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Microstructural Evolution in Coated Single Crystal Ni-Based Superalloys

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A doctoral thesis submitted in partial fulfilment of the requirements for the award of Doctor of Philosophy

November 2007
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Abstract

Ni-based superalloys are primarily used in the manufacturing of critical gas turbine components, such as rotating blades. The drive for increased efficiency has led to a continuous rise in engine operating temperatures, and therefore these components are exposed to conditions that can ultimately compromise their mechanical integrity and therefore limit their service life. There is a desire to extend the component’s life and also to avoid any premature failures, and therefore understanding of the material’s stability and properties throughout component life is increasingly important.

The identification of features in the microstructure of Ni-based superalloys which change systematically with time and temperature may allow it to be used as a ‘time-temperature’ recorder. This could enable a determination of the effective temperature a component will have experienced, and in conjunction with known values of operating stress, an estimate of the remaining service life can be made.

This research was concerned with the microstructural evolution as a function of time and temperature in two different coated Ni-based superalloy systems and in particular, the interactions which occur at the coating/substrate interface. The coated samples were isothermally exposed to various temperatures to simulate the possible service conditions experienced by industrial gas turbine blades. A variety of experimental techniques, including field emission gun scanning electron microscopy (FEGSEM), energy dispersive x-ray (EDX) analysis and transmission electron microscopy (TEM) have been utilised for phase characterisation. Detailed examinations have been made of the substrate alloy, the coating system and the interactions between the coating and substrate. Where possible, thermodynamic equilibrium calculations were also performed using a commercial software package in conjunction with a thermodynamic database for Ni-based superalloys to provide information about the likely phase stability at equilibrium.

Significant microstructural transformations were observed as a result of thermal exposure within both the MCrAIY and Pt aluminide diffusion coated superalloy systems examined. In the MCrAIY coatings, the depletion of Al from the coating by the formation and growth of the
oxide scale at the coating surface and the interdiffusion with the substrate, resulted in the depletion of \( \beta \)-NiAl phase. Both the oxide thickness and \( \beta \) depleted zones were seen to increase with increasing ageing time and temperatures. However, in the Pt aluminide diffusion coatings, the diffusion of Al from the coating out towards the oxide and in towards the substrate alloy resulted in the phase transformation from the Al-rich \( \beta \) matrix to the \( \gamma' \) phase. The amount and size of the \( \gamma' \) particles within the coating were seen to increase with temperature and exposure time, with the majority located in the central regions of the coating and towards the coating/substrate interface. Diffusion of elements across the coating/substrate interface in both coating systems led to complex interdiffusion zone structures, including the formation of carbides, such as MC and M\(_{23}C_6\), and intermetallic TCP phases, including \( \sigma \), \( \mu \) and P.

A one-dimensional diffusion-based model was developed in a parallel project, to predict the concentration profiles associated with the oxidation and interdiffusion that occurs in MCrAlY coated superalloys. The model was capable of simultaneously managing multiple components, multi-phases, and oxidation using a flexible grid-design, flexible component numbers and moving phase boundaries. The model incorporated an oxidation model to deal with the alumina scale formation process, a diffusion model to predict the redistribution of alloy elements across the coating substrate system and thermodynamic software application to calculate the phase constitution and its evolution with time. Extensive comparisons have been made in this research between the experimental results obtained and the predictions of the model, in order to validate the model and make suggestions for future improvements. Such a model can therefore act as a time temperature recorder, to allow the prediction of the effective operating temperature of a component and as a result (in combination with other information such as operating stress) estimate its remaining life in service.
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Chapter 1
Introduction

Turbine blades are critical components for both aeronautical and industrial gas turbines. The realisation that the temperature at which the material operates is linked to the efficiency of the overall engine led to a demand for materials which could retain their strength at high temperatures; subsequently Ni-based superalloys have become the major material used for this application because of their high creep strength at temperature. Turbine blades operate within an aggressive environment, hence there is a need to protect the materials from excessive oxidation and corrosion.

Coatings are used on superalloys to allow their use at high temperatures and extend the component life by inhibiting the interaction between the substrate material and the working environment. The environments in which superalloys are used are potentially damaging, with the possibility of metal dissolution due to the oxidation and corrosion reactions occurring at the surface of the substrate. This corrosion/oxidation can subsequently lead to a reduction in mechanical properties through the diffusion of harmful species into the alloy and through loss of section thickness. Coatings attain their protective action from the interaction/reaction of elements such as Al and Cr in the coating with oxygen present in the working environment. This interaction with oxygen forms dense, adherent oxide scales on the surface of the coating, which as a result inhibits the diffusion of damaging elements such as oxygen, nitrogen and sulphur into the substrate material. Therefore, the life of the coating can be related to its ability to form the protective scales and/or replace the scale as and when required. The thermal stability of coatings is deemed one of the key variables which can be expected to influence performance. The durability of protective coatings is a crucial issue for gas turbines, since coating life mainly controls the refurbishment and/or replacement of many engine parts, such as blades and vanes.

A complete understanding of the diffusion assisted degradation processes and the microstructural changes that take place within the coating, interdiffusion zone and substrate material is crucial in order to develop more accurate life prediction procedures for coatings and coated Ni-based superalloys. Modelling of these diffusion processes which occur during
service can be an important tool to predict coating and substrate degradation as a function of time and operating temperature. Such a tool is of great advantage in the estimation of long term component performance, and for the selection and/or development of optimum coating/substrate combinations.

The aim of this research was to gain a fundamental understanding of the microstructural evolution as a function of time and temperature in two different coated Ni-based superalloy systems. The focus of the research therefore was the microstructural interactions which occur as a result of interdiffusion between the coating and substrate. Both MCrAlY and Pt aluminide diffusion coatings have been isothermally aged at various times and temperatures representative of the service conditions experienced by industrial gas turbine blades. Detailed microstructural characterisation allowed the identification of features in the coated Ni-based superalloys which change systematically with time and temperature, and which therefore could be used as an indicator of effective thermal exposure.

The literature relevant to this research is reviewed in Chapter 2, and includes discussion of the major phases that can form in Ni-based superalloys during heat treatment or service exposure conditions. The various coating processes which can be applied to superalloys are also discussed, with reference to microstructural evolution as a result of interdiffusion in particular.

Chapter 3 presents details of the materials used in this work and reviews the experimental methodology followed. Thermodynamic equilibrium calculations have been used during this research in order to predict the amount and chemical composition of the phases that will occur within the material at equilibrium as a function of temperature, which in turn assists in phase identification. The majority of the microstructural characterisation was carried out by means of scanning electron microscopy (SEM) because it enables the resolution of features not observable by means of optical microscopy. Energy dispersive X-ray analysis (EDX) was used in conjunction with the SEM to determine the composition of the various phases present to aid in their identification. A dual beam focussed ion beam/FEGSEM was used to produce site specific samples for high resolution analysis. This procedure allowed the extraction of particles within the complex interdiffusion zone, where the preparation of thin foils and carbon replicas would have been very difficult to achieve and hence provide the desired information. Conclusive identification of particles in the site-specific samples was possible.
with the combined use of selected area electron diffraction (SAED) and EDX analysis within the transmission electron microscope (TEM).

Chapter 4 discusses the results of the microstructural investigations carried out on the two main variants of CMSX4 alloy used in the research, referred to as 'standard' CMSX4 and CMSX4 HC respectively and which differed primarily in the amount of carbon they contained. Thermodynamic equilibrium calculations were carried out on the substrate CMSX4 alloys in order to predict the amount and chemical composition of the phases occurring at equilibrium as a function of temperature, which in turn assisted in phase identification. Microstructural characterisation of the two CMSX4 alloys was also carried out using scanning electron microscopy (SEM) and EDX for chemical analysis to establish a baseline for the subsequent examination of coated samples.

The detailed microstructural characterisation carried out on the MCrAlY coated CMSX4 samples is presented in Chapter 5. Round bar samples were isothermally aged in air at temperatures ranging from 850 - 1050°C at times up to 10,000 hours. Examination of the samples and determination of phase stability as a function of temperature, time and position relative to the coating/substrate interface was carried out using a variety of microscopy techniques. A multi-component diffusion model capable of simulating the evolution in microstructure of a coated Ni-based superalloy system was developed in parallel to this research in order to be useful as a predictive tool for assessing microstructural evolution and therefore the effective thermal exposure of coated turbine blade systems, and also for designing new coated alloy systems. The model was capable of predicting the changes in concentration and phase stability across the coated superalloy system after a given thermal history. In addition, the model was also capable of estimating the losses due to oxidation and the likely remaining life of the coating based on a concentration and/or phase fraction dependent failure criteria. In Chapter 6, the model was compared to the experimental data presented in Chapter 5 in order to validate the model, assess its capabilities and suggest future improvements.

Platinum modified aluminide diffusion coatings are produced by both inward and outward growth methods, and each mechanism forms a distinctive coating microstructure. Chapter 7 presents a detailed study of the microstructural evolution of two commercial Pt modified aluminide diffusion coatings, RT22 and CN91, applied to the Ni-based superalloy CMSX4.
The RT22 coatings, which were the subject of the bulk of the experimental work, were inward grown, whereas the CN91 coatings were outward grown. This was followed by a detailed microstructural investigation carried out on RT22 coated CMSX4 ex-service blades presented in Chapter 8, in order to make comparisons with the microstructures observed in the isothermally aged RT22 coated CMSX4 samples. It has shown that microstructural maps can be used as an indicator of effective thermal exposure for coated systems, although for a complete life prediction methodology, models are required which link the diffusion mechanisms and phase transformations to the effects of both temperature and stress, and ideally corrosion and oxidation phenomena.
Chapter 2
Literature Review

2.1 Introduction

Turbine blades are critical components of both aeronautical and industrial gas turbines. The demand for materials which could retain their strength at high temperatures increased due to the realisation that the temperature at which the material was operated at is linked to the efficiency of the overall engine; subsequently Ni-based superalloys have become the major material used for this application because of their high strength at temperature and stability in aggressive environments. This chapter reviews the history of superalloys, illustrating the major developments in alloy composition and processing techniques. The microstructure of superalloys can be quite complex, and this chapter considers the major phases that can form in Ni-based superalloys during heat treatment or service exposure conditions, thus highlighting the relationship between composition, structure and properties. Coatings are used on superalloys to allow their use at high temperatures, together with inhibiting the interaction between the substrate material and the working environment. This chapter also describes the types of coatings and coating processes which have been developed to provide protection for superalloy substrates at high temperatures.

2.2 Principles of Gas Turbine Engines

The basic principle of a gas turbine engine is the generation of energy by the combustion of fuel which in turn increases the total energy of the air stream passing through the engine. Gas turbines usually operate on an open cycle known as the Brayton cycle\textsuperscript{[1,2]} as illustrated in Figure 2.1.
Fresh air at ambient conditions is drawn into the compressor, in which it's temperature and pressure are raised. The high pressure air then proceeds into the combustion chamber, in which the fuel is burnt at constant pressure, resulting in an increase in energy of the system. The main requirement of the engine is for stable and efficient combustion to be maintained over a wide range of operating conditions. The resulting high-temperature gases then enter the turbine, where they continue to expand to atmospheric pressure through a row of nozzle guide vanes. This expansion causes the turbine blades to rotate, and in turn provides the necessary power to drive the compressor via various networks of shafts. In the case of aero engines the expansion of the gas is continued through a propelling nozzle providing the required thrust. However, in industrial gas turbine engines the rotating turbine blades proceed to turn a shaft held inside a magnetic coil. This rotation within the magnetic coil induces an electric current. The compression and expansion processes are both carried out by means of rotating elements in which the energy transfer between fluid and rotor is affected by means of kinetic action, rather than by positive displacement as in reciprocating machinery\(^3\).

Efficient gas turbine operation is ultimately achieved with high compression ratios and high turbine entry temperatures. Despite the severe environmental conditions experienced by high-pressure turbine blades, turbine entry temperatures have more than doubled since the Whittle engine\(^4\), which has been achieved both by material development and by the adoption and development of blade cooling technology. The main elements of the gas turbine cycle are: the compressor, the combustion chamber and the turbine.

\[\text{Figure 2.1 Schematic diagram illustrating the Brayton closed cycle}^1\]
2.2.1 Compressor Section

Efficient compression of large volumes of air is essential for a successful gas turbine engine. Two main types of compressors are utilised within gas turbine engines; the axial-flow compressor and the centrifugal or radial-flow compressor. Most modern power plant compressors are axial-flow. The object of a good compressor design is to obtain the most air through a given diameter compressor with a minimum number of stages while retaining relatively high efficiencies and aerodynamic stability. The compressors contain a row of rotating blades followed by a row of stationary (stator) blades, in which a stage consists of both a row of rotor and stator blades. In modern turbines several compressors are usually needed, e.g. one low and two high pressure compressors. All work done on the working fluid is by the rotating rows, with the stators present to convert the fluid’s kinetic energy to pressure and directing the fluid into the next rotor. The fluid enters with an initial velocity relative to the blade and leaves with a final relative velocity at a different angle.

The temperature loading through the compressor ranges from -50 to 500°C, in which low alloy and ferritic stainless steels have proved to have adequate mechanical properties for these conditions. For advanced gas turbine designs increased temperatures, pressure ratios and rotor speeds are being introduced within the compressor\(^5\). This requires the use of high strength steels, as well Ni-based alloys for the rotating components in gas turbines in the rear stages of the compressor. However, the use of these materials would significantly increase the cost of the system. Manufacturing complexity would also be introduced which can include operational difficulties such as component handling, overhaul and repair of such components.

2.2.2 Combustion Section

The function of the combustion chamber is to accept the air from the compressor and to deliver it to the turbine at the required temperature, ideally with no loss of pressure. The combustion chamber receives air from the compressor, which mixes with fuel sprayed from nozzles in the front of the chamber. The mixture is then burnt at temperatures up to 2000°C to generate the maximum possible heat energy. The fuel is commonly in a gaseous or liquid state, normally hydrocarbons. Gases used are typically natural gas, mostly methane and butane, and the liquids range from highly refined gasoline through to kerosene and light diesel oil, to a heavy residual oil. However, with increasing amounts of legislation introduced
recently on reduced emissions, alternative fuels such as gases derived from biomass and syngas with high hydrogen contents are being proposed\[6\].

Combustor exit temperatures can range from 1150 to 1500°C depending on the engine size. Therefore, the combustors are exposed to a combination of loads, including high temperature creep and oxidation, high cycle fatigue and thermomechanical fatigue. The materials used within this area are generally wrought or sheet formed Ni-based superalloys; these provide excellent thermomechanical fatigue, creep and oxidation resistance and can be formed into complex shaped components. The high thermal loading incurred by these materials and the need to limit the cooling air used has led to the use of ceramic thermal barrier coating systems to protect these components. The general multilayer coating systems comprise of a bond coat and a ceramic topcoat applied to the substrate. The application of this system aims to reduce the maximum temperatures to between 900 and 950°C; increased operating temperatures in the future and corrosive fuels will thus require further development of coating technologies\[7-9\].

2.2.3 Turbine Section

Gas turbines move relatively large quantities of air through the cycle at very high velocities. Each turbine consists of one or more stages of alternate stationary and rotating blades. The rotating turbine blades are carried on discs, which are connected by a shaft to the compressor. The stationary blades or nozzle guide vanes are housed within the turbine casing. The hot compressed air is then allowed to expand through the turbine stages hence reducing the pressure and temperature and increasing its volume. During the expansion the turbine extracts energy from the hot exhaust gases to drive the compressor by means of the connecting shaft.

The high-pressure turbine blades operate under the most arduous conditions of temperature and stress of any component in the engine. The blades not only experience the high temperatures and direct stress from the accelerated airflow, but furthermore they experience rapid temperature transients at various points in the cycle. The turbine section of the engine encounters hot gases leaving the combustion chamber, and therefore due to the high temperatures encountered, turbine blades and discs continue to be manufactured from cast and wrought Ni-based superalloys. To meet the demand for higher performance, advanced materials have been introduced into the turbine, including various coatings to provide protection against high temperature oxidation and corrosion. The use of thermal barrier
coatings (TBC) and internal cooling have also been increasingly utilised to reduce the material temperatures.

2.3 History of Ni-based Superalloys

The term 'superalloys' is used to describe a wide range of high temperature materials which combine high strength and corrosion at temperatures above 650°C, usually based on group VIIA elements. Superalloys are divided into 3 classes; Ni-based, Co-based and Fe-based superalloys. Superalloys are utilised at a high proportion, rapidly approaching 80 - 90%, of their melting temperature. The face centred cubic (fcc) structure of the matrix phase is common to all superalloys. Co-based alloys and Ni-based sheet alloys use solid solution hardening and carbides to obtain the required strength, whereas, wrought and cast Ni and Fe-based alloys additionally use the precipitation of intermetallic phases within the matrix to provide additional strengthening.

Rapid developments in high temperature materials for the use in aerospace technologies occurred as a direct result of the onset of World War II. This was closely followed by the requirements of the industrial gas turbines, which demanded strength at high temperatures plus the additional reliability and economic feasibility. The need for materials that could retain their strength at high temperatures increased due to the realisation that the temperature at which the material was operated was linked to the efficiency of the overall engine.

Prior to the development of superalloys, the materials that were deemed to have the highest strength were that of the austenitic steel family which have a face centred cubic (fcc) structure\[1,10\]. The main strengthening phase within Ni-based superalloys is the $\gamma'$ phase, which was introduced within the initial superalloys in 1929 by Bedford, Pilling and Mercia\[1\]. This phase enabled the alloys to retain their strength at temperatures above 650°C. The initial development of these alloys involved the gradual increase of elements that promote the $\gamma'$ phase such as Al and Ti, which in turn varied the volume fraction, and hence the resulting mechanical properties. Due to the high reactivities of these elements, their increased content within Ni-based superalloys required the development of alternative processing methods such as vacuum induction melting (VIM). This progress was accompanied by the control of solid strengthening elements such as W, Re, Mo and Ta within the alloys in order to prevent local precipitation of embrittling phases during solution heat treatments or under service conditions.
Grain boundaries in cast components were thought to be points of weakness, which ultimately led to the production of directionally solidified (DS) alloys. The basis for creating DS alloys is to align (or eliminate) grain boundaries parallel to the stress axis. This grain morphology is achieved by pouring the liquid metal into a mould that contains a water-cooled bottom plate. Solidification first occurs at the bottom plate, after which the mould is slowly withdrawn from the furnace, allowing the metal inside to directionally solidify from bottom to top. The DS alloys have displayed a considerable improvement in the creep strength and ductility of the alloy compared to conventionally cast alloys, whilst maintaining a high level of strength.

Single crystal (SC) alloys were developed from the DS casting processes. SC castings are produced in a similar fashion to DS with the addition of the selection of a single grain, via a grain selector. During solidification, this single grain grows to encompass the entire part. The benefits offered by the removal of grain boundaries within a component are improved creep rupture strength, thermal fatigue properties, resulting in superior performance and durability. The absence of grain boundaries made it possible to remove elements that were used as grain boundary strengtheners, such as carbon, boron and zirconium, which inadvertently increased the solidus temperature and allowed for further alloy development via heat treatments. Both directionally solidified and single crystal types are currently being used at higher service temperatures than conventionally cast components. Figure 2.2 shows an example of a conventionally cast, directionally solidified and single crystal turbine blade.
2.3.1 Chemistry

In order to obtain all of the desired effects of the various element additions together with ensuring the ideal microstructure, the chemical composition must be carefully balanced. Ni-based superalloys can be defined as predominately consisting of Ni with significant amounts of alloying elements, each one having its own role within the superalloys, whether it is for corrosion protection or for strengthening purposes. The complexity of superalloy compositions has grown with each stage of development. Consequently creating a balance of these elements in order to obtain the optimum properties for a given application proves exceptionally difficult. Elemental additions within the Ni-based superalloys can be categorised as shown in Table 2.1.

<table>
<thead>
<tr>
<th>Category</th>
<th>Elements</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\gamma$ phase promoters</td>
<td>Co, Cr, Mo, W, Fe</td>
</tr>
<tr>
<td>$\gamma'$ phase promoters</td>
<td>Al, Ti, Nb, Ta, Hf</td>
</tr>
<tr>
<td>Carbide formers</td>
<td>Cr, Mo, W, Re, Nb, Ta, Ti</td>
</tr>
<tr>
<td>Oxide formers</td>
<td>Cr, Al</td>
</tr>
<tr>
<td>Segregate to grain boundaries</td>
<td>B, C, Zr</td>
</tr>
</tbody>
</table>

Table 2.1 Categorisation of the main elements present within Ni-base superalloys
In the early stages of development, the matrix was either Fe or Ni-based with the addition of sufficient amounts of Cr to produce adequate corrosion resistance, and also to strengthen the matrix to a certain extent. Cr was initially added in substantial quantities to the alloy to increase the corrosion resistance; however, this was soon proved to be a hindrance to the strength. However, reducing the chromium amount led to the onset of hot corrosion, and therefore a balance had to be achieved. Small additions of Al and Ti were made, which are the principal γ' forming elements. Ta can also replace Ti to an extent in single crystal superalloys as it both strengthens the γ' and raises the solidus temperature. The volume fraction of γ' was steadily increased over the course of superalloy development and resulted in an increase in the creep resistance within the alloy.

In the early developments of Ni-based superalloys, Co was used extensively in the compositions with values up to 20 wt.%[13]. The large price increase of cobalt during the 1970's initiated a close examination of the element's role within the superalloy compositions. It was subsequently found upon this examination that Co appeared to have little effect on strengthening within the alloy as its atomic size was very similar to that of Ni. The element's main influence is indirect regarding the solidus temperature, which can lead to higher volume fractions of γ' at low temperatures[1,10].

Refractory metal additions such as Mo, W, Nb, Ta, and more recently Re and Ru, were added to alloys in order to strengthen the matrix through solid solution strengthening. The high melting point of these elements can increase the high temperature properties of superalloys; this is partly achieved by inhibiting the atomic diffusion throughout the crystal lattice. As temperature increases so does the rate of diffusion, therefore the addition of refractory elements can reduce the diffusion rate by increasing the activation energy required to move the atoms in the system. However, excessive amounts of these elements within the alloy promote topologically closed-packed phases such as σ, μ and Laves which have plate-like morphologies and are often seen as detrimental due to their brittle nature. The amount of these refractory elements are thus limited despite their beneficial effect on creep strength at high temperatures and particle coarsening[10,14-16].

Carbon has been present within superalloys during these developments, because it forms carbides which act as point strengtheners together with having beneficial grain boundary
The effects. The most recent developments of single crystal alloys illustrate that these are not needed due to their lack of grain boundaries. However, for large single crystals components, it has proven difficult to avoid casting defects, such as freckles and misoriented grains. Carbon additions have recently been shown to significantly reduce the frequency of solidification defects\(^{17-21}\) and to reduce the formation of surface scale on single crystal Ni-based superalloy castings. Consequently, controlled amounts of carbon have been recently reintroduced into a number of commercial Ni-based single-crystal alloys. Elements such as B, Zr and Hf are added to promote grain boundary effects other than precipitation or carbide formation\(^{22}\). Minor alloying additions and trace elements can be present within Ni-based superalloys and can have a significant impact on the performance of cast components. These elements can be divided into two groups: detrimental and beneficial, however, beneficial elements can become detrimental if present in higher levels than ppm. The classifications of these elements are shown in Table 2.2. The control of these critical elements is the key to optimising alloy castability and properties.

<table>
<thead>
<tr>
<th>Class</th>
<th>Type</th>
<th>Elements</th>
</tr>
</thead>
<tbody>
<tr>
<td>Detrimental</td>
<td>Residual gasses</td>
<td>O, H, N, Ar, He</td>
</tr>
<tr>
<td></td>
<td>Non-metallic impurities</td>
<td>S, P</td>
</tr>
<tr>
<td></td>
<td>Metallic impurities</td>
<td>Pb, Bi, Sb, As, Se, Ag, Cu, Tl, Te</td>
</tr>
<tr>
<td>Beneficial</td>
<td>Refining aids</td>
<td>Ca, Mg, Ce, La</td>
</tr>
<tr>
<td></td>
<td>Minor alloying additions (ppm)</td>
<td>B, Hf, Mg, C</td>
</tr>
<tr>
<td></td>
<td>Alloying additions (&lt;1.5 wt.%)</td>
<td>Hf, Zr</td>
</tr>
</tbody>
</table>

Table 2.2 Classification of impurities and trace elements in Ni-based superalloys\(^{11}\)

2.4 Microstructure of Ni-based Superalloys

The microstructure of Ni-based superalloys can be quite complex due to the potential for a variety of phases that can form during heat treatment or service exposure conditions. The major phases found to be present within Ni-based superalloys are listed below:

- FCC γ matrix
- L1\(_2\) ordered γ' (Ni\(_3\)Al) precipitate
- Carbides
- Borides
2.4.1 The γ phase

The basic microstructure of any superalloy consists of a gamma (γ) matrix. The γ matrix is a continuous matrix with a face centred cubic (fcc) crystal structure, which contains a high percentage of solid solution elements promoting solid solution strengthening, such as Cr, Co, W and Mo. Solid solution strengthening causes strengthening of the matrix by creating lattice distortion which increases with atomic size difference up to a maximum of 10%\(^{10}\). Elements with high melting points can also be utilised as they provide strong lattice cohesion within the matrix and thus reduce diffusion at increased temperatures. Slow diffusing elements such as Mo and W have proved to be the greatest hardeners at high temperatures and can also be seen to lower the diffusivity of Ti and Cr at 900°C. The basis of Ni as the main alloying elements is due to its substantial alloying abilities without inducing phase instability and when alloyed with Cr has the ability to produce protective scales\(^{11}\). Figure 2.3 shows a schematic of a typical fcc crystal structure.

![Schematic diagram illustrating the fcc lattice structure of the γ matrix phase](image)

2.4.2 The γ’ phase

The gamma prime (γ’) phase is a coherent precipitating phase with an ordered L1\(_2\) fcc crystal structure, which exhibits long range order. The nominal composition of γ’ commonly encountered within Ni-based superalloys is Ni\(_3\)(Al,Ti). The γ’ phase has a lattice structure with a slight mismatch compared with that of the γ matrix. The mismatch is defined as the normalised difference in lattice parameters between γ and γ’. The resulting coherency strain produced by the mismatch can contribute significantly to the overall hardening of the alloy.
The compatibility of the $\gamma'$ L1$_2$ structure with $\gamma$ matrix allows the homogeneous nucleation of precipitates with low surface energy. This consequently allows the superalloy to maintain its mechanical properties up to very high temperatures for relatively long exposure times. The $\gamma'$ phase contributes to the superalloys strength by hindering the movement of dislocations. The strength and ductility of the $\gamma'$ increases with temperature which in turn prevents the phase from being a source of failure within the alloy. The factors that affect the degree of hardening created by the $\gamma'$ are the size and spacing of the particles, and therefore their volume fraction within the matrix. With low volume fractions the interparticle spacing is large and the precipitates are coarse which allows dislocations within the matrix to bend round the particles by means of the Orowan mechanism. The volume fraction of $\gamma'$ within a superalloy system can be up to 70% within single crystals, which represents an optimum value for high creep strength\textsuperscript{[10]}.

The degree of lattice mismatch between the $\gamma$ and $\gamma'$ phase determines the morphology of the $\gamma'$ phase. For small values of lattice mismatch 0 – 0.2% the $\gamma'$ particles are spherical. As the mismatch increases from 0.5 – 1.0% the particle shape evolves into cubes, finally changing into plates at mismatches greater than 1.25%\textsuperscript{[1,22]}. Coarsening increases the size of the precipitates at a greater rate and in turn facilitates in dislocation bypassing. Reducing the potential for coarsening assists in retaining long time creep resistance. The coarsening rate of the $\gamma'$ decreases significantly as the Cr and Mo amount is increased within the alloy as this reduces coherency strains\textsuperscript{[1]}, additions of Al and Ti to the alloy have the opposite effect. The loss of creep resistance during $\gamma'$ coarsening is dependent on the volume fraction of $\gamma'$. Low volume fractions coarsen faster than high volume fractions, therefore to retard the coarsening effect, the volume fraction of $\gamma'$ is increased within the alloy or alternatively slow diffusing elements are added to the $\gamma'$, such as Nb and Ta.
2.4.3 Carbides

Carbides are formed within the microstructure of a superalloy by the use of minor additions of carbon, boron, zirconium and hafnium. Carbides that precipitate on grain boundaries strengthen the superalloy by increasing the boundary cohesion, therefore preventing or retarding grain boundary sliding and permitting stress relaxation. Strengthening due to carbide precipitation at grain boundaries is utilised within both conventionally cast (CC) and directionally solidified (DS) components. Carbides have proved to have a beneficial effect on rupture strength at high temperatures, and they can also influence the ductility and chemical stability of the matrix by the removal of reactive elements. Carbides are found in a number of forms within Ni-based superalloys including MC, M₆C and M₂₃C₆. Heat treatments carried out on the superalloys can result in the decomposition of the MC carbides, producing the lower carbides M₂₃C₆ and M₆C which often begin to form at grain boundaries.

The MC carbides have fcc structures which are dense and closely packed, resulting in substantial strength and stability. These carbides usually form when the metal is in a molten state and are therefore invariably 'frozen' in the microstructure both in inter and transgranular positions. The 'M' represents elements such as Ta, Ti, Hf, Nb or W. These carbides prove to be the major source of carbon within the alloy for use during heat treatment and within service\[1,24\]. It has been reported that the preferred order of formation of MC carbides is HfC, TaC, NbC and TiC, with decreasing stability\[22\]. The morphology of the MC carbide tends to be a coarse random cube or a script-like particle.

The M₂₃C₆ carbide tends to form in abundance within alloys that contain high amounts of Cr. These carbides form during heat treatments and in service typically at the lower temperatures of 760 - 980°C. It has also been established that they can be a product of the dissolution of MC carbides. These carbides have a tendency to precipitate at grain boundaries and occasionally along twin lines, stacking faults and at twin ends, occurring as irregular discontinuous blocky morphologies, and in some cases, they have been observed to form as plates and regular geometric forms. M₂₃C₆ carbide can also have a significant effect on the alloys properties, because their presence on the grain boundaries promotes an effect on the rupture strength through inhibition of grain boundary sliding. However, this can be initiated by fracture or by decohesion of the M₂₃C₆ interface.
The $M_6C$ carbide also has an fcc structure and is formed at a slightly higher temperature than $M_{23}C_6$ at approximately 815-980°C, and precipitates in a blocky form at grain boundaries, and in rare circumstances in Widmanstätten intragranular morphology. This carbide is similar to $M_{23}C_6$ but is usually formed when there is a substantial concentration of Mo or W in the alloy. This stability at higher temperatures makes it more beneficial as a grain boundary precipitate, and hence controlling the grain size within wrought and cast alloys\textsuperscript{[22,25]}.

2.4.4 Borides

Boron is usually present in superalloys within the range of 50 – 500 ppm. Borides form on the grain boundaries as $M_3B_2$ and block the onset of grain boundary tearing under creep rupture loading. These particles are hard refractory particles at grain boundaries, the shape of which can vary from blocky to half moon in appearance, but are usually observed in much smaller quantities than carbide phases.

2.4.5 Topologically Closed Packed (TCP) Phases

Topologically closed packed (TCP) phases are intermetallic compounds that generally form in service after long times at elevated temperatures due to the high concentrations of refractory elements such as W, Re, Mo, Cr and Ta. TCP phases include $\pi$, $\mu$, $\chi$ and $\sigma$ phases and are characterised by close packed layers of atoms forming “basket weave” morphologies generally aligned with the octahedral planes in the FCC matrix\textsuperscript{[19,26]}, as illustrated in Figure 2.5.

![Figure 2.5 SEM micrograph of deep-etched TCP platelets from alloy SX-2 revealing the characteristic "basket weave" pattern\textsuperscript{[19]}](image-url)
The TCP phases are known to be similar in composition and crystallography, which can result in the coexistence of several of the phases within a single structure. The main criterion used to distinguish the phases is their distinct crystallographic structures. The $\mu$ and R phase precipitates have a rhombohedral crystal structure, whereas the $\sigma$ phase is tetragonal and the P phase orthorhombic\cite{14,27}. The lattice parameters are given in Table 2.3. These phases are often regarded as detrimental to the properties of the alloy due to their high hardness and plate-like morphologies. As the TCP phases precipitate and grow with time and temperature, they deplete the surrounding matrix of refractory solid solution strengthening elements, consequently weakening the matrix and allowing for the initiation and propagation of cracks within the structure\cite{27,28}.

<table>
<thead>
<tr>
<th>TCP Phase</th>
<th>System</th>
<th>Lattice parameter ($\AA$)</th>
<th>$\alpha$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\sigma$</td>
<td>Tetragonal</td>
<td>$a = b = 9.3, c = 4.86$</td>
<td>90°</td>
<td>[14]</td>
</tr>
<tr>
<td>P</td>
<td>Orthorhombic</td>
<td>$a = 17.2, b = 4.86, c = 9.2$</td>
<td>90°</td>
<td>[14]</td>
</tr>
<tr>
<td>$\mu$</td>
<td>Rhombohedral</td>
<td>$a = b = 4.75, c = 25.8$</td>
<td>120°</td>
<td>[29]</td>
</tr>
<tr>
<td>R</td>
<td>Rhombohedral</td>
<td>$a = b = 10.9, c = 19.3$</td>
<td>120°</td>
<td>[27]</td>
</tr>
</tbody>
</table>

Table 2.3 Crystallography of the TCP phases

The low diffusivities of the refractory elements such as W, Re and Ta at high temperatures result in reactions being very slow, which can result in precipitates forming from the concentrations of the elements as isolated plate or cellular morphologies. The formula of TCP's are generally (Cr, Mo)$_x$(Ni, Co)$_y$ where $x$ and $y$ can be $1 - 7$. Superalloys have been designed in the attempt to avoid the formation of TCP phases using methods such as PHACOMP ('phase composition') or, more recently, thermodynamic equilibrium calculations to predict the tendency for TCP phase to form\cite{14,30}.

2.4.6 Segregation

During solidification of complex Ni-based superalloys, elements used for the purpose of solid solution strengthening such as W, Re and Ta can cause solute segregation. This results in the formation of concentration gradients within the microstructure, and may affect the mechanical
properties of the material. Segregation can also cause the formation of secondary phases in the interdendritic regions. Which can prove detrimental, depending on the size and morphology of the phases, as these can initiate cleavage fracture within the alloy\cite{31}. The segregation of certain elements within the alloy has been extensively investigated, illustrating that W and Re strongly segregate to the dendrite core whereas the Ta separates preferentially to the interdendritic region\cite{17-19}. The cooling rate of the alloy influences the amount of segregation, which becomes more severe when the solidification process is rapid, because fast cooling limits the time allowed for the diffusional exchange of elements between the liquid/solid interfaces.

Homogenising heat treatments are used to redistribute the solute in order to produce a homogeneous microstructure. However, complete redistribution within these alloys has proved difficult due to the low diffusivities of the heavy refractory elements. The time required for this operation can be substantial, which in turn increases the cost of the process. This increase in time spurred a compromise to be made, producing shorter standard solution treatments which result in a residual chemical segregation that proves not too detrimental to the mechanical properties of the alloy. A typical industrial solution treatment of a single crystal superalloy is to hold the material for 3 hours at a temperature approximately 1300°C. As a result of slow diffusion this still results in heavy elements such as W, Ta and Mo not being uniformly distributed.

Homogenising heat treatments take place between the \( \gamma' \) solvus and solidus temperatures for the alloy. Care has to be taken when selecting solution treatment temperatures, if they are too high incipient melting will occur with detrimental consequences on the mechanical properties of the alloy, due to the resulting change of volume leading to micro-porosity after re-solidification. Techniques have been established for the quantification of the segregation characteristics of elements within superalloys, the main one being a Scheil-type analysis\cite{17,19} of quantitative EDX data. Within this procedure compositional measurements are taken at the dendrite core and the interdendritic regions to identify the partitioning behaviour of particular elements within the alloy. Square grids are then indexed over an area that most represents the dendritic microstructure; quantitative point measurements are subsequently collected to provide a general distribution of the elements within these regions\cite{18}. 

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2.5 Microstructural Evolution at High Temperatures

Microstructural changes occur in superalloys as a result of high temperature exposure during service. The changes in shape and size distribution of constituent phases which occur at elevated temperatures can affect the mechanical properties of the alloy. A knowledge of how the phases evolve with temperature and time is required for the realistic estimation of service life within components in order to avoid premature failures during service.

2.5.1 Changes in $\gamma/\gamma'$ Morphology

The initial heat treatment of an alloy and subsequent exposure to thermal ageing greatly affects the size, shape, distribution and volume fraction of the $\gamma'$ precipitates, which in turn determines the properties of the alloy. Increased understanding of these changes in shape and size potentially allows for more reliable life prediction techniques.

**Coarsening**

Coarsening refers to the mechanism by which there is an increase in average particle size at a constant volume fraction. Particle coarsening is the result of an exchange of solute atoms between the precipitate and the matrix\[^{[10]}\]. As a consequence of coarsening, larger particles will tend to grow at the expense of smaller ones, which is known as Ostwald ripening. $\gamma'$ precipitates have been observed to undergo several morphology changes as they grow. In order to minimise the surface energy the initial shape formed is a sphere. As the precipitate grows the misfit strain energy continues to increase so that gradually the cuboidal morphology associated with Ni-based superalloys is produced, therefore minimising the total energy of the precipitate\[^{[32,33]}\].

In the absence of applied stress the driving force for coarsening is the minimisation of interfacial energy, hence the specific free energy of the $\gamma'$ precipitate/matrix interface\[^{[10,34,35]}\].

A decrease in interfacial energy can be achieved by reducing the $\gamma/\gamma'$ lattice mismatch, which in turn increases its coherency. For low growth rates of the $\gamma'$ precipitates, a coherent $\gamma/\gamma'$ interface and low lattice mismatch ($\delta$) is required, as defined by Equation 2.1, where $a_\gamma$ and $a_{\gamma'}$ are the lattice parameters for the $\gamma$ and $\gamma'$ phases respectively.

\[^{[20]}\]
The majority of single crystal Ni-based superalloys have a negative lattice mismatch, meaning that the lattice constant of the $\gamma'$ phase is smaller than that of the $\gamma$ phase. However, the mismatch is seen to vary with temperature due to different thermal expansion coefficients of the $\gamma$ and $\gamma'$ phases. The microstructural changes that occur for the reduction of the total interfacial energy is the decrease in area of the various interfaces. This is achieved by precipitate coarsening, shape changes of the precipitates and interactions of phase and grain boundaries.

The $\gamma'$ particles are observed to increase in size with increase in temperature and change their morphology. The initially cuboidal precipitates can group together, forming chain and block-like structures, that have a tendency to coalesce, as illustrated in Figure 2.6. These grouped precipitates can orientate in a specific direction depending on the degree of anisotropy such as residual chemical gradients resulting from segregation\textsuperscript{[10]}

\[
\delta = 2 \frac{(a_{\gamma'} - a_{\gamma})}{(a_{\gamma'} + a_{\gamma})}
\]  

[2.1]  

Rafting  

Coarsening that occurs during high temperature exposure and under an externally applied stress is referred to as 'rafting'. Under the combined influence of stress and temperature, the cuboidal $\gamma'$ precipitates coalesce to form a rafted $\gamma'$ morphology as illustrated in Figure 2.7. Rafting within single crystal superalloys is known to occur when subjected to stress at temperatures above 900°C\textsuperscript{[36]}. Rafting is strongly influenced by the lattice parameters, lattice mismatch and elastic constants between the $\gamma$ and $\gamma'$ phases\textsuperscript{[10,36]}. The specific direction of
The degree of rafting is not usually uniform throughout components such as gas turbine blades, as it depends on the gradients of both temperature and stress as a function of time. During service, the response to load across gas turbine blades is not uniform, therefore, differences in temperature and stress are experienced over the surface of the aerofoil, therefore resulting in variations in rafting direction. However, generally, the rafting of the $\gamma'$ precipitates is orientated perpendicular to the blade axis, as it is along this axis the centrifugal stresses act. With this in mind it is possible to assess the remaining life of a component by the development and growth of rafting, including the width and size, which are dependent on the time of load applied at elevated temperatures$^{[39]}$.

### 2.5.2 Carbide Reactions

During heat treatments and service exposure MC decomposes slowly, giving rise to the formation of lower carbides, such as $M_{23}C_6$ and $M_6C$. However, elements such as Nb and Ta can significantly enhance the thermal stability of the MC carbides, therefore making it more difficult for them to break down. This major carbide reaction$^{[1,22,24]}$ in simplified form can be represented as:

$$MC + \gamma \rightarrow M_{23}C_6 + \gamma'$$  \[[2.2]\]
The γ' precipitates that are generated by the reaction can have a beneficial effect on the mechanical properties as they surround the carbides and the grain boundary, producing a relatively ductile, creep resistant layer. However, if the M23C6 produced has a cellular morphology instead of a blocky one, this can result in the reduction of the ductility. Generally the alloy is resistant to this if abundant γ' is formed at the grain boundaries.

2.6 High Temperature Oxidation and Corrosion

Operating temperatures within gas turbine engines are constantly being increased with the need to increase efficiency. The combination of these high temperatures and aggressive environments leads to increased rates of oxidation and hot corrosion attack upon the gas turbine components, which can significantly reduce their mechanical properties. It is therefore necessary to have sufficient oxidation and corrosion resistance at high temperatures in order to provide a satisfactory component life. In most modern situations Ni-based superalloys are coated to enhance the oxidation resistance.

2.6.1 Oxidation

Oxygen in the working environment interacts with the alloys at high temperatures to form oxides. Initial oxidation occurs when oxygen is adsorbed on the alloy surface, which results in the formation of individual oxide nuclei which grow laterally to form a continuous oxide film. Once this occurs the oxide film separates the metal from the oxidising environment, therefore the reaction can only proceed through solid state diffusion of the reactants through the film. The rate of scale growth is therefore dependent on the transport mechanisms of both the oxygen and metal through the oxide scale.

High temperature oxidation resistance of superalloys requires the formation of a chemically and mechanically stable oxide, which is able to inhibit the diffusion of damaging species into the substrate material. Ni-based superalloys and high temperature coatings usually form protective Cr2O3 and Al2O3 scales for oxidation resistance. The kinetics of Al2O3 formation are slower than that of Cr2O3, therefore in order to produce a Al-rich oxide scale of substantial thickness to provide adequate protection requires substantionally higher temperatures. Therefore, the Al2O3 scales generally provide better oxidation resistance at higher
temperatures and yield lower oxidation rates than \( \text{Cr}_2\text{O}_3 \). However, the ability of the alloy to produce these protective oxides is limited by the \( \text{Al} \) and/or \( \text{Cr} \) concentrations.

### 2.6.2 Hot Corrosion

Hot corrosion is defined as accelerated corrosion, resulting from the presence of salt contaminants such as \( \text{Na}_2\text{SO}_4 \) and \( \text{NaCl} \) that combine to form molten deposits, which in turn damages the protective surface oxides. Hot corrosion is divided into two forms, type I, known as high temperature hot corrosion and type II, known as low temperature hot corrosion. The development of these two forms can be affected by several parameters such as the alloy composition and thermomechanical condition, contaminant composition and flux rate, temperature and temperature cycle, gas composition and velocity, and erosion processes\(^{[40]}\).

#### Type I Hot Corrosion (HTHC)

Type I hot corrosion occurs mainly within the temperature range \( 850 - 950^\circ\text{C} \) and initiates with the condensation of fused alkali metal salts on the surface of the alloy. A cycle of subsequent chemical reactions takes place, initially attacking the protective oxide film and then continuing on to deplete the chromium element from the substrate material. With chromium depletion, oxidation of the base material is accelerated and a porous scale can form. The principal salt within HTHC is \( \text{Na}_2\text{SO}_4 \) due to its high thermodynamic stability and is formed during combustion within the engine, from sodium and sulphur, the latter being present in the fuel. Other impurities either in the fuel or in the air such as vanadium, phosphorous, lead and chlorides can combine with sodium sulphate to form a mixture of salts with a lower melting temperature, thus broadening the range of attack. Within the combustion gases, \( \text{NaCl} \) will react with sulphur dioxide and oxygen, forming \( \text{Na}_2\text{SO}_4 \) via the following reaction\(^{[40,41]}\):

\[
2\text{NaCl} + \text{SO}_2 + \text{O}_2 \rightarrow \text{Na}_2\text{SO}_4 + \text{Cl}_2
\]  

The initiation of HTHC is often attributed to failure of the protective layer, which allows the molten salt to access directly the substrate alloy. This failure may arise from thermal stresses, erosion-corrosion and chemical reactions. HTHC can be divided into four progressive stages from initial onset to failure\(^{[40]}\):

\[24\]
1. Slight roughening of the surface caused by some growth and localised breakdown of the oxide scale layer is evident. At this stage, Cr depletion in the substrate layer and loss of mechanical integrity are not observed.

2. The roughness of the surface is more marked as oxide layer breakdown continues. While chromium depletion commences at this stage, mechanical integrity is still not affected.

3. Oxidation of the base material has penetrated to significant depth, with obvious build up of scale. At this stage, mechanical integrity should be considered as jeopardised and the blades removed from the service. Progression to stage 4 will accelerate with or without the continued presence of sodium.

4. Catastrophic attack occurs by penetrating deeply into the blade while forming a large ‘blister’ of scale. Failure is likely to occur at this stage due to loss of structural material.

The macroscopic appearance of HTHC can be characterised in the majority of cases by severe peeling of the substrate alloy and by significant colour changes in the area of accelerated attack.

**Type II Hot Corrosion (LTHC)**

Type II hot corrosion is observed mainly within the lower temperature range of 650 - 800°C. LTHC typically forms pitting, resulting from the formation of mixtures of Na₂SO₄ and CoSO₄ with low melting temperatures\(^{[1]}\). CoSO₄ is a corrosion product from the reaction with Co-based alloys whereas the formations of Na₂SO₄-NiSO₄ eutectics are associated with Ni-based superalloys. The localised nature of the attack is related to failure of the scale as a result of chloride attack, thermal cycling or erosion.

2.7 **Protective Coatings for Ni-based Superalloys**

Coatings are used on superalloys to allow their use at high temperatures, together with inhibiting the interaction between the substrate material and the working environment. The environments in which superalloys are used are potentially damaging, causing metal dissolution due to the oxidation and corrosion reactions occurring at the surface of the substrate. This corrosion can consequently lead to a reduction in mechanical properties through the diffusion of harmful species into the alloy.
Coatings attain their protective action from the interaction/reaction with oxygen present in the working environment. This interaction with oxygen forms dense, adherent oxide scales on the surface of the coating, which as a result inhibits the diffusion of damaging elements such as oxygen, nitrogen and sulphur into the substrate material. To form this dense oxide layer the coating needs to be rich in elements that readily form protective oxide scales such as Al, Si and Cr, and therefore the life of the coating is related to its ability to form the protective scales and/or replace the scale as and when required. The thermal stability of coatings is deemed one of the key variables which can be expected to influence the performance capability. The durability of protective coatings is a crucial issue for gas turbines, since coating life mainly controls the refurbishment and/or replacement of many engine parts such as blades and vanes\textsuperscript{42,43}.

Extensive use of coatings on superalloy substrates is evident within gas turbine engines such as combustors, blades and vanes. These components operate within a highly aggressive environment; the constant increase in turbine inlet temperatures seen through the development of gas turbine engines has consequently caused excessive oxidation of the superalloys. This increase in damage due to oxidation of critical components led to the development of simple aluminide coatings. Hot corrosion of superalloy components became an apparent problem within the use of industrial and power generation gas turbines due to the fuels used containing harmful species such as sulphur and sodium. The aluminide coatings initially developed had proved effective in aircraft engines at inhibiting oxidation attack but proved futile in regard to inhibiting severe hot corrosion attack\textsuperscript{44}. This finding initiated the development of alternative systems such as MCrAIY coatings, aimed at reducing the damaged caused by hot corrosion.

With engine operating temperatures constantly being increased in order to increase efficiency, the need to cool the temperature of the superalloy components became apparent. This cooling of blades has been effectively achieved by the combination of internal cooling passages within the component together with the use of thermal barrier coatings, which utilise a ceramic layer on top of the coating.

It has been identified that various compositions of coating and application processes are required to meet the needs of varying applications. There are several factors that are seen to affect the coating selection are as follows;
• Protection against working environment – application of component
• Effects of coating/process on mechanical and thermal properties of the superalloy
• Effects of interdiffusion between coating and substrate during high temperature exposure
• Geometry of components together with coating process
• Cost of coating and coating lifetime, which in industry is deemed as the controlling factor.

There are two main coating types; diffusion coatings and overlay coatings. In the case of diffusion coatings, the outer layer of the substrate is altered by the contact and interaction with certain chemical species such as Al and Cr. Overlay coating systems involve the deposition of metallic species which create a protective layer on the substrate surface. The typical microstructures of a diffusion and an overlay coating are illustrated in Figure 2.8.

2.7.1 Diffusion Coatings

Diffusion coatings improve resistance to high temperature oxidation and corrosion of the alloy substrate by enriching the surface with elements such as Al, Cr and Si. The most widely used diffusion coatings are the aluminide coatings, in which Al is diffused into the alloy surface.

Aluminide coatings are protected by an Al₂O₃ scale, which is produced by oxygen combining with the Al within the coating at the surface and forming the dense protective oxide. If the oxide scale cracks due to thermal cycling, the procedure repeats and the Al diffuses to the surface to reform the protective scale. The coatings degrade both due to Al consumption at the coating surface, as a result of the growth of the oxide, and also due to the interdiffusion
between the coating and the substrate. As Al is depleted from the coating by diffusion the \( \beta \)-
NiAl matrix phase gradually transforms to \( \gamma' \)-Ni\(_3\)Al and finally to \( \gamma \)-Ni solid solution\(^{[1,22]} \). Once the Al levels falls below 4-5 wt.\% it is no longer considered to be sufficient for the formation of protective \( \text{Al}_2\text{O}_3 \), therefore oxidation of the coated superalloy occurs more rapidly\(^{[1]} \).

The corrosion resistance and mechanical properties of diffusion coatings have a strong dependence on the substrate composition. It has been reported that the Al content within the substrate affects the rate at which the Al diffuses out of the coating to produce its protective oxide layer and hence its service life. Numerous investigations have been carried out which show that certain elements within the substrate diffuse into the coating during service exposure, and are known to either enhance (Cr, Hf and Ta) and degrade (Ti, V, W and Mo) the oxidation resistance\(^{[1]} \). When aluminide coated superalloys are exposed to high temperature, interdiffusion occurs. The solubility of elements W, Re, Mo and Cr are lower in the Al rich phase \( \beta \) and \( \gamma' \) than in \( \gamma \), therefore precipitation of TCP phases can also occur. The presence of plate-like TCP precipitates below the interdiffusion zone has been reported to have a detrimental influence on the mechanical properties of the superalloy\(^{[45]} \). Their occurrence increases the risk of anisotropic embrittlement. The formation of these precipitates also causes local depletion of elements that provided solid solution hardening within the substrate.

**Modified Aluminide Coatings**

Modified aluminide coatings are produced by depositing an interlayer prior to the aluminising process. Alloying additions that have been utilised include Cr, Si, Ta, various rare earth metals and precious metals. Additions of chromium have been reported to offer improved performance against low temperature corrosion in industrial and marine turbines burning high sulphur containing fuels\(^{[10,44,46,47]} \). It has also been concluded that silicon modified aluminide coatings have higher phase stability at service temperatures together with improved hot corrosion resistance. The disadvantages, however, include a reduction in the ductility and chemical incompatibility with the substrate materials\(^{[48,49]} \). In comparison to other types of coatings these modified aluminide coatings have received renewed interest, as they offer an economic alternative to the expensive equipment of electron beam physical vapour deposition and plasma spraying used to deposit the overlay coatings.
The most significant improvement to high temperature oxidation and hot corrosion performance was reported with the development of platinum modified aluminide coatings\([46,50,51,52]\). Pt is used within these coatings to significantly improve the high temperature oxide and hot corrosion performance\([46]\), although there are discrepancies in the literature on how this is achieved. Authors have reported improved oxide adherence, whereas other works have reported that Pt excludes refractory transition elements such as Mo, V and W from the outer coating layer\([44,53,54]\), which promotes selective oxidation of Al, thus decreasing the oxide growth rate and the onset of oxide spallation. Pt has also been reported to have an effect on the stability of matrix phases within the coating such as the rate by which β-NiAl transforms to the Al rich \(\gamma'\) - Ni\(_3\)Al phase beneath the oxide scale\([55]\). Furthermore Pt has been observed to reduce the amount of Al lost by interdiffusion with the substrate compared to simple aluminide coatings\([56]\). Active element additions to diffusion coatings have also been investigated and present conflicting findings. Additions of Y to diffusion coatings have been reported to increase the oxidation resistance\([57]\). However in high activity Pt aluminide coatings both Y and Hf additions present a lower oxidation resistance than an untreated coating\([58]\).

**Coating Processes**

Diffusion coatings have been applied to gas turbines components using a variety of techniques which include pack cementation and more recently chemical vapour deposition, however, technically pack diffusion coatings may be considered as being produced by a CVD process carried out with the aid of a powder mixture\([59]\). Pack cementation is regarded as the traditional process used to apply diffusion coatings to turbine components and is still extensively used today. However, the disadvantage of the pack cementation process is that it can cause blockage of cooling holes within components which then requires removal after the coating process\([44]\).

**Pack Cementation**

The reactant used consists mainly of an Al containing powder together with various additives, which are chemical activators and inert fillers. The reactant is then heated within an inert atmosphere to prevent oxidation together with the component requiring the coating. The metal powder and activator react, thus forming a vapour which reacts with the surface of the
component, depositing Al on the surface and forming phases such as NiAl and Ni$_3$Al in the case of Ni-based superalloys. Under these conditions, the following equilibrium reactions can be found, where M is usually Al or Cr:

\[
\begin{align*}
MCl_2 & \leftrightarrow M + Cl_2 \\
\text{or} \quad MCl_2 + H_2 & \leftrightarrow M + 2HCl
\end{align*}
\]

The factors controlling the reaction are the concentrations of the reactant and the temperature at which the reaction occurs. The morphology of the coating is thus controlled by the time held at temperature and the resultant heat treatment conducted following the coating process$^{[48,60]}$.

In the case of diffusion coatings, the activity of Al maintained at the surface of the substrate defines two categories of deposition methods; outward ‘low activity’ and inward ‘high activity’ diffusion. An inward coating occurs when the activity of the aluminium is much greater than that of the nickel with the substrate therefore the aluminium diffuses into the substrate at a greater rate than the nickel outwards. This inward diffusion of aluminium results in the formation of the brittle Ni$_2$Al$_3$ phase. The diffusivity of Al is reported to be very high within this phase, therefore substantial amounts of Al can diffuse further into the substrate$^{[44,61]}$. Following the aluminisation process the component is heat treated so that Ni diffuses outwards through the coating and the Ni$_2$Al$_3$ phase transforms to $\beta$ - NiAl. This step is usually combined with the heat treatment required to recover the mechanical properties of the substrate. Due to the inward growth of high activity coatings, slow diffusing alloy elements such as W, Re, Ta, Mo and Cr may be entrapped within the coating$^{[61]}$. An outward coating occurs under the opposite conditions, allowing the nickel from the substrate to diffuse outwards at a faster rate than the aluminium inwards, and results in the direct formation of a nickel rich NiAl layer. This type of coating is usually produced at a higher temperature than the inward grown coatings. The major difference in the outward coating is that there is a lower amount of slowly diffusing elements within the coating. The typical morphologies produced from either coating type are illustrated in Figure 2.9.
These two types of coatings both contain a $\beta$-NiAl phase in which the solubility of substrate elements is small. This rejection of elements results in the precipitation of various carbides and intermetallic phases, such as topologically closed packed (TCP) phases within the interdiffusion zone between the outer coating layer and substrate. The characteristics of the coating change with the varying compositions and grain structures within the Ni-based superalloy, in particular respect to the phase associated with the interdiffusion zone.

**Chemical Vapour Deposition (CVD)**

Within the chemical vapour deposition (CVD) process a vapour of specific composition is introduced into a chamber containing the component to be coated and subsequently reacting with it under controlled conditions. The main advantages of this process is the ability to uniformly coat extremely complex geometries, an example of which are the internal cooling passages within turbine blades\(^{[44,62]}\). In addition the chemistry of the coating can be carefully controlled in the CVD process, therefore enabling additional elements to be incorporated into the coatings at precise levels\(^{[63]}\).

### 2.7.2 Overlay Coatings

Overlay coatings involve the deposition of metallic species of a required composition which create a protective layer on the surface of the substrate, which typically exhibit a two phase
microstructure of $\beta$ and $\gamma$ depending on the composition and temperature. In contrast to diffusion coatings, these coatings do not require interdiffusion in order to produce the desired coating structure and composition. The presence of $\gamma$ increases the ductility of the coating, thereby improving the thermal fatigue resistance$^{[1]}$. The reduced substrate interactions, choice of corrosion resistant alloy and the ability to deposit thicker coatings results in greater design flexibility. High temperature exposure results in depletion of the Al, both to the thermally grown oxide formed on the surface of the coating and to the substrate by interdiffusion as for aluminide diffusion coatings. The $\beta$ phase reduces in stability as the Al concentration lowers, and is therefore often described as an aluminium reservoir, and the coating life is often measured in terms of depletion of $\beta$.

The composition of the M-Cr-Al (M being Ni and/or Co) system is selected to give a good balance between the corrosion resistance and coating ductility, whereas active element additions such as Y, Si, Ta and Hf can enhance oxide scale adhesion and decrease oxidation rates$^{[64-68]}$. The early MCrAlY coatings were based on cobalt. The CoCrAlY coatings proved to have adequate hot corrosion and oxidation resistance at low temperatures $\sim$ 650 - 800°C where type II hot corrosion is predominant. However, these coatings failed to meet ductility requirements for turbine blades in high performance commercial and military engines. NiCrAlY variants proved to have limited hot corrosion resistance, therefore a compromise was sought which led to the development of NiCoCrAlY coatings. These new coatings showed significantly improved ductility with the necessary oxidation and hot corrosion properties$^{[44,67]}$.

It was initially thought that the coating composition and performance would be independent of the substrate composition; however, this has subsequently been shown to be incorrect due to the high diffusion rates experienced within the materials used in these high temperature applications$^{[69]}$. The substrate composition affects the diffusion of the substrate elements, with increased time at temperature and can therefore affect the oxidation resistance of the overlay coating. The interdiffusion of elements across the coating/substrate interface can result in the formation of intermetallic TCP phases, carbides, voids and porosity, which may have a detrimental influence on the system's mechanical properties$^{[1]}$. Several methods have been investigated to improve the standard M-Cr-Al coating performance. These new coatings have been developed with additions of multiple active elements such as Y and Hf. The benefit of small additions of active elements to MCrAlY coatings are well documented$^{[63,67,68,70]}$. 
including the improvement of scale adhesion and the scale growth mechanism. The inclusion of elements such as Y and Hf have been reported to decrease the oxide growth rate, decrease the amount of voidage at the oxide/coating interface, leading to improved mechanical properties. Y and Hf can also act as sulphur getters within the coating system\(^7\). The incorporation of precious metal additions\(^4\) and compositionally graded coatings known as smart overlay coatings\(^7\) have also been investigated, as described in more detail below. Also the benefits of surface modifications have been examined using CVD, electroplating and re-processing with high-energy beams\(^7\).

**Smart Overlay Coatings**

One of the most recent technological advances in overlay coating technology is the development of ‘smart’ coatings, which are compositionally graded coating systems\(^7\). These coating systems attempt to address the problems associated with the differences in temperature experienced over the surface of an aerofoil. Temperatures are reported to vary from a maximum of the order of 1100°C at the leading and trailing edges to approximately 650°C in the centre of the airfoil surfaces and near the airfoil roots. Due to the wide range of temperatures experienced, the nature of the environmental degradation varies from oxidation through type I hot corrosion to type II hot corrosion. The smart coatings are required to respond to the local temperatures in such a way that they will form either an alumina or chromia protective layer as appropriate. Coatings most suitable for protection from type II hot corrosion are stated to be high in Cr content and low in Al, and for protection from type I hot corrosion roughly equal amounts of Cr and Al represent optimised compositions. The relative oxidation and corrosion resistance of the possible coating systems are illustrated in Figure 2.10.
In a smart overlay coating the oxidation and corrosion resistance at varying temperatures are achieved through a chemically graded coating structure enriched in Al and Cr. The coating developed by Nicholls et al\textsuperscript{[72]} comprises of a base coating of standard MCrAlY composition, which is pre-treated to form an intermediate layer rich in chromium, followed by an aluminising treatment producing an outer layer enriched in aluminium as illustrated in Figure 2.11.

In high temperature oxidation conditions the enriched aluminium layer within the coating produces a protective alumina layer, and the chromium rich layer behaves as a diffusion
barrier, thus limiting the loss of aluminium by diffusion into the coating and/or substrate alloy. Within the low temperature range that type II hot corrosion is predominant, the main form of protection comes from the chromium rich interlayer, which forms rapidly growing chromia protective scales at these temperatures.

**Coating Processes**

Overlay coatings have been deposited using a range of techniques, including plasma spraying and electron beam physical vapour deposition (EBPVD). Plasma spraying has the advantage that high deposition rates are possible with little change in composition, however, the limitations are that the coating process is 'line-of-sight'.

**Electron Beam Physical Vapour Deposition (EBPVD)**

The initial production method for depositing overlay coating was by the EBPVD technique\[44,48\]. However, due to the high cost of this process, alternative methods such as plasma spraying were developed. The EBPVD technique consists of vaporising an ingot of required coating composition with a focused electron beam. As the vapour comes in contact with the heated component, they react forming a solid phase that is deposited onto the component, as illustrated in Figure 2.12. The composition of the coating in most cases will be different to that of the starting ingot. Heat treatments are performed on the component after the coating process to allow small amounts of interdiffusion to take place between the coating and the substrate. This interdiffusion ensures a greater amount of bonding between the two surfaces. The EBPVD process results in a columnar coating structure that is typically orientated perpendicular to the substrate surface. The coating density can be improved by varying the substrate temperature or by bombarding the substrate with energetic particles that can break up the columnar structure\[48\].
**Plasma Spraying**

The plasma spraying process is most commonly used in atmospheric condition and referred to APS. This coating technique involves the injection of the required coating material in powder form into a high temperature plasma gas stream. On contact with the plasma the powdered coating material will melt and be accelerated towards the component’s surface, as illustrated in Figure 2.13.

As the molten metal contacts with the component it spreads out in a direction parallel to the surface, creating 'splat-like' morphologies. The adhesion of the coating is primarily mechanical, which then requires post coating heat treatments to ensure good adherence. Sprayed coatings typically have a percentage of porosity and oxide particles included between the molten metal deposits. Carrying out the plasma spraying process in a reduced pressure, known as low-pressure plasma spraying (LPPS), or in a vacuum chamber (VPS), permits close
control of the gaseous environment. This removes the possibility of oxide defects within the coating and undesirable gas/metal reactions and also permits high particle velocities giving improved adhesion and higher densities. A high velocity oxygen fuel (HVOF) spraying process has been developed to produce extremely high spray velocities, which in turn increases the density and strength of the coating. In addition HVOF coatings have demonstrated lower residual stresses which enable thicker coatings to be applied to the substrate alloys.

2.7.3 Thermal Barrier Coatings

A thermal barrier coating system is defined as a multilayer coating system consisting of an insulating ceramic layer (TBC) and a metallic inner layer known as a bond coat. The function of the ceramic layer is to insulate the substrate material from temperatures which they are unable to withstand. The use of thermal barrier coatings has resulted in significant improvements in the life of service components. The temperature gradient created through the coating can depend on several factors such as the thermal conductivity of the ceramic and the coating thickness. At high temperature exposure, oxygen easily penetrates the low density ceramic layer reacting with the bondcoat, which oxidises and produces a protective thermally grown oxide (TGO) at the interface between the ceramic layer and the bondcoat. The role of the bondcoat is also to ensure proper adherence of the coating system and to accommodate the strains that are built up by the mismatch in thermomechanical properties between the substrate and the ceramic topcoat. Within the aero industry TBCs have a typical thickness of ~ 125 μm, whereas industrial and automotive applications may require much thicker coatings up to 400 μm thick\[^76\]. It has been recognised that for the ceramic to be efficient in the role as a thermal barrier coating it must meet fundamental requirements such as:

- High melting point,
- Low density,
- High surface emissivity
- High thermal shock resistance,
- Low vapour pressure,
- Resistance to oxidation or chemical environment,
- Low thermal conductivity,
- High coefficient of thermal expansion,

37
• Resistance to gaseous and particulate erosion

When these requirements are all considered, few ceramics meet the extensive criteria. Stabilised zirconium oxide (ZrO₂) is the optimum material used for the thermal barrier coating due to its very low thermal conductivity and relatively high coefficient of thermal expansion (CTE). Despite having a high coefficient of thermal expansion, partially stabilised ZrO₂ is regarded as having excellent thermal shock resistance due to micro cracking and transformation toughening [76]. Over the years, several other ceramics have been investigated for use as thermal barrier coatings or anticorrosion coatings within engines. These include 3Al₂O₃-2SiO₂ (mullite), Ca₂SiO₄, MgAl₂O₄, CaTiO₃, ZrSiO₄ and ZrTiO₄ [76,77], however, these materials have not been developed to the extent that would rival the use of ZrO₂. Pure ZrO₂ transforms from the monoclinic to tetragonal phase at approximately 1180°C, and from the tetragonal to cubic phase at approximately 2370°C, as illustrated within the phase diagram in Figure 2.14.

Figure 2.14 Phase diagram of the ZrO₂–YO₁.₅ system illustrating the various phase region [77]

A volume change of 4 – 6% is known to occur as a result of these phase transformations. This volume change experienced results in severe spalling when thermally cycled through the monoclinic-tetragonal transformation temperature. In order for ZrO₂ to be used within engine
applications, it is required to be stable from the high temperature tetragonal form down to ambient temperatures. The oxides that are currently used to stabilise ZrO₂ include CaO, MgO, Y₂O₃, CeO₂ and the majority of the rare earth oxides. Quantitative comparisons have proved difficult between the various stabilising oxides; however, it is known that the stabilising effect occurs to different degrees together with different stabilising mechanisms⁷⁶,⁷⁸.

**Coating Processes**

The two principle means at present for applying TBCs are plasma spraying and electron beam physical vapour deposition (EB-PVD). Each method produces its own largely distinctive structure in the resultant TBC.

**Plasma Spray Deposition**

The bonding mechanism of these coatings is largely mechanical, with a coating structure being typically laminar. A schematic diagram showing a cross section of a typical plasma-sprayed thermal barrier coating is given in Figure 2.15. As in the overlay coating process, porosity can be introduced into the structure as the molten droplets splat down, the amount of which within the zirconia layer is critical in determining the heat insulation, thermal shock, thermal cycle tolerance and erosion resistance of the TBC. Standard plasma sprayed coatings have a typical porosity of 10 – 20 %. In general, the more porous the zirconia layers the better the heat insulation and spalling resistance, whereas a reduced amount of pores within the layers give improved erosion resistance. Lack of reproducibility has been a traditional problem in the plasma spraying of zirconia TBCs. It has been suggested that the characteristics of the individual plasma spray powders are the cause of this variability. Experiments have been carried out to determine how the physical, crystallographic and chemical makeup of the powders influences the thermal cycle life and erosion resistance of the coatings. The results illustrated that the most critical factors were determined to be the particle size and its uniformity, the chemical homogeneity of the powder and the method of manufacture⁴¹,⁴⁸.
Figure 2.15 (a) Schematic diagram and (b) representative micrograph, illustrating the structure of plasma sprayed zirconia thermal barrier coatings.\textsuperscript{[76,78]}

\textit{Electron Beam Physical Vapour Deposition (EBPVD)}

Zirconia thermal barrier coatings can also be deposited by an EB-PVD process. Thermal barrier coatings produced by this process are characterised by their columnar structure, as illustrated in Figure 2.16. During the process of EB-PVD a thin, dense $\text{ZrO}_2$ layer forms between the bond coat surface and the upper columnar zirconia structure. This phase grows under oxygen-deficient conditions at the start of $\text{ZrO}_2$ deposition, the thickness of which is controlled by how quickly the oxygen bleed is activated. The most effective adhesion between the TBC and the bond coat is obtained when the bond coat surface is smooth or preferably polished, in contrast to plasma sprayed TBCs, which require a rough bond coat surface. This implies that the adhesion of EBPVD TBCs involve a chemical bond rather than a mechanical one. The coating process is followed by high temperature post coating heat treatments, which act to improve and strengthen the bond quality.

The major advantage of EBPVD thermal barrier coatings is in their columnar structure. The individual columns prevent the build up of tensile stresses and match the coefficient of thermal expansion differences between the TBC and the base metal. The nature of the EBPVD columnar structure offers better resistance than the plasma sprayed laminar structure to erosion type failure. The main disadvantage of the columnar structure is that it has a higher thermal conductivity compared to the plasma sprayed TBCs, therefore exposing the components to higher temperatures. EBPVD TBCs are reported to be more suitable for applications on rotating components as they have a greater strain tolerance\textsuperscript{[44]}. 
Failure Mechanisms of Thermal Barrier Coatings

In general, the final failure of TBCs is related to fracture and spallation in or close to the interface between the ceramic topcoat and the bondcoat\(^{1,78-81}\). To obtain an accurate prediction of the life expectancy of a coating, it is necessary to understand the nature of the failure. Failure mechanisms are very complex and usually are a combination of several mechanisms, some of which are:

- **Mismatch in thermo-mechanical properties:** Heating and cooling give rise to thermal stresses due to the mismatch in physical and thermal properties between the different zones in the coating system. After several cycles, propagating cracks may have reached a stage where the top coat spalls off\(^{82}\).

- **Sintering of the topcoat:** At very high temperatures sintering of the ceramic microstructure occurs, this increases the thermal conductivity of the TBC and can increase the total amount of elastic energy stored in the coating, which provides additional driving force for cracking and spalling of the coating\(^{1}\).

- **Chemical degradation of the ceramic:** This degradation can occur when the zirconia is destabilised due to contact with corrosive species such as molten Na\(_2\)SiF, SO\(_3\) and Na\(_2\)SO\(_4\)\(^{78,79}\). This means that the equilibrium phase tetragonal zirconia is formed, which is in turn transformed into monoclinic zirconia upon cooling, causing detrimental volumetric stresses.

- **Bondcoat oxidation:** The thermally grown oxide (TGO) has a major influence on TBC durability\(^{82-85}\). This alumina scale is needed for protection, but it also develops swelling...
stresses during growth and can cause large residual compressive stresses during cooling due to the thermal expansion misfit with the substrate

- **Surface roughness of TGO:** The surface roughness at the topcoat/bondcoat interface has been considered. A non-flat interface as produced in plasma sprayed TBCs combined with microcracks will favour irregular oxidation at the interface, which further accelerates the cracking process. The microcracks eventually coalesce into buckling or spallation cracks\(^{[85-87]}\).

- **Spinel formation at TGO:** It has been shown that Ni, Co and Cr rich spinel oxides are formed in the vicinity of the TGO region. These spinels show poorer mechanical properties than alumina and may induce premature cracking.

- **TBC erosion:** Particle erosion causes continued wearing away of the coating, and with large particles cracks can occur in the coating and along the interface between the TBC and the bond coat\(^{[88]}\).

---

### 2.8 Summary

This chapter has reviewed the history of superalloys, illustrating the major developments in alloy composition and processing techniques. Major phases that can form within the microstructure during heat treatment or service exposure conditions have been discussed. The types of coatings and coating processes which have been developed to provide protection for superalloy substrates at high temperatures and their effect on microstructural evolution have also been reviewed.
3.1 Introduction

This chapter presents details of the materials used in this work and reviews the experimental methodology followed. A variety of experimental techniques have been utilised for the microstructural characterisation of the coated superalloys, with particular interest focused on the interdiffusion between the coating and substrate. Techniques used include field emission gun scanning electron microscopy (FEGSEM) and energy dispersive x-ray (EDX) analysis, together with the use of a dual beam focused ion beam / FEGSEM to make site specific samples for high resolution analysis in the transmission electron microscope (TEM). Furthermore, thermodynamic equilibrium calculations were carried out in order to predict the amount and chemical composition of the phases occurring at equilibrium within the multicomponent systems as a function of temperature and composition.

3.2 Materials

3.2.1 Substrate Alloys

The substrate materials investigated within this study were three CMSX4 alloys of slightly different compositions. CMSX4 is a second generation Re-containing Ni-based single crystal superalloy that has been successfully used in numerous aero and industrial gas turbine applications. The three CMSX4 alloys are defined by their differing amounts of carbon, with the bulk of the alloying elements being virtually identical. The 'standard' CMSX4 contains carbon in the range of 0.0021 - 0.0029 wt.% and was supplied by both RWE npower (Snp) and Howmet (Sh). The differing process parameters of these companies used during the alloy production will result in very slight compositional differences, but are not likely to be large enough to affect the resultant microstructure. The CMSX4 HC, again supplied by RWE npower, contains a larger amount of carbon at 0.0229 wt.%. Full chemical compositions of the alloys are presented in Table 3.1.
The samples were all provided in the form of cylindrical bars of various lengths, with the diameter dependent on the CMSX4 variant. The 'standard' CMSX4 supplied by RWE npower (Snp) and Howmet (Sh) had diameters of 13 and 12 mm respectively, whereas the CMSX4 HC sample bars had a 10 mm diameter. The samples were supplied in the 'as-received' condition, which involved a commercial high temperature solution heat treatment, followed by aging at a lower temperature before being air-cooled. The details regarding the solution heat treatments received by the samples are presented in Tables 3.2 - 3.4. All samples provided had a longitudinal crystal orientation of <001> and had met acceptance standards such that the primary crystal orientation was less than 15 degrees off the longitudinal axis of the sample.

<table>
<thead>
<tr>
<th>Elements (wt.%)</th>
<th>'Standard' CMSX4 (Snp)</th>
<th>'Standard' CMSX4 (Sh)</th>
<th>CMSX4 HC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>Balance</td>
<td>Balance</td>
<td>Balance</td>
</tr>
<tr>
<td>Al</td>
<td>5.63</td>
<td>5.64</td>
<td>5.64</td>
</tr>
<tr>
<td>Ti</td>
<td>1.02</td>
<td>1.03</td>
<td>1.01</td>
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<tr>
<td>Cr</td>
<td>6.4</td>
<td>6.4</td>
<td>6.4</td>
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<tr>
<td>Co</td>
<td>9.6</td>
<td>9.6</td>
<td>9.6</td>
</tr>
<tr>
<td>Mo</td>
<td>0.59</td>
<td>0.59</td>
<td>0.6</td>
</tr>
<tr>
<td>Ta</td>
<td>6.5</td>
<td>6.5</td>
<td>6.5</td>
</tr>
<tr>
<td>W</td>
<td>6.4</td>
<td>6.4</td>
<td>6.4</td>
</tr>
<tr>
<td>Re</td>
<td>2.9</td>
<td>2.9</td>
<td>2.9</td>
</tr>
<tr>
<td>Hf</td>
<td>0.09</td>
<td>0.10</td>
<td>0.19</td>
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<tr>
<td>Fe</td>
<td>0.051</td>
<td>0.045</td>
<td>0.024</td>
</tr>
<tr>
<td>Nb</td>
<td>0.05</td>
<td>0.03</td>
<td>0.05</td>
</tr>
<tr>
<td>C</td>
<td>0.0021</td>
<td>0.0029</td>
<td>0.0229</td>
</tr>
<tr>
<td>Si</td>
<td>0.02</td>
<td>0.02</td>
<td>0.01</td>
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<tr>
<td>Zr</td>
<td>0.002</td>
<td>0.003</td>
<td>0.0014</td>
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<tr>
<td>B</td>
<td>0.002</td>
<td>0.002</td>
<td>0.0093</td>
</tr>
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</table>

Table 3.1 Chemical composition of the three CMSX4 variants investigated in this research
<table>
<thead>
<tr>
<th>Heat Treatment Stage</th>
<th>Details</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solution Heat Treatment</td>
<td>Heat to 1277°C - hold for 120 min</td>
</tr>
<tr>
<td></td>
<td>Heat to 1288°C - hold for 180 min</td>
</tr>
<tr>
<td></td>
<td>Heat to 1296°C - hold for 180 min</td>
</tr>
<tr>
<td></td>
<td>Heat to 1304°C - hold for 180 min</td>
</tr>
<tr>
<td></td>
<td>Heat to 1313°C - hold for 120 min</td>
</tr>
<tr>
<td></td>
<td>Heat to 1316°C - hold for 120 min</td>
</tr>
<tr>
<td></td>
<td>Heat to 1318°C - hold for 120 min</td>
</tr>
<tr>
<td></td>
<td>Heat to 1321°C - hold for 120 min</td>
</tr>
<tr>
<td></td>
<td>Rapid gas fan quench</td>
</tr>
<tr>
<td>Ageing 1</td>
<td>1140°C for 120 min - air cool</td>
</tr>
<tr>
<td>Ageing 2</td>
<td>870°C for 1200 min - air cool</td>
</tr>
</tbody>
</table>

Table 3.2 Details of pre-service heat treatments applied to the ‘standard’ CMSX4 samples supplied by RWE npower

<table>
<thead>
<tr>
<th>Heat Treatment Stage</th>
<th>Details</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solution Heat Treatment</td>
<td>Heat to 1312°C - hold for 360 min</td>
</tr>
<tr>
<td>Ageing 1</td>
<td>1140°C for 120 min - air cool</td>
</tr>
<tr>
<td>Ageing 2</td>
<td>870°C for 1200 min - air cool</td>
</tr>
</tbody>
</table>

Table 3.3 Details of pre-service heat treatments applied to the ‘standard’ CMSX4 samples supplied by Howmet
### Heat Treatment Details

<table>
<thead>
<tr>
<th>Stage</th>
<th>Details</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stress Relief in Air</td>
<td>Heat evenly to 1218°C - hold for 120 min</td>
</tr>
<tr>
<td></td>
<td>Air cool to room temperature</td>
</tr>
<tr>
<td>Solution Heat Treatment</td>
<td>Heat to 954°C in 90 min</td>
</tr>
<tr>
<td></td>
<td>Back fill furnace with argon (99.9% purity)</td>
</tr>
<tr>
<td></td>
<td>Hold at 954°C for 90 min</td>
</tr>
<tr>
<td></td>
<td>Heat to 1052°C in 20 min - hold for 120 min</td>
</tr>
<tr>
<td></td>
<td>Heat to 1202°C in 30 min</td>
</tr>
<tr>
<td></td>
<td>Heat to 1302°C in 250 min - hold for 510 min</td>
</tr>
<tr>
<td></td>
<td>Gas fan cool to less than 1082°C at a minimum 27°C/min</td>
</tr>
<tr>
<td>Ageing 1</td>
<td>1140°C for 120 min - argon fan quench</td>
</tr>
<tr>
<td>Ageing 2</td>
<td>871°C for 1200 min - argon fan quench</td>
</tr>
</tbody>
</table>

Table 3.4 Details of pre-service heat treatments applied to the CMSX4 HC samples

### 3.2.2 Coatings

The coatings investigated in this study included both MCrAlY overlay coatings and modified diffusion coatings. The overlay coating was a NiCoCrAlY type coating denoted Amdry-997, the nominal composition of which is given in Table 3.5. The coating was applied to the ‘standard’ CMSX4 samples supplied by RWE npower by a low pressure air plasma spray (LP-APS) process. Prior to coating, the samples were cleaned using a very light grit blasting, then shot peened with alumina. Following the coating procedure the specimens were given an additional standard diffusion heat treatment as detailed in Table 3.6, to establish increased adhesion between the coating and substrate layers. The MCrAlY coatings were approximately 360 μm thick, although it was noted that there was some variability around the surface of the samples.

<table>
<thead>
<tr>
<th>Elements (wt.%), Amdry-997</th>
<th>Ni</th>
<th>Co</th>
<th>Cr</th>
<th>Al</th>
<th>Ta</th>
<th>Y</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bal</td>
<td>23.0</td>
<td>20.0</td>
<td>8.5</td>
<td>4.0</td>
<td>0.6</td>
<td></td>
</tr>
</tbody>
</table>

Table 3.5 Nominal composition of Amdry-997 NiCoCrAlY overlay coating
### Heat Treatment Stage Details

<table>
<thead>
<tr>
<th>Heat Treatment stage</th>
<th>Details</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diffusion Heat Treatment</td>
<td>Heat to 1140°C - hold for 4 hours followed by air cooling</td>
</tr>
<tr>
<td>Ageing</td>
<td>Heat to 870°C - hold for 20 hours followed by air cooling</td>
</tr>
</tbody>
</table>

Table 3.6 Details of post-coating heat treatment received by Amdry-997 coated CMSX4

Two commercial Pt modified aluminide diffusion coatings have also been investigated during this research, RT22 and CN91. Both of these coatings were manufactured by Chromalloy UK. The RT22 coating was applied to the CMSX4 HC material. The process involves electrolytic deposition of Pt onto the surface approximately 7 ± 2 μm thick, followed by a diffusion heat treatment of 1 hour at ~ 1010°C. The aluminisation was performed by a pack cementation process, believed to be for 20 hours at ~ 875°C [89]. Finally the samples were heat treated between 800 and 900°C for 16 hours in order to restore the required substrate microstructure.

The CN91 coating was applied to the ‘standard’ CMSX4 material supplied by Howmet (Sh). The process involved similar electrodeposition of Pt but to a thickness of ~ 5 μm, followed by a diffusion heat treatment in a vacuum for 1 hour at ~ 1100°C. The vapour phase aluminising is believed to be conducted at 1080°C for 5 hours and, as in the case of the RT22 coating, it is likely this was followed by a commercial heat treatment.

### 3.3 Heat Treatment

A heat treatment programme was carried out to enable systematic microstructural characterisation of the coated systems as a function of time and temperature. The temperatures were chosen to be representative of the service conditions experienced by industrial turbine blades. The NiCoCrAlY coated CMSX4 specimens were isothermally exposed in a laboratory furnace air environment at temperatures of 850, 900, 950, 1000 and 1050°C for times of 190, 500, 1000, 2000, 5000 and 10000 hours, followed by cooling in air. Exact details of heat treatments are provided in Table 3.7, in which the coloured ticks represent the samples analysed in detail during this investigation.
The Pt-modified aluminide coated CMSX4 samples were isothermally exposed in a combustion gas atmosphere at Cranfield University. The dry combustion gas consisted of 1% argon, 3.4% CO$_2$ and 15% O$_2$ with the balance being N$_2$ by volume percentage. Steam at approximately 6 volume % was also added to the gas via a bubbling water bath. The combustion gas was introduced to simulate the environment in which industrial gas turbine blades are operated. The samples were isothermally exposed at temperatures of 850, 900, 950, 1000 and 1050°C for times of 1000, 2000, 4000 and 10,000 hours, followed by cooling in air. It should be noted that the coated samples were monitored for weight gain every 1000 hours which involved cooling to room temperature. Exact details of heat treatments are provided in Table 3.8, in which the red coloured ticks represent the samples analysed in detail during this investigation. All RT22 coated CMSX4 samples up to 10,000 hours were analysed, however for the CN91 coated CMSX4 only the sample aged for 1000 hours at 1000°C was analysed for comparison purposes in this research.

<table>
<thead>
<tr>
<th>Temp (°C)</th>
<th>Time (hours)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>190</td>
</tr>
<tr>
<td>850</td>
<td>✓</td>
</tr>
<tr>
<td>900</td>
<td>✓</td>
</tr>
<tr>
<td>950</td>
<td>✓</td>
</tr>
<tr>
<td>1000</td>
<td>✓</td>
</tr>
<tr>
<td>1050</td>
<td>✓</td>
</tr>
</tbody>
</table>

Table 3.7 Heat treatment times and temperatures carried out on the NiCoCrAlY coated CMSX4 samples in a lab furnace in air

<table>
<thead>
<tr>
<th>Temp (°C)</th>
<th>Time (hours)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1000</td>
</tr>
<tr>
<td>850</td>
<td>✓ ✓</td>
</tr>
<tr>
<td>900</td>
<td>✓ ✓</td>
</tr>
<tr>
<td>950</td>
<td>✓ ✓</td>
</tr>
<tr>
<td>1000</td>
<td>✓ ✓</td>
</tr>
<tr>
<td>1050</td>
<td>✓ ✓</td>
</tr>
</tbody>
</table>

✓ RT22
✓ CN91
✓ Samples investigated in detail

Table 3.8 Heat treatment times and temperatures carried out on the RT22 and CN91 coated CMSX4 samples in a lab furnace in a combustion gas atmosphere
3.4 Metallographic Sample Preparation

After isothermal aging at varying times and temperatures, the specimen bars were cut perpendicular to the longitudinal axis using an Accutom 5 circular saw, equipped with a 357 CA Al₂O₃ blade. The samples were cut at speeds of 0.030 mm s⁻¹ using considerable amounts of cooling fluid, to avoid any recrystallisation which could take place within the single crystal material due to mechanical stresses induced by the saw. No evidence of recrystallisation was found within these samples.

Samples of approximately 13 mm in diameter and 5 mm thick, as shown in Figure 3.1, were produced for examination using metallographic techniques. The cylindrical cut sections were prepared by mounting in edge retaining conducting Bakelite, thus protecting the specimen’s edge and maintaining the integrity of the material’s surface features, which is important for examination of the interdiffusion phenomena associated with the coating/substrate interface. The samples were then ground on successively finer grades of silicon carbide paper from 320, 800, 1200 and 2400 grit to eliminate deep scratches, before final polishing with 6 and 1 μm diamond paste.

![Figure 3.1 Schematic diagram illustrating the samples produced from the cylindrical bars](image)

Within electron backscatter diffraction (EBSD) analysis the diffracted electrons escape from within only a few tens of nanometres of the specimen surface hence the specimen preparation for EBSD is critical to achieve good results. If material near the surface is deformed, or has any surface contaminant, oxide or reaction product layers present, then the EBSD pattern formation may be reduced. In addition to the standard sample preparation a final polishing stage is required to achieve a finish suitable for EBSD, with the use of a 0.02 μm Struers colloidal silica suspension for approximately 30 – 45 minutes.
3.5 Etching Techniques

The purpose of etching is to optically enhance microstructural features such as grain size and phase features in particular. Etching selectively alters these microstructural features based on composition, stress and/or crystal structure. The most common technique is known to be chemical etching, however, other techniques such as molten salt, electrolytic, thermal and plasma etching can be used for specialised applications\(^9\). Electrolytic etching is often used for specimens that do not respond well to basic chemical etching techniques; this technique requires the specimen to be conductive and is therefore limited primarily to metals. Molten salt etching is useful for grain size analysis for hard to etch materials such as ceramics as this technique takes advantage of the higher internal energy associated with grain boundaries. Plasma etching can be used for accurate etching of selected areas producing higher resolution patterns.

For this investigation electrolytic etching with an acidic solution was employed. Etching by this technique is conducted by setting up an electrochemical cell, in which an electrical potential is applied to the specimen by means of an external circuit. The electrolytic cell is set up by placing a platinum gauze on the inside rim of a beaker, which is then made to be the cathode within the system by connecting it to the negative terminal of the power supply. The sample is placed in the centre of the beaker and covered with the etchant solution such that both the sample and the gauze are submerged. The positive terminal is then connected to a stainless steel needle, and a direct electric current applied by means of the needle, thus setting the sample as the anode. The needle was placed at the edge of the specimen and a potential of 5 V was used and the surface was etched for 3 seconds at a time until a dendrite formation was observed within the substrate section of the sample. The chemical composition of the etchant used within the investigation was 10% orthophosphoric acid in water, as literature studies have shown this etchant promotes the dissolution of the \(\gamma\) phase within the material, whilst leaving the \(\gamma'\) particles in relief\(^9\). On completion of the etching process, the specimen was rinsed in clean water to remove the chemicals and stop any reactions from proceeding further. This was followed by rinsing in alcohol and drying in a stream of warm air. The use of alcohol speeds up the drying action and inhibits the formation of water spots.

It was observed through this procedure that preferential etching of the coating was occurring, thus producing an under-etched substrate and an over etched coating. Etching with the probe
connected to the centre of the sample also caused preferential etching of the coating and pitting within the substrate together with under etched features, therefore a compromise was established according to the features required for characterisation. Optical microscopy was unable to reveal significant features, other than the coating thickness on the samples therefore proved inappropriate for detailed characterisation. Consequently, the samples were primarily investigated using scanning electron microscopy (SEM).

3.6 Scanning Electron Microscopy (SEM)

The majority of the microstructural characterisation was carried out using scanning electron microscopy (SEM) because it enables the resolution of features not observable by means of optical microscopy. Images in the SEM were viewed either in secondary electron (SE) or backscatter (BSE) modes. Secondary electrons have low energies; therefore these detected electrons are created relatively near the sample surface, making them sensitive to topography. Backscattered electrons have greater energies than that of the secondary electrons and are considered to be electrons that are reflected or back-scattered out of the specimen. The high energy of these electrons allows them to escape from within a greater depth of the sample known as the interaction volume, illustrated in Figure 3.2. The backscattered electrons may be used to detect contrast between areas with different chemical compositions because the intensity of the signal is proportional to the atomic number of the elements within the sample. The higher the atomic number, the stronger the signal emitted, resulting in a brighter appearance.

The samples were prepared as described in Section 3.4 and electrolytically etched as described in Section 3.5 for examination in the scanning electron microscope (SEM). The SEM was employed to examine both the microstructures and phase compositions of the samples. The studies used a Leo VP 1530 field emission gun scanning electron microscope (FEGSEM) with an EDAX Pegasus energy dispersive x-ray (EDX) system. The SEM was generally operated at 20 kV with a varying working distance, typically 11 - 18 mm.
With EBSD analysis the sample was placed within the chamber of the SEM at a tilted angle of 70° so that a small angle, ~ 20°, is made between the incident electron beam and the sample. This ensures that the angular geometries are appropriate for both EBSD and EDX operating simultaneously. The operating voltage used was mainly 20 kV with working distances ranging from 16 to 18 mm. The FEGSEM is equipped with an EDAX EBSD system with OIM 4 DC and analysis packages. The software allows simultaneous chemical and crystallographic data to be collected during scans. Crystallographic data such as pole figure and image quality were subsequently analysed by the package OIM 4 Analysis.

3.6.1 Electron Backscatter Diffraction (EBSD)

The atoms in a material inelastically scatter a fraction of the electrons with a small loss of energy to form a divergent source of electrons close to the surface of the sample. Some of these electrons are incident on atomic planes at angles which satisfy the Bragg equation:

\[ n\lambda = 2d \sin \theta \]  

[3.1]

where \( n \) is an integer, \( \lambda \) is the wavelength of the electrons, \( d \) is the spacing of the diffracting planes, and \( \theta \) is the angle of incidence of the electrons on the diffracting plane. Backscattered electrons that satisfy Bragg’s law for a given plane emanate in diffraction cones from both the
front and back surface of the plane. When these cones intersect the phosphor screen sets of parallel lines are formed; these are known as the Kikuchi lines, as illustrated in Figure 3.3.

Figure 3.3 Schematic diagram showing the origin of Kikuchi lines produced in EBSD. These parallel lines formed are known as a Kikuchi band, and these bands are representative of the lattice planes in the diffracting crystal, as shown in Figure 3.4. Each Kikuchi band is defined by their distinct width and intensity which corresponds to the d-spacing of atoms in the crystal planes, and the symmetry of the crystal lattice is reflected in the pattern.

Electrons of all energies scattered from the sample form a background to the diffraction pattern, which reduces the contrast of the Kikuchi bands. The background intensity can be collected and then subtracted to improve the visibility of the Kikuchi bands. The background can be measured by scanning the beam over many grains in the sample to average out the diffraction information. The background can be removed by subtraction from, or division into, the original pattern. This proved difficult because the material under investigation was a single
crystal, resulting in only one diffraction pattern and therefore the background was determined over the grains within the coating in this case.

3.7 Transmission Electron Microscopy (TEM)

Transmission electron microscopy (TEM) is a technique that allows high resolution analysis of electron transparent samples, revealing internal microstructural features and crystallographic data. An image is formed when an electron beam passes through a sample of thickness typically less than 300 nm, and is projected onto a fluorescent screen. During the investigation a Jeol JEM-2000FX TEM operated at an accelerating voltage of 200 kV was used. The TEM was operated in bright field imaging mode. The brighter areas of the image show regions where the electrons have travelled through the sample without significant deflection and the darker areas are produced when large amount of electrons have been deflected as a result of increased sample thickness, density or specific microstructural features.

3.7.1 Sample Preparation

Samples were prepared for TEM directly from the bulk samples by focused ion beam (FIB) milling/welding using an fei Nova Nano Lab 600 dual beam (FEG-SEM/FIB) system. The (FIB) system uses a finely focused beam of gallium ions to raster over the surface of a sample. The Ga+ beam sputters a small amount of surface material which leaves the surface as either secondary ions or neutral atoms; continued removal of material is known as milling. The dual beam system combines a FIB and a FEGSEM column whereby the ion beam can be used for milling and the electron beam for imaging. This system has an advantage over more traditional techniques, such as carbon extraction replicas and thin foils, of being able to extract specific areas or particles for analysis. The 'insitu lift out' technique was used to provide site specific electron transparent cross sections of ~ 20 x 5.0 μm as illustrated in Figure 3.5. The area of interest and size of the sample are defined by the user. Initially a protective platinum layer was deposited onto the surface of the sample to prevent removal of material from the ion beam over the location of the sample to be extracted. This was followed by the milling of stepped trenched either side of the defined area of interest, and finally a U shaped cut was made underneath which results in the sample being attached by two small ligaments either side. The lift out of the sample was manually controlled with the use of an Omniprobe micromanipulator. The manipulator was then welded onto the sample with platinum, allowing
the sample to be cut away from the bulk sample using the ion beam. The manipulator was then used to transfer the sample to a copper TEM grid, to which it was finally welded, once again using platinum. Final thinning was carried out by FIB milling using progressively smaller currents from 1000 - 100 pA with inclination angles of 1-1.2° to the plane of the sample. This reduces the sample thickness to approximately 200 nm, ready for examination in the TEM.

Figure 3.5  Micrographs illustrating the steps of the ‘insitu lift out’ technique showing a) the defined area of interest on the sample’s surface, b) Stepped trenches milled either side of the defined area of interest, c) the ‘u’ shaped cut process in the detachment of the specimen, d) removal of the specimen with the use of a micromanipulator, e) attachment of specimen to copper grid and f) final thinning of specimen to the required thickness for examination in the TEM

3.7.2 Analysis of Diffraction Patterns

When an electron beam is directed on to a thin sample, some of the electrons pass through without interactions while others are scattered (change direction) due to interactions with crystallographic planes within the sample. The scattered electrons create an arrangement of
spots known as a diffraction pattern, the spatial distribution of which provides crystallographic data. Simple geometry is used to relate the distance between the spots to the values for the interplanar spacing (d) within a crystal lattice. The electrons which pass straight through the sample interact with the phosphor screen a distance L from the sample known as the camera length. The scattered electrons are assumed to diffract through an angle of 2θ by the crystal planes within the sample, as illustrated in Figure 3.6. The diffracted beam is displaced by a distance ‘r’ from the undiffracted beam resulting in the equation:

$$\tan 2\theta = \frac{r}{L}$$ \hspace{1cm} [3.2]

However, for small angles of θ it can be assumed that tan 2θ ≈θ, therefore;

$$2\theta = \frac{r}{L}$$ \hspace{1cm} [3.3]

Combining this relationship with Bragg's Law results in the following equation:

$$rd = L\lambda = \text{camera constant}$$ \hspace{1cm} [3.4]

where λ is the wavelength of the electrons and d is the spacing of the diffracting planes. The camera length (L) and wavelength (λ) are independent of the sample, therefore the spacing of the crystal planes can be determined by measuring ‘r’ on the diffraction pattern.

![Figure 3.6 Schematic diagram of the geometry related to diffraction pattern formation](image-url)
Diffraction patterns were analysed in addition to compositional data to assist in the identification of phases within the samples, in conjunction with known lattice parameters for reference phases. The diffraction patterns were produced using the selected area diffraction technique, which can be used on regions larger than 1 μm in diameter; below this, it is possible that electrons in the region around the area may contribute to the pattern\(^{92,94}\). The sample must accurately lie at eucentric height preventing it from moving laterally when tilted during acquisition of diffraction patterns. The diffraction patterns were analysed directly from the photographic film, to avoid any risk of dimensional distortion during reproduction.

The relationship \( rd = L \lambda \) was used for the determination of the spacing of the diffracting planes \((d)\), once the distance between the spots \((r)\) has been measured and the camera constant \((L \lambda)\) calculated.

1. The distance between three diffraction spots \((r)\) close to the centre of the pattern were measured, as illustrated in Figure 3.7. The distance was measured with the use of a ruler, with the average distance taken over several spots.

2. The acute angles between the 3 pairs of vectors \((\alpha, \beta \text{ and } \gamma)\) were measured

3. \(d_1, d_2 \text{ and } d_3\) were determined from equation 3.4, if the camera length is known

4. The crystal system, lattice parameters of which are presented in Table 3.9, calculated ‘d’ values and measured angles were inputted into the software program Practical Crystallography version 1.6 developed by H.K.D.H. Bhadeshia. This program determines any possible matches to the relevant phases present within the sample.

![Figure 3.7 Schematic diagram of a diffraction pattern illustrating the distances and angles measured to aid in phase identification](image-url)
<table>
<thead>
<tr>
<th>Phase</th>
<th>Crystal structure</th>
<th>Lattice parameters (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>σ</td>
<td>tetragonal</td>
<td>a_o = 9.12 - 9.3 and c_o = 4.72 - 4.86</td>
</tr>
<tr>
<td>μ</td>
<td>rhombohedral</td>
<td>a_o = 4.73 - 4.75 and c_o = 25.54 - 25.8</td>
</tr>
<tr>
<td>P</td>
<td>orthorhombic</td>
<td>a_o = 17.2, b_o = 4.86 and c_o = 9.2</td>
</tr>
<tr>
<td>α-Cr</td>
<td>body-centred cubic (bcc)</td>
<td>a_o = 2.88</td>
</tr>
<tr>
<td>α-W</td>
<td>body-centred cubic (bcc)</td>
<td>a_o = 3.16</td>
</tr>
<tr>
<td>M₂₃C₆</td>
<td>face-centred cubic (fcc)</td>
<td>a_o = 10.368</td>
</tr>
<tr>
<td>MC</td>
<td>face-centred cubic (fcc)</td>
<td>a_o = 4.4 - 4.7</td>
</tr>
</tbody>
</table>

Table 3.9 Crystal system and the corresponding lattice parameters used in the identification of phase

3.8 Energy Dispersive X-ray (EDX) Analysis

Energy dispersive X-ray (EDX) analysis was used in both the SEM and TEM to investigate and identify particles and phases by determining their chemical composition. The SEM is equipped with an EDAX Pegasus energy dispersive x-ray (EDX) system and the TEM with an Oxford instruments Inca ISIS system. The principles of EDX analysis are the same in both the SEM and TEM, such that when the sample is bombarded by an electron beam, electrons are excited from inner to outer shells. A resulting electron vacancy is subsequently filled by an electron dropping down from a higher shell, and an x-ray is emitted to balance the energy difference. Each of the elements present within the surface of the specimen is identified according to the energy possessed by the x-rays which it emits. The main difference between these two systems is the volume of the sample which is penetrated by electrons (known as the activation volume) and the volume of the specimen from which the detected X-rays originate, as illustrated in Figure 3.8. Consequently the number of electrons emitted from a thin sample for a given probe current is lower than that for a bulk sample and therefore chemical compositions of very small phases are likely to be more accurate from the TEM.
Limitations are also to be considered when using this analytical technique; low atomic weight elements such as carbon and oxygen can be detected due to the use of a super ultra thin polymer window detector available on both systems, however, accurate quantification cannot be achieved due to uncertainties in their mass absorption coefficients\[94\]. Overlap of different energy peaks can also occur, thus affecting the quantification of these elements. This problem mainly arose with the heavier elements such as W, Ta, Re and Hf. In the acquisition of chemical data, it has been proved that the software has an increased prospect of discriminating between the overlapping energy peaks where there is a greater amount of a particular composition. Within the resulting spectra it has been observed that the M lines are in close proximity to each other and hence prove difficult to separate, consequently the quantitative data needs to be determined from the L lines which have a greater separation, but which are lower in intensity. The main overlap problems occurred during the collection of chemical data in this work was related to the Ta and W Lα energy peaks as these are seen to overlap with each other, as well as overlapping with the Ni Kβ energy peak. Consequently the EDX elemental composition obtained in such cases within this investigation should therefore be handled with some caution.

### 3.8.1 EDX Maps and Matrix Scans

EDX elemental maps were performed within the SEM. The maps illustrated the variations in x-ray intensity, thus indicating the relative elemental concentrations within the pre-defined area.
Multipoint EDX analysis was performed on the samples in order to obtain chemical composition profiles for the main alloying elements across a pre-defined distance. The EDAX software stores the measured spectra and calculated concentrations for each point on the defined matrix. The matrix used consisted of 75 points in the y-axis and 4 in the x-axis which included the coating, interdiffusion zone and part of the substrate, as shown in Figure 3.9. Due to the number of phases present within these systems the x-axis points were averaged in order to reduce any variation in single elements as a direct result of the underlying phases, therefore providing an average elemental concentration across the coating, interdiffusion zone and into the substrate.

Figure 3.9 Typical matrix locations for EDX multipoint analysis producing compositional profiles across the coating and interdiffusion zone

3.9 Thermodynamic Equilibrium Calculations

Phase diagrams have been used for a long time to predict the equilibrium structure of binary, ternary and higher order systems, the experimental determination of which is a time-consuming and costly task. This becomes even more pronounced as the number of components increases. The ‘calculation of phase diagrams’ (CALPHAD) method reduces the effort required to determine equilibrium conditions in a multicomponent system.

Thermodynamic modelling is extensively used to predict the amount and chemical composition of the phases occurring within multicomponent systems as a function of temperature and composition. The main approach for determining thermodynamic equilibrium is through a Gibbs free energy minimisation process. When the Gibbs energy, $G$, of the system is at a minimum, the chemical potentials of the components are equalised throughout the
system. Equilibrium can therefore be computed by minimising the Gibbs energy of the system\cite{95,96}.

\[ G = \sum_{i=1}^{p} n_i G_i = \text{minimum} \quad \text{[3.5]} \]

where \( n_i \) is the number of moles, and \( G_i \) is the Gibbs energy of phase \( i \). A thermodynamic description of a system requires the assignment of thermodynamic functions for each phase. The CALPHAD method employs a variety of models to describe the temperature, pressure, and concentration dependencies of the free-energy functions of the various phases\cite{97}. The contributions to the Gibbs energy of a phase \( j \) can be written as:

\[ G^\phi = G^\phi_T(T,x) + G^\phi_p(p,T,x) + G^\phi_m(T_c, \beta_0, T, x) \quad \text{[3.6]} \]

where \( G^\phi_T(T,x) \) is the contribution to the Gibbs energy by the temperature \( (T) \) and the composition \( (x) \), \( G^\phi_p(p,T,x) \) is the contribution of the pressure \( (p) \), and \( G^\phi_m(T_c, \beta_0, T, x) \) is the magnetic contribution of the Curie or Néel temperature \( (T_c) \) and the average magnetic moment per atom \( (\beta_0) \). The temperature dependence of the concentration term of \( G^\phi \) is usually expressed as a power series of \( T \).

\[ G = a + b \cdot T \cdot c \cdot T \cdot \ln(T) + \sum d_n \cdot T^n \quad \text{[3.7]} \]

where \( a, b, c, \text{ and } d_n \) are coefficients, and \( n \) are integers. To represent the pure elements, \( n \) are typically 2, 3, -1, and 7 or -9\cite{98}. This function is valid for temperatures above the Debye temperature; in each of the equations in the following models describing the concentration dependence, the \( G \) coefficients on the right-hand side can have such a temperature dependence. Frequently, only the first two terms are used for the representation of the excess Gibbs energy. For multicomponent systems, it has proven useful to distinguish three contributions from the concentration dependence to the Gibbs energy of a phase, \( G^\phi \).

\[ G^\phi = G^0 + G^{ideal} + G^{ex} \quad \text{[3.8]} \]

The first term, \( G^0 \), corresponds to the Gibbs energy of a mechanical mixture of the constituents of the phase; the second term, \( G^{ideal} \), corresponds to the entropy of mixing for an ideal solution, and the third term, \( G^{ex} \), is the so-called excess Gibbs energy term.
A variety of software packages can be used for the calculation of phase diagrams, using Gibbs free energy minimisation. The most frequently used software packages are MTDATA\textsuperscript{1} and Thermo-Calc\textsuperscript{II}, although all of these software packages can be used for the calculation of phase equilibria, their features and user interfaces differ.

The thermodynamic equilibrium calculations within this investigation have been performed using the commercial thermodynamic equilibrium software package MTDATA. MTDATA was used in conjunction with a thermodynamic database for Ni-based superalloys Ni-DATA\textsuperscript{10} version 4.74, which contains the relevant thermodynamic coefficients. This database incorporates data for Ni, Al, Co, Cr, Fe, Hf, Mo, Nb, Re, Ta, Ti, W, Zr, B, C and N, however, there are some limitations as to the range of compositions of the Ni-based alloys for which this database can be used. This database was produced primarily for Ni-based superalloys, therefore the coating compositions with significantly lower amounts of Ni may be subject to some error. In addition yttrium is not allowed for within the database, therefore care should be taken when performing calculations on MCrAlY coatings. The phases included in the database\textsuperscript{10} are given in Table 3.10. The main phases covered are the matrix phase $\gamma$, $\gamma'$ and $\beta$, carbides such as MC, M\textsubscript{23}C\textsubscript{6} and M\textsubscript{7}C, TCP phases such as $\sigma$, $\mu$, P and R phase and finally several forms of borides.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Liquid</th>
<th>$\eta$</th>
<th>$\sigma$</th>
<th>M\textsubscript{23}(B,C)\textsubscript{6}</th>
<th>M\textsubscript{2}B\textsubscript{orth}</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\gamma'$ (Ni\textsubscript{3}Al)</td>
<td>$\alpha$-(Cr,Mo,W)</td>
<td>M</td>
<td>M\textsubscript{6}C</td>
<td>M\textsubscript{2}B\textsubscript{tetr}</td>
<td></td>
</tr>
<tr>
<td>$\beta$ (NiAl)</td>
<td>$\delta$-NiMo</td>
<td>R phase</td>
<td>M\textsubscript{7}(B,C)\textsubscript{3}</td>
<td>M\textsubscript{3}B\textsubscript{2}</td>
<td></td>
</tr>
<tr>
<td>Ni\textsubscript{3}Nb</td>
<td>Laves\textsubscript{C14}</td>
<td>P phase</td>
<td>M\textsubscript{2}N</td>
<td>Cr\textsubscript{5}B\textsubscript{3}</td>
<td></td>
</tr>
<tr>
<td>$\gamma''$</td>
<td>Laves\textsubscript{C15}</td>
<td>M(C,N)</td>
<td>M\textsubscript{3}B</td>
<td>TiB\textsubscript{2}</td>
<td></td>
</tr>
</tbody>
</table>

Table 3.10 List of phases allowed within the Ni-DATA base\textsuperscript{10} used within this research

\textsuperscript{1} MTDATA is developed and maintained by the Materials Thermochemistry Group at the National Physical Laboratory, Teddington, Middlesex, TW11 0LW, U.K.

\textsuperscript{II} Thermo-Calc was developed by the Department of Materials Science and Engineering, The Royal Institute of Technology, Stockholm, S-100 44, Sweden, and is maintained by Thermo-Calc software AB, Stockholm, Sweden
3.10 Summary

This chapter has presented and discussed the various techniques used in the detailed microstructural characterisation of different coated CMSX4 samples. Thermodynamic equilibrium calculations have been used in order to predict the amount and chemical composition of the phases that will occur within the material at equilibrium as a function of temperature, which in turn assists in phase identification. The majority of the microstructural characterisation was carried out by means of scanning electron microscopy (SEM) because it enables the resolution of features not observable by means of optical microscopy. Energy dispersive X-ray analysis (EDX) was used in conjunction with the SEM to determine the composition of the various phases present to aid in identification.

A dual beam focussed ion beam/FEGSEM was used to produce site specific samples for high resolution analysis. This procedure allowed the extraction of particles within the complex interdiffusion zone, where techniques such as thin foils and carbon replicas would have failed. Consequently, conclusive identification of particles was possible with the combined use of selected area electron diffraction (SAED) and EDX analysis within the transmission electron microscope (TEM). The results of the detailed characterisation are discussed in Chapter 4 for the substrate, Chapter 5 for the MCrAlY coated samples and Chapters 7 and 8 for the Pt aluminide coated samples.
Chapter 4
Microstructural Characterisation of CMSX4 Alloys

4.1 Introduction
This chapter discusses the microstructural characterisation of the two main CMSX4 substrate alloys used in this work with slight variations in composition referred to as ‘standard’ CMSX4 and CMSX4 HC, using both theoretical and experimental techniques. Scanning electron microscopy (SEM) was used to carry out the detailed microstructural characterisation of the substrate alloys, with the use of EDX for chemical analysis. Thermodynamic modelling has been utilised to predict the amount and chemical composition of the phases occurring at equilibrium within these alloys as a function of temperature.

4.2 Thermodynamic Equilibrium Calculations
Thermodynamic equilibrium calculations have been performed using the commercial thermodynamic equilibrium software package MTDATA, in conjunction with a critically assessed thermodynamic database for Ni-based superalloys\cite{101}, as explained in Chapter 3. These calculations have been performed on all three alloys with the two ‘standard’ CMSX4 alloys (Snp) and (Sh) containing 0.0021 and 0.0029 wt.% C respectively and the CMSX4 HC containing an increased amount, 0.0229 wt.% C. The ‘standard’ CMSX4 reported on in this chapter is CMSX4 (Snp) as the slight variation in composition was not great enough to affect the predicted phases and resultant microstructure. These calculations can be used to predict the phases that will occur within the material at equilibrium and give an indication of the amount and composition of each phase present as a function of temperature. In all calculations performed, the alloy composition was used as an input over a temperature range of 600 - 1500°C. The chemical compositions for each CMSX4 alloy as reported in Table 3.1 were inputted into the software, with the exception of B and Zr due to their very small concentrations within the alloys.

For both the ‘standard’ CMSX4 and CMSX4 HC, a total of 7 phases are predicted to be present within the materials at equilibrium. The phases present at temperatures above 600°C are; liquid, γ, γ’, carbides MC and M23C6, and TCP phase’s μ and α, some of which are only
stable over a limited temperature range. The total amount of each of the phases predicted are presented in Figures 4.1 and 4.2. The overall wt.% of elements present within each of the phases predicted by the calculations over the temperature range are presented in Figures 4.3 and 4.4.

Figures 4.1 and 4.2 show that for both alloys the proportion of $\gamma$ increases with temperature at the expense of $\gamma'$. The fraction of $\gamma'$ within the alloys is seen to be at its maximum of $\sim 72$ wt.% at 600°C when $\gamma$ is at a minimum of $\sim 19$ wt.%. The increase in C content of the CMSX4 HC shows no significant changes in the amount of $\gamma$ and $\gamma'$ present within the alloy and the profile with increasing temperature. This therefore suggests that the $\gamma$ and $\gamma'$ phases are not greatly affected by the change in C content. The thermodynamic calculations indicate that both the $\gamma$ and $\gamma'$ phases are predominantly Ni based, containing $\sim 54$ and 67 wt.% respectively. Figures 4.3 a), b) and 4.4 a), b) show how the compositions of both $\gamma$ and $\gamma'$ vary with temperature. The main differentiating factors between $\gamma$ and $\gamma'$ are the concentration of elements Cr, Co, Al and Ta. The calculations show that in both alloys the $\gamma$ phase holds a greater amount of Cr and Co in solution at 600°C $\sim 18$ and 23 wt.%, as opposed to 1.7 and 5.5 wt.% respectively for the $\gamma'$ phase. The Cr and Co content within the $\gamma$ phase is predicted to decrease with temperature leading to a corresponding increase in Ni content. The $\gamma'$ phase ($\text{Ni}_3\text{Al}$), is known to contain a greater amount of Al than that of the $\gamma$; this is confirmed by the calculations, resulting in predictions of $\sim 7.6$ wt.% for $\gamma'$ compared to $\sim 0.8$ wt.% for the $\gamma$ phase. The majority of the elements predicted within the $\gamma'$ can be seen to remain relatively constant throughout the temperature range in which it is stable.
Figure 4.1 Predicted equilibrium quantities of the various phases in ‘standard’ CMSX4 as a function of temperature, showing (a) full scale and (b) expanded scale

Figure 4.2 Predicted equilibrium quantities of the various phases in CMSX4 HC as a function of temperature, showing (a) full scale and (b) expanded scale
The calculations have predicted the existence of MC and $M_{23}C_6$ carbides within both the 'standard' CMSX4 and CMSX4 HC. However, the carbides in the 'standard' CMSX4 are present in amounts less than 1% due to the alloy containing only 0.0024 wt.% C. Figures 4.1 b) and 4.2 b) illustrate that with the increase in C content, the fraction of MC and $M_{23}C_6$ carbides present increases from a maximum of 0.03 and 0.05 to 0.32 and 0.45 respectively. This would be expected as there is more C present to combine with reactive elements within the alloy. Due to the low amounts of carbides predicted for the 'standard' CMSX4 it can be assumed that virtually no carbides will be present within the actual alloy. The plots illustrate that the MC carbides form upon cooling from the melt as seen in many Ni-base superalloys. The temperature range at which the phases are stable has also changed due to the increase in C content. The temperatures in which the MC carbides are predicted to be stable in the 'standard' CMSX4 and CMSX4 HC, ranges from 1000 to 1280°C and 880 to 1360°C. The $M_{23}C_6$ carbide has been predicted to form at lower temperatures in both alloys and is thermodynamically stable up to ~980°C in the 'standard' CMSX4 and 1000°C in the CMSX4 HC. This therefore illustrates some overlap in the stability of the MC and $M_{23}C_6$ carbides in the CMSX4 HC, showing that both carbides are stable between 880 and 1000°C.

Figures 4.3 c), d) and 4.4 c), d) present the predicted compositions of the MC and $M_{23}C_6$ as a function of temperature. In both alloys the MC carbide consists mainly of Hf and Ta, the amount of each being strongly dependant on temperature. At the lower stability temperature of 940°C in the 'standard' CMSX4 the Hf and Ta contents are similar at ~47 and 44 wt.% respectively, with the Hf decreasing to 14 wt.% as the temperature increases. This results in the MC carbides being predominantly Ta-rich at high temperatures with ~73 wt.%. The CMSX4 HC again proves to be rich in Hf and Ta, however a greater difference in amounts at the lower temperature is predicted, with ~74 wt.% Hf and ~19 wt.% Ta. The Ta content increases to almost 74 wt.% which is similar to the 'standard' CMSX4. The Hf content shows the opposite trend, decreasing to ~11 wt.% at the higher temperatures. MC carbides form from the liquid at higher temperature and therefore it is likely that those observed in the microstructure of the substrate will be rich in Ta rather than Hf. Figures 4.3 c) and 4.4 c) show the predicted compositions of $M_{23}C_6$ as a function of temperature in 'standard' CMSX4 and CMSX4 HC respectively, indicating significant differences with the increase in C content. In the 'standard' CMSX4 the $M_{23}C_6$ carbide at the lower temperatures is predicted to be Cr-rich containing substantial amounts of Mo, approximately 64 and 16 wt.% respectively. The wt.% of each element predicted in this phase remains relatively constant up to ~880°C, after
which the Mo rapidly decreases to less than 0.01 wt.%, with a corresponding increase in Re content. In the CMSX4 HC the $\text{M}_{23}\text{C}_6$ appears to consist primarily of Cr and Re with a maximum of ~ 77 and 16 wt.% respectively, which remains relatively constant throughout the temperature range.

The TCP phases predicted to be present in both alloys are $\sigma$ and $\mu$ phase, both of which are rich in refractory solid solution strengthening elements. Figures 4.1 b) and 4.2 b) show that in the 'standard' CMSX4 and the CMSX4 HC respectively, the $\sigma$ and $\mu$ phases are increasingly stable at lower temperatures, but are not predicted to be stable above 920 and 1060°C respectively. The temperatures over which these phases are stable does not appear to be affected by the increase in C content. However, the maximum amount of $\sigma$ phase present decreased from 4.0 wt.% in the 'standard' CMSX4 to 3.5 wt.% in the CMSX4 HC. Figures 4.3 e) and 4.4 e) show the change in composition for $\mu$ as a function of temperature in both alloys. The composition of $\mu$ phase remains relatively unaffected by the increase in C content and is seen to consist primarily of W with substantial amounts of Re, ~ 40 and 25 wt.% respectively. The remaining elements constituting the phase are Co, Cr, Mo and Ni, which remain relatively constant within the range of 7 - 12 wt.%. Figures 4.3 f) and 4.4 f) show the $\sigma$ phase has been predicted to be rich in Re with significant amounts of Cr, the maximum and minimum values of which changing slightly with the increase in C content. The trends of the elements prove similar in each alloy, with the amount of Re and W increasing with temperature at the expense of Cr.
Figure 4.3 Thermodynamic equilibrium plots illustrating the wt.% of elements as a function of temperature in 'standard' CMSX4, a) γ, b) γ', c) \(\text{M}_2\text{C}_6\) carbide, d) MC carbide, e) μ phase and f) σ phase
Figure 4.4  Thermodynamic equilibrium plots illustrating the wt.% of elements as a function of temperature in CMSX4 HC. a) \( \gamma \) b) \( \gamma' \) c) \( M_23C_6 \) carbide, d) MC carbide, e) \( \mu \) phase and f) \( \sigma \) phase.
4.3 Microstructure of CMSX4 Alloys

This section presents and discusses the results of the microstructural investigations carried out on the different CMSX4 alloys. The two CMSX4 alloys contain different amounts of carbon, with the ‘standard’ CMSX4 containing ~ 0.002 wt.% and the CMSX4 HC 0.0229 wt.%. Full compositions of the alloys are reported in Chapter 3. The investigation illustrates any differences in microstructure of the two alloy compositions. Experimental techniques used in the study include field emission gun scanning electron microscopy (FEGSEM) and energy dispersive x-ray analysis (EDX).

4.3.1 ‘Standard’ CMSX4

The main constituent of Ni-based superalloys is a γ matrix containing ordered intermetallic γ’ precipitates. The microstructure of the ‘standard’ CMSX4 in its as-received condition, following a commercial solution heat treatment, is shown in Figure 4.5.

![Figure 4.5 SEM micrographs of ‘standard’ CMSX4 in as-received condition, showing a) the γ/γ’ structure and b) at higher magnification of the same area](image)

The γ’-(Ni₃Al) precipitates of cuboidal morphology are uniformly distributed throughout the alloy. The lattice mismatch between the γ and γ’ phases is known to determine the morphology of the γ’ precipitates[1,22]. Therefore, the cuboidal morphology of the γ’ precipitates indicates that the lattice mismatch between the γ and γ’ phase lies in the range of
The size of the $\gamma'$ precipitates ranges from $\sim 0.4 - 0.7 \, \mu m$. There were no $\gamma/\gamma'$ eutectic or carbides detected within the alloy. Thermodynamic calculations discussed in Section 4.2 did indicate the presence of carbides, however, these were in very small amounts less than 0.1 wt.% and were not seen in the alloy. The chemical analysis reported in Table 4.1 shows that the $\gamma'$ particles consist mainly of Ni with smaller amounts of Ta, Al and Co, approximately 10.5, 6.6 and 7.3 wt.% respectively. These values lay close to the range predicted by the thermodynamic equilibrium calculations for Ta $\sim 9 - 13$ wt.%, Al $\sim 7.5 - 7.6$ wt.% and Co $\sim 5.5 - 7.0$ wt.%, therefore proving predicted and experimentally determined compositions were in close agreement. The etchant used throughout this work promotes the dissolution of the $\gamma$ phase, therefore chemical analysis of this phase was unachievable at this scale. Figure 4.6 shows structures which were observed throughout the microstructure. These are lines of slightly coarsened $\gamma'$ particles that are seen to disrupt the $\gamma$ matrix, and in some instances the $\gamma'$ precipitates have a slightly dendritic morphology rather than cuboidal. Chemical analysis of these $\gamma'$ particles showed that there were no substantial differences compared to the primary $\gamma'$. It has been reported that this structure is often observed after solution heat treatments and can be due to varying precipitation conditions at planar defects. Additionally it has been suggested that these structures are low angle grain boundaries[10], however, no harmful effects have been identified. With isothermal ageing the structures remain present throughout the microstructure and show no significant changes in morphology. However, the $\gamma'$ observed in the surrounding areas does appear to become significantly rafted after extended ageing, as shown in Figure 4.7. It has been reported that the coalescence of $\gamma'$ particles can be induced by residual chemical gradients resulting from segregation[10]. However, no substantial differences in composition were observed within an EDX map across these areas. Additionally it is possible that this localised rafting can be induced by residual internal stresses within the structures, and therefore the minimisation of this stress can be a driving force for coarsening.
### Table 4.1 EDX analysis results of γ', γ', structures and TCP phases present within the bulk of the 'standard' CMSX4 alloy

<table>
<thead>
<tr>
<th>Phase</th>
<th>Ni (wt.%)</th>
<th>Al (wt.%)</th>
<th>Ti (wt.%)</th>
<th>Cr (wt.%)</th>
<th>Co (wt.%)</th>
<th>Ta (wt.%)</th>
<th>W (wt.%)</th>
<th>Re (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>γ'</td>
<td>60.4 - 61.3</td>
<td>6.5 - 6.7</td>
<td>1.1 - 1.2</td>
<td>3.5 - 3.9</td>
<td>7.2 - 7.3</td>
<td>10.2 - 10.7</td>
<td>4.6 - 6.2</td>
<td>1.3 - 1.6</td>
</tr>
<tr>
<td>γ''</td>
<td>61.5 - 62.2</td>
<td>6.7 - 7.2</td>
<td>1.2 - 1.36</td>
<td>2.9 - 3.9</td>
<td>6.4 - 7.2</td>
<td>11.1 - 11.2</td>
<td>3.8 - 5.2</td>
<td>0.7 - 0.8</td>
</tr>
<tr>
<td>TCP</td>
<td>11.3 - 13.7</td>
<td>-</td>
<td>-</td>
<td>8.1 - 10.9</td>
<td>7.8 - 9.3</td>
<td>0.0 - 3.1</td>
<td>26.3 - 31.9</td>
<td>30.1 - 39.7</td>
</tr>
</tbody>
</table>

γ', γ'' alignment structures

Figure 4.6 SEM micrographs of 'standard' CMSX4 in the as-received condition, showing a) and b) structures which disrupt the γ matrix
Figures 4.7 SEM micrographs of 'standard' CMSX4 thermally exposed at 950°C for 10,000 hours showing the localised rafting surrounding the aligned structures.

Figures 4.8 and 4.9 illustrate the change in morphology of the γ' particles in the substrate with increased temperature and exposure length. After 2000 hours at 850°C the γ' particles still retain their general cuboidal structure, with only a slight rounding of the edges. This rounding effect is due to the minimisation of interfacial energy between the γ' precipitate and the γ matrix and is regarded as the onset of coarsening. The γ' particles continue to coarsen with temperature and exposure length, resulting in 'chain' and 'block-like' structures that have a tendency to coalesce, as shown in Figure 4.9 b). Furthermore, clusters of blocky and needle-type precipitates are observed within the bulk of the substrate. Small amounts of these precipitates are present after ageing for 2000 hours at 900°C and increase significantly in volume fraction with temperature and exposure length. Chemical analysis showed these precipitates to contain large amounts of Re and W, ranging from 30 - 40 wt.% and 26 - 32 wt.% respectively. Full compositions of these precipitates are reported in Table 4.1. The high W and Re content suggests these precipitates are TCP phases, with closest agreement to the μ phase predicted by the thermodynamic equilibrium calculations. However, the calculations predicted the primary elements within the μ phase to be W and Re with approximately 41 wt.% and 22 wt.% respectively, which is in contrast to those observed in the actual CMSX4 alloy. Conclusive identification of these phases would require the determination of their crystal structure.
Figure 4.8 SEM micrographs of 'standard' CMSX4 showing the $\gamma'$ morphology in a) the as-received condition and b) exposed at 850°C for 2000 hours.

Figure 4.9 SEM micrographs of 'standard' CMSX4 isothermally aged at 1050°C for 10,000 hours showing a) low magnification image of the overall microstructure, including the clusters of TCP phases, b) rafting of the $\gamma'$ and c) TCP phases observed throughout the alloy.
4.3.2 CMSX4 HC

Figure 4.10 shows the microstructure of the higher carbon (HC) CMSX4 in its as-received condition, following a commercial heat treatment.

Figure 4.10 SEM micrographs of HC CMSX4 in as-received condition, a) low magnification of the alloy structure and b) higher magnification showing the γ' structure.

As observed in the 'standard' CMSX4 alloy, γ' precipitates of cuboidal morphology with an average size of 0.6 μm are uniformly distributed throughout the alloy, which lies in the range of 0.4 - 0.7 μm observed in the 'standard' CMSX4. Structures consisting of closely spaced coarsened γ' precipitates, similar to those observed in the 'standard' CMSX4 are present throughout the microstructure. Regions comprising of large γ' particles were also observed within the microstructure; these were identified as γ/γ' eutectics. These eutectic regions display different morphologies with sizes ranging from ~11 - 47 μm, as illustrated in Figure 4.11. Eutectic γ/γ' within Ni-based alloys is characteristic of segregated areas within the alloy microstructure and occurs as a result of varying diffusion rates of solute elements during solidification. Chemical analysis of the eutectic γ/γ' showed it to be slightly richer in Ta compared to the primary γ', ~11.6 and 9.1 wt.% respectively. This illustrates the partitioning concentration of the liquid and solid, as the eutectic is the last to solidify upon cooling. The acceptable level of eutectic γ/γ' within CMSX4 is below ~3 % for industrial applications. This was measured by means of image analysis, which confirmed that the area fraction of eutectic γ' observed was 2.2 % and therefore lay within acceptable tolerance levels.
Particles appearing bright in backscattered mode were also observed throughout the microstructure, in particular, in the areas surrounding the eutectic $\gamma'$. Chemical analysis showed these particles to be rich in Ta, Hf and C, approximately 72, 5 and 4 wt.% respectively. Due to the high proportions of Ta and the presence of C, the particles were likely to be MC carbides, as predicted in the thermodynamic calculations. MC carbides are known to form in the molten state and therefore are invariably ‘frozen’ in the microstructure\textsuperscript{[1,22]}. These are present in various morphologies, such as coarse block and script, as shown in Figure 4.12. With increase in temperature and exposure length, the MC carbides become surrounded by bands of $\gamma'$, as shown in Figure 4.13. It has been suggested that a layer of $\gamma'$ can develop around the MC core as the MC carbide reduces in stability, resulting in the outward diffusion of C and inward diffusion of elements from the substrate such as Al and Ni. This outwards diffusion of carbon is known to instigate reactions forming lower carbides such as $M_{23}C_6$, represented in Equation 4.1.

$$MC + \gamma \rightarrow M_{23}C_6 + \gamma'$$ \text{[4.1]}

However, no other carbides such as $M_{23}C_6$ were detected throughout the microstructure as predicted to occur at equilibrium.
Figure 4.12 SEM micrographs of HC CMSX4 in the as-received condition, showing a) low magnification image of the alloy indicating the varying MC carbide morphologies, with examples of b) block type structures and c) script morphology.

Figure 4.13 SEM micrographs of HC CMSX4 isothermally aged for 1000 hours at 1050°C, a) and b) showing the development of $\gamma'$ bands surrounding the MC carbides within increase in temperature.
4.4 Summary

This chapter has presented and discussed the results of the microstructural investigations carried out on the two main variants of CMSX4 alloy used, referred to as 'standard' CMSX4 and CMSX4 HC. Thermodynamic equilibrium calculations were carried out on the CMSX4 alloys in order to predict the amount and chemical composition of the phases occurring at equilibrium as a function of temperature, which in turn assisted in phase identification. Microstructural characterisation of the two CMSX4 alloys was carried out using scanning electron microscopy (SEM) and EDX for chemical analysis.

The thermodynamic equilibrium calculations carried out on the two CMSX4 alloys showed that the increase in C content of the CMSX4 HC resulted in no significant change in the amount and composition of the γ and γ′ phases present within the alloy. Therefore, suggesting that the matrix phases remain relatively unaffected by C content. In contrast increasing the C content by approximately a factor of 10 from the 'standard' CMSX4 to the CMSX4 HC, the fraction of MC and M23C6 carbides were predicted to increase by the same factor.

The 'standard' CMSX4 microstructure consisted of primary γ′ precipitates of cuboidal morphology uniformly distributed throughout the alloy. No carbides were observed within the 'standard' CMSX4 alloy, however, these were predicted by thermodynamic calculations to be present in amounts less than 0.1 wt.%, initially indicating the possible absence of these phases. Structures comprising of lines of slightly coarsened γ′ particles that disrupt the γ matrix were present throughout the microstructure. The γ′ particles in the area surrounding these structures became rafted after extended ageing. It was suggested that the rafted-like structure was induced by residual chemical gradients resulting from segregation, however, no evidence of this was observed. After continued thermal ageing clusters of blocky and needle-type precipitates were observed within the bulk of the substrate. Due to the high W and Re content of these precipitates these are most probably TCP phases, with a close agreement to the μ phase predicted by the thermodynamic equilibrium calculations.

As observed in the 'standard' CMSX4, the CMSX4 HC microstructure consisted of primary γ′ precipitates of cuboidal morphology uniformly distributed throughout the alloy. In addition large regions of γ′, identified as γ′γ′ eutectics were observed within the microstructure. Chemical analysis of the eutectic γ′γ′ showed it to be slightly richer in Ta compared to the
primary $\gamma'$, therefore illustrating the partitioning of Ta in the liquid and solid during solidification, as the eutectic is the last to solidify upon cooling. MC carbides rich in Ta and Hf, as predicted in the thermodynamic calculations, were observed with various morphologies including coarse block and script throughout the microstructure. After thermal ageing the MC carbides became surrounded by bands of $\gamma'$. 

The focus of this research is the microstructural interactions which occur as a result of interdiffusion between the coating and substrate which are discussed in the following chapters.
Chapter 5
Microstructural Characterisation of NiCoCrAlY Coated CMSX4

5.1 Introduction
This section presents and discusses the theoretical and experimental results of the detailed microstructural investigations carried out on a NiCoCrAlY coated CMSX4 system. Thermodynamic modelling has been utilised to predict the amount and chemical composition of the phases occurring at equilibrium within this multicomponent system as a function of temperature and composition. Thermodynamic ‘thought’ calculation studies have been additionally carried out in order to get an indication of the phases which will be present in the material, as a consequence of the diffusion of elements between the substrate and the coating, as a function of temperature. The results of the microstructural characterisation on the NiCoCrAlY coating system are discussed including samples in the as-received condition, as well as samples exposed to isothermal ageing. Samples were isothermally aged in air at 850°C, 950°C and 1050°C for 190, 2000 and 10,000 hours. These temperatures were chosen to provide a detailed investigation of the microstructural evolution within the coating system and to be representative of the possible service conditions experience by industrial gas turbine blades. A variety of experimental techniques have been utilised in the study of the coating system. These include field emission gun scanning electron microscopy (FEGSEM) and energy dispersive x-ray analysis (EDX). A dual beam focussed ion beam FEGSEM has also been utilised to make site specific samples for high resolution transmission electron microscopy (TEM) analysis.

5.2 Thermodynamic Equilibrium Calculations
Thermodynamic equilibrium calculations were performed for the NiCoCrAlY overlay coating, Amdry-997, applied to the substrate superalloy, the composition of which is presented in Table 3.5. These calculations have been used to give an indication of the phases and their proportions that will occur within the material at equilibrium, together with the composition of each phase present as a function of temperature. All calculations were performed over a temperature range of 600 - 1500°C.
The database predicts the presence of five phases within the material at equilibrium. The phases present at temperatures above 600°C are; liquid, $\gamma$, $\gamma'$, $\beta$, and $\sigma$, some of which are only stable over a limited temperature range. It should be noted that for these calculations performed on the coating, yttrium is not allowed for within the thermodynamic database. However, Y is generally thought to form oxides within such coatings; therefore the predictions of the phases within the bulk of the coating are likely to be a reasonable representation. The weight % (wt.%) of each of the phases predicted by the database are presented in Figure 5.1. The overall wt.% of elements present within each of the phases predicted by the database over the temperature range are presented in Figure 5.2.

![Figure 5.1](image)

*Figure 5.1 Predicted equilibrium quantities of the various phases present in the NiCoCrAlY coating*

Figure 5.1 shows that the proportion of $\gamma$ phase decreases from a maximum value of ~ 78 wt.% at 1280°C, finally becoming thermodynamically unstable below 840°C. The opposite trend is observed for $\gamma'$, whereby the proportion increases with a decrease in temperature up to ~ 42 wt.% at 840°C. This is followed by a small increase to the maximum value of ~ 47 wt.% observed at 600°C. $\beta$ phase is predicted to remain stable over the majority of the temperature range, within which no significant change in wt.% of the $\beta$ phase was observed. Figure 5.2 a) shows that the $\gamma$ phase holds in solution greater amounts of Cr and Co with similar values of each ranging between 25 and 40 wt.%, which is in a similar range to the amount of Ni present within the phase. The Ni content within the $\gamma$ phase is seen to gradually increase with temperature from ~ 38 wt.% at 600°C to ~ 42 wt% at 1300°C. The $\gamma'$ phase is
predominantly more Ni based with ~ 70 wt.% of Ni and significantly lower amounts of the Cr, Al, Co and Ta. The proportions of these elements can be seen to remain relatively constant throughout the temperature range in which the phase is stable, with only the Ta content increasing from ~ 10 wt.% at 850°C to ~ 19 wt.% at 1020°C. $\gamma$, $\gamma'$ and $\beta$ are nominally Ni, Ni$_3$Al and NiAl respectively and therefore the most significant compositional difference is the Al concentration. This is confirmed with predictions of ~ 5, 10 and 20 wt.% of Al present within $\gamma$, $\gamma'$ and $\beta$ respectively. Figure 5.2 c) shows that $\beta$ phase contains a high concentration of Co ~ 21 wt.% at the lower temperatures, this is seen to decrease with temperature and is coupled with an increase in Ta content resulting in similar amounts of the two elements at ~ 11 wt.% above 1000°C. Also predicted by the database was the presence of $\sigma$ up to temperatures of ~ 1000°C, as illustrated in Figure 5.2 d), which is predicted to be a Cr rich phase ~ 62 wt.% with significant amounts of Co, together with smaller amounts of Ni.
Figure 5.2 Thermodynamic equilibrium plots illustrating the wt.% of elements as a function of temperature in, a) γ, b) γ', c) β and d) η phase
5.2.1 Thermodynamic Equilibrium ‘Thought’ Calculations

Thermodynamic equilibrium calculations have been performed on both the NiCoCrAlY coating and CMSX4 substrate (Chapter 4) and have been regarded to as separate systems. However, in reality this is not the case. It is well documented that interdiffusion of elements between the coating and substrate alloy at high temperatures results in complex microstructures, with the precipitation and dissolution of phases occurring at the interface. Thermodynamic ‘thought’ calculations were therefore carried out in order to provide an indication of the effect that diffusion across the coating/substrate interface has on the amount and type of phase predicted. The diffusion of elements was simulated from proportional concentrations of the coating and substrate. These were taken as coating/substrate and substrate/coating ratios of 9:1, 8:2 and 7:3 as described in Figure 5.3. This part of the work is not based on diffusional data, however, the microstructural model discussed in Chapter 6 incorporates all of these factors to give an accurate simulation of the interdiffusion that occurs within this system.

![Figure 5.3: Schematic diagram illustrating the different composition proportions used for the thermodynamic equilibrium 'thought' calculations across the substrate/coating interface](image)

The phases predicted by the thermodynamic calculations with the differing proportional concentrations are illustrated in Table 5.1, which illustrates the stability of the various phases with slight changes in composition. The Υ and Υ' phases are predicted to be stable throughout the different composition proportions with no significant changes in composition as a function of temperature. Figures 5.4 and 5.5 illustrate that from the substrate across the interface into the coating, the Υ and Υ' show slight overall increases in Cr, Co, Al with corresponding decreases in the Ni and Ta contents.
<table>
<thead>
<tr>
<th>Phase</th>
<th>Coating: Substrate ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Coating 9:1 8:2 7:3 3:7 2:8 1:9 Substrate</td>
</tr>
<tr>
<td>Liquid</td>
<td>✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓</td>
</tr>
<tr>
<td>γ</td>
<td>✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓</td>
</tr>
<tr>
<td>γ'</td>
<td>✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓</td>
</tr>
<tr>
<td>β</td>
<td>✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓</td>
</tr>
<tr>
<td>MC</td>
<td>✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓</td>
</tr>
<tr>
<td>M\textsubscript{23}C\textsubscript{6}</td>
<td>✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓</td>
</tr>
<tr>
<td>σ phase</td>
<td>✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓</td>
</tr>
<tr>
<td>μ phase</td>
<td>✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓</td>
</tr>
<tr>
<td>P phase</td>
<td>✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓</td>
</tr>
</tbody>
</table>

Table 5.1 The stability of the phases predicted by thermodynamic equilibrium calculations with varying proportional concentrations of the coating and substrate

Figure 5.4 Thermodynamic equilibrium plots illustrating the change in wt.% elements within the γ phase as a function of temperature with varying compositions for coating:substrate ratios of a) 1:9 and b) 7:3
Figure 5.5  Thermodynamic equilibrium plots illustrating the change in wt.% of element of the γ' phase as a function of temperature with varying compositions in regards to coating:substrate ratios of a) 1:9 and b) 7:3

Table 5.1 shows that the β phase is predicted to be stable only at the coating:substrate ratios of 9:1, 8:2 and 7:3. Figure 5.6 illustrates that although the phase is stable, the fraction decreases and it becomes thermodynamically unstable at the lower temperatures of ratio 7:3. The β phase at equilibrium is only predicted to be stable in the coating and therefore at and above an Al and Cr content of 6.4 and 10.5 wt.% respectively associated with the ratio 7:3.

Figure 5.6  Thermodynamic equilibrium plots illustrating the change in quantities of the β phase as a function of temperature with varying compositions for coating:substrate ratios of a) 9:1 and b) 7:3

The sensitivity studies shown in Figures 5.7 and 5.8 illustrate the effects of varying the Al and Cr content within the coating composition. The calculations were conducted by making step changes in the Al and Cr concentrations at 900°C and 1000°C, with Ni always set as the balancing element. The nominal Al and Cr content for the NiCoCrAlY coating are 8.5 and 20
wt.% respectively. The results indicated that with separate decreases in Al and Cr content the weight fraction of $\beta$ phase decreases. However, in contrast to the proportional change in concentrations, $\beta$ was seen to remain stable at concentrations of 6 wt.% Al and 10 wt.% Cr separately. This, therefore, suggests that the combined reduction in Al and Cr content has a more pronounced effect on the stability of the $\beta$ phase.

Figure 5.7 Sensitivity study illustrating the effects of Al content in the NiCoCrAlY coating at a) 900°C and b) 1000°C

Figure 5.8 Sensitivity study illustrating the effects of Cr content in the NiCoCrAlY coating at a) 900°C and b) 1000°C

It is well known that the differences in chemical composition between the coating and substrate promote chemically driven diffusion of certain elements across the interface. Although this work is not based on diffusional data, it can still be assumed that the elements that have the largest wt.% difference between the coating and the substrate will have the greatest effect on the composition of the phases predicted. Apart from Ni, the largest differences in composition between the coating and substrate are Cr and Co. This therefore
suggests that the phases rich in these elements such as $M_{23}C_6$ carbides and the TCP phase $\sigma$, will show more pronounced changes in stability and composition as a function of temperature.

The $M_{23}C_6$ carbides were predicted to be stable across the majority of the proportional concentrations, as illustrated in Table 5.1. For the coating:substrate ratio of 1:9, shown in Figure 5.9 a) the $M_{23}C_6$ was predicted to be Cr and Re rich at the lower temperatures of 600°C, however, at 620°C the Cr and Re content decreases with a subsequent increase in Mo and W. This was followed by a reduction in the Mo and W content to less than 0.1 wt.% at 870°C and an increase in Re content to $\sim$15 wt.%. This change in composition as a function of temperature indicates that the $M_{23}C_6$ was stabilised by Mo and W at the lower temperatures, with Re being the high temperature stabiliser. As the composition proportions move from the substrate towards the coating, the temperature range in which Mo stabilises the $M_{23}C_6$ carbide decreases until the phase is stable with a constant Re content of $\sim$10 wt.% as shown in Figure 5.9 c). The smaller amounts of elements predicted present remain relatively constant throughout the temperature range.

Figures 5.10 a) shows that the $\sigma$ phase was predicted to be rich in Cr and Re within the stable temperature range. The Re content is predicted to increase with temperature from $\sim$ 26 to 42 wt.% at the same time the Cr shows the opposite trend, with the lines intersecting at 820°C. Similar trends were observed for the wt.% of elements predicted for coating:substrate ratio of 2:8. However, at the lower temperatures the overall Re content has decreased together with an increase in Cr and Co. This change in content of elements results in a Cr and Co rich phase with smaller amounts of Ni, Re and W.
Figure 5.9 Thermodynamic equilibrium plots illustrating the change in wt.% of element of the $M_2C_6$ carbide as a function of temperature with varying compositions in regards to coating:substrate ratios of a) 1:9, b) 3:7 and c) 8:2.

Figure 5.10 Thermodynamic equilibrium plots illustrating the change in wt.% of element of the $\alpha$ phase as a function of temperature with varying compositions in regards to coating:substrate ratios of a) 1:9, b) 2:8 and c) 7:3.
5.3 Microstructure of NiCoCrAlY Coated CMSX4 System

5.3.1 Microstructure of NiCoCrAlY Coated CMSX4: As-received

The microstructure of the NiCoCrAlY coated CMSX4 system in its as-received condition is shown in Figure 5.11.

![SEM micrograph illustrating the overall structure of the substrate and coating of the sample in its as-received condition, including the coating, interdiffusion zone and the substrate](image)

The NiCoCrAlY coating in its as-received condition has a thickness of \(~216\ \mu\text{m}\), which comprises of a three phase structure consisting of \(\beta\) (NiAl), \(\gamma'\) (Ni3Al) and \(\gamma\) (Ni). The \(\beta\) phase (NiAl), appearing mid-grey in backscattered mode, was observed throughout the coating with an average size of \(1.9\ \mu\text{m}\), as shown in Figures 5.12 and 5.13. Chemical analysis of the \(\beta\) phase indicates high concentrations of Al \(~16.8\ \text{wt.}\%\) and Co \(~14.5\ \text{wt.}\%\), which are in close agreement to values predicted by the thermodynamic equilibrium calculations. Within NiCoCrAlY coating systems the \(\beta\) phase is regarded as the Al reservoir, enabling the formation of the protective oxide scale at the coating surface. As the amount of Al decreases, the \(\beta\) phase tends to dissolve, however there is no sign of \(\beta\) depletion in the as-received condition. Figures 5.12 and 5.13 show areas throughout the coating, of the \(\gamma\) matrix containing finely dispersed particles, tens of nanometres in size. Due to the size of the particles, an accurate chemical analysis proved hard to obtain, therefore compositions were taken over several of the precipitates. The concentration of Ni, Al and Ta reflects quite closely with those...
predicted for the γ' phase within the coating. However, in contrast, the γ' showed an increase in Co levels, which can be attributed to the underlying γ matrix. These areas of γ and γ' are referred to as γ/γ' domains.

Figure 5.12 SEM micrographs of NiCoCrAlY coated CMSX4 in as-received condition, showing a) the coating microstructure, b) the fine γ' particles in the γ/γ' domains and c) the coating surface.

Large, light grey particles with an average size of 4.3 μm were scattered throughout the top half of the coating and in some cases at the coating surface, as shown in Figures 5.12 and 5.13. Observed within the centre of these particles are areas of bright appearance. Chemical analysis of the bright areas showed them to be rich in Ta, Ni and C, approximately 81.4, 5.1 and 5.3 wt.% respectively. Due to the high proportions of Ta and the presence of C, the particles were thought to be MC carbides. MC carbides are known to form in the molten state and therefore are invariably ‘frozen’ in the microstructure. It has been reported that alloys with high Ta contents contain MC carbides that do not break down easily during solution heat treatments, therefore supporting the occurrence of these MC carbides within the as-received condition. The initial source of carbon is unclear. Thermodynamic calculations reported
in section 5.2.1 have indicated that the 0.0021 wt.% C present within the substrate alloy does not allow the formation of MC carbides in the bulk of the coating. It is therefore possible that the carbon was introduced into the system during the coating processes. Chemical analysis of the particles encasing the MC carbides indicated a Ni:Al ratio similar to that of the \( \gamma' \) phase in the coating. It has been suggested that a transition zone consisting of \( \gamma' \) can develop around the original MC core\(^{11} \). This zone forms as the MC carbide degrades, resulting in the outward diffusion of C and inward diffusion of elements from the coating such as Al and Ni.

![Figure 5.13 SEM micrographs of NiCoCrAlY coated CMSX4 in as-received condition, showing a) and b) the phases within the bulk of the coating](image)

Interdiffusion of elements occurs at the coating/substrate interface during the commercial heat treatment following the coating process. The differences in chemical composition between the coating and substrate promote chemically driven diffusion of certain elements. This interdiffusion of elements has resulted in the formation of an interdiffusion zone at the interface, as shown in Figure 5.14. In this work the interdiffusion zone was characterised as the area at the interface affected by the interdiffusion of elements, resulting in a distinct microstructure unlike that of the coating and/or substrate. Particles with high atomic contrast are observed precipitating in a linear array parallel to the coating/substrate interface, as shown in Figures 5.14 a) and b). Once more the high proportions of Ta ~ 76.5 wt.% and the presence of C, indicated the particles were MC carbides. In contrast to the carbides observed in the bulk
of the coating, small proportions of Ti and Hf were also detected. The presence of Ti and Hf indicates that they may be a result of outwards diffusion from the substrate into the coating.

A coalescence of γ' particles was observed within the substrate, adjacent to the coating/substrate interface. This has resulted in the formation of a γ' layer with a thickness of 5 μm. It has been reported that a γ' layer can form at the coating/substrate interface, due to the interdiffusion of Al and Ni\[^{42,52,89,103}\]. The net increase of Al in the substrate and Ni in the coating results in the transformation of the γ phase in the substrate adjacent to the coating into γ'. Small precipitates rich in Cr, Re and W were also observed within this γ' layer. The high content of refractory elements suggests that these precipitates are TCP phases, and prove to have good correlation to the σ phase predicted by thermodynamic calculations discussed in Section 5.2.1. However, conclusive identification of these phases would require the determination of their crystal structure. These phases are known to form to accommodate the excess Cr and Re produced as a result of the phase transformation from γ to γ', due to their reduced solubility in γ' compared to γ.
Figure 5.14 SEM micrographs of NiCoCrAlY coated CMSX4 in the as-received condition, showing a) the coating at the interdiffusion zone, b) the interdiffusion zone and c) the substrate at the interdiffusion zone.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Elements (wt.%), Ni Al Ti Cr Co Ta W Re Hf C</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \gamma' \gamma' )</td>
<td>47.3 - 59.6, 5.9 - 8.3, 0.0 - 0.3, 7.8 - 15.3, 14.3 - 22.2, 4.9 - 8.0, 0.0 - 0.7, - - -</td>
</tr>
<tr>
<td>( \gamma'_{\text{EV}} )</td>
<td>53.0 - 55.9, 6.2 - 7.9, - 4.2 - 5.4, 11.8 - 13.4, 15.4 - 19.4, - - - -</td>
</tr>
<tr>
<td>( \beta )</td>
<td>55.1 - 58.6, 15.6 - 17.9, 0.0 - 0.2, 4.9 - 5.7, 13.9 - 15.1, 0.6 - 2.6, 0.0 - 1.8, - - -</td>
</tr>
<tr>
<td>MC(_{\text{BC}})</td>
<td>5.4 - 6.3, 1.2 - 1.3, - 1.7 - 2.5, 2.5 - 3.3, 81.8 - 8.31, - - - 4.7 - 4.9</td>
</tr>
<tr>
<td>MC(_{\text{IDZ}})</td>
<td>3.5 - 7.7, 0.9 - 1.4, 3.7 - 3.9, 0.8 - 1.4, 1.8 - 2.6, 73.5 - 80.0, 1.1 - 1.3, 0.5 - 2.2, 5.3 - 5.4</td>
</tr>
</tbody>
</table>

\( \gamma' \gamma' \) - \( \gamma' \gamma' \) in \( \gamma' \gamma' \) domains
\( \gamma'_{\text{EV}} \) - \( \gamma' \) Envelopes
MC\(_{\text{BC}}\) - MC carbides in coating
MC\(_{\text{IDZ}}\) - MC carbides in IDZ

Table 5.2 EDX analysis results of the phases present within the bulk of the coating and the interdiffusion zone (IDZ) of the sample in its as-received condition (obtained using SEM)

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5.3.2 Microstructure of NiCoCrAlY Coated CMSX4 Thermally Exposed at 850°C

**Thermal Exposure at 850°C for 190 hours**

The microstructure of the NiCoCrAlY coated CMSX4 system after thermal exposure at 850°C for 190 hours is illustrated in Figure 5.15.

The external scale present on the coating surface was approximately 1.5 μm thick. This oxide scale consisted mainly of an Al/O rich layer, thought to be Al2O3, containing small amounts of solid solution elements Cr and Ni ~ 6.1 and 2.9 wt.% respectively. The main phases observed within the bulk of the coating are β (NiAl) and γ' (Ni3Al) in a γ (Ni) matrix. The majority of the γ' phase is present as very fine spherical precipitates of the order of 100 nm in diameter. These precipitates were dispersed over areas of the γ matrix and are referred to as γ'/γ' domains, as illustrated in Figures 5.16 b) and c). The Al-rich β phase is present throughout the coating with an average size of 2 μm.

Figure 5.16 a) shows an area of agglomerated γ' precipitates present at the coating surface. This is an area of the coating that has been affected by oxidation. Within this area a depletion of the β precipitates was also observed. This depletion is thought to be due to the Al diffusing...
out towards the coating surface, thus creating and sustaining the protective oxide layer. The depletion of the Al from the Al-rich \( \beta \) phase has resulted in a phase transformation from \( \beta \rightarrow \gamma' \). As a result, the phase transformation creates a greater area fraction of \( \gamma' \) precipitates at the coating surface, resulting in an agglomeration of the particles. Large agglomerated particles of \( \gamma' (\gamma'_{\text{Agg}}) \) with an average size of 3 - 4.5 \( \mu \text{m} \) were also observed precipitating in a linear array through the central section of the coating. Chemical analysis reported in Table 5.3 shows these particles to contain a greater amount of Ta than that of the very fine spherical \( \gamma' \) precipitates within the coating. This increase in Ta is suggested to be a result of the decomposition of the Ta-rich MC carbides that were observed within \( \gamma' \) envelopes in the as-received sample.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Ni</th>
<th>Al</th>
<th>Cr</th>
<th>Co</th>
<th>Ta</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \gamma )</td>
<td>26.0 - 29.4</td>
<td>2.7 - 4.8</td>
<td>22.9 - 28.1</td>
<td>28.8 - 34.5</td>
<td>2.4 - 5.8</td>
</tr>
<tr>
<td>( \gamma' )</td>
<td>47.3 - 48.9</td>
<td>6.1 - 7.3</td>
<td>8.5 - 9.2</td>
<td>16.4 - 17.6</td>
<td>14.2 - 16.2</td>
</tr>
<tr>
<td>( \gamma'_{\text{Agg}} )</td>
<td>51.5 - 53.5</td>
<td>6.5 - 7.5</td>
<td>4.3 - 4.9</td>
<td>12.4 - 13.6</td>
<td>16.3 - 19.5</td>
</tr>
<tr>
<td>( \beta )</td>
<td>52.8 - 58.2</td>
<td>15.2 - 16.1</td>
<td>5.8 - 8.4</td>
<td>15.5 - 18.5</td>
<td>2.6 - 5.4</td>
</tr>
</tbody>
</table>

\( \gamma'_{\text{Agg}} \) - Agglomerated \( \gamma' \)

Table 5.3 EDX analysis results of \( \gamma', \gamma' \) and \( \beta \) phases present within the bulk of the coating of sample aged for 190 hours at 850°C (obtained using SEM)

The diffusion of Cr from the coating into the substrate alloy has encouraged the formation of Cr-rich phases of globular morphology. These phases were observed within the coating adjacent to the interdiffusion zone, as illustrated in Figure 5.16 c) and confirmed by the EDX elemental maps shown in Figure 5.18. Chemical analysis of these precipitates indicated a significantly higher Cr content and lower Co content compared to that predicted for \( \sigma \) phase, compositions of which are reported in Table 5.4. The precipitates were further identified as \( M_{23}C_6 \) carbides (\( a_0 = 10.638 \text{ Å} \)) using a combination of selected area diffraction patterns and EDX analysis. Typical SAED patterns are illustrated in Figure 5.19. The Cr-rich \( M_{23}C_6 \) carbides were located within a similar area of the interdiffusion zone to that of the MC carbides observed in the as-received sample. It has been well documented that \( M_{23}C_6 \) carbides are more stable at lower temperatures and can form from the degeneration of MC carbides. This breakdown results in the presence of available carbon in a relatively high chromium region, leading to the formation of Cr-rich \( M_{23}C_6 \) carbides.
Figure 5.16 SEM micrographs of NiCoCrAlY coated CMSX4 thermally exposed for 190 hours at 850°C, showing a) the coating surface, including the oxide scale, b) phases within the bulk of the coating, c) low magnification image showing the agglomerated $\gamma'$, and d) the coating adjacent to the interdiffusion layer.
A continuous $\gamma'$ layer ranging from 6.0 - 7.7 $\mu$m in thickness was observed within the interdiffusion zone, separating the coating from the substrate, as illustrated in Figure 5.17. Coarse and irregular 'vein-like' $\gamma'$ particles were seen to extend from this $\gamma'$ layer into the coating. These particles connect, resulting in areas containing an abundance of small spherical $\gamma'$ precipitates similar to those associated with the coating structure. It has been suggested that this continuous layer has formed due to the net increase of aluminium in the substrate and nickel in the coating. This subsequently leads to the transformation of the $\gamma$ phase from the substrate adjacent to the coating into the $\gamma'$ layer\textsuperscript{[89]}. In addition to the $\gamma'$ layer, the interdiffusion of elements such as Cr, Re and W across the coating/substrate interface encouraged the formation of several intermetallic phases. Small precipitates rich in Cr, Re and W were observed within the $\gamma'$ layer. The high content of these elements and their needle-like structure suggests these precipitates are topologically closed packed (TCP) phases. Selected area diffraction (SAED) and EDX analysis across the continuous $\gamma'$ layer enabled the identification of the TCP phases. The main TCP phase present after aging for 190 hours was the Cr-rich $\sigma$ phase ($a_0 = 9.3\text{Å}$ and $c_0 = 4.86\text{Å}$) with approximately 35 wt.% Cr and 22 wt.% Re together with small additions of Co, Mo and W. Typical SAED patterns are shown in Figure 5.20, and their compositions given in Table 5.4.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Elements (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ni</td>
</tr>
<tr>
<td>$M_23C_6$</td>
<td>15</td>
</tr>
<tr>
<td>$\sigma$ phase</td>
<td>8.81</td>
</tr>
</tbody>
</table>

Table 5.4 EDX analysis results of $M_23C_6$ carbide and $\sigma$ phase present within the interdiffusion zone of sample aged for 190 hours at 850°C (obtained using TEM)

The $\gamma'/\gamma'$ structure observed within the substrate near to the coating/substrate interface was rafted, as shown in Figure 5.17 b). The direction of the rafting was seen to vary with the position around the samples surface. It is not fully understood why the differing angles occur. However, it has been suggested that this rafting was caused by biaxial compressive stresses induced due to the formation of the continuous $\gamma'$ layer at the coating/substrate interface. Furthermore the differing thermal expansion coefficients of the coating and substrate materials during aging, are reported to have an effect on rafting within this area\textsuperscript{[104]}. 

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Figure 5.17 SEM micrographs of NiCoCrAlY coated CMSX4 thermally exposed for 190 hours at 850°C, showing a) the interdiffusion layer and b) γ' layer containing TCP phases.

Figure 5.18 SEM micrographs of NiCoCrAlY coated CMSX4 thermally exposed for 190 hours at 850°C, showing a) the precipitates within the interdiffusion zone; EDX elemental maps of area illustrating the concentration of b) Cr and c) Al.
Figure 5.19 Micrographs and selected area diffraction patterns (SADP) of $M_6C_6$ precipitates within the coating adjacent to the IDZ: a) Micrograph highlighting area of interest, b) bright field image (BF); c) SADP of $M_6C_6$ carbides; zone axes are labelled.

Figure 5.20 Micrographs and selected area diffraction patterns (SADP) of the $\sigma$ phase within the $\gamma'$ layer of the IDZ: a) Micrograph highlighting area of interest, b) bright field image (BF); SADP of c) $\sigma$ phase; zone axes are labelled.
Thermal Exposure at 850°C for 2000 hours

The microstructure of the NiCoCrAlY coated CMSX4 coated system after thermal exposure at 850°C for 2000 hours is illustrated in Figure 5.21.

Figure 5.21  SEM micrograph illustrating the overall structure of the substrate and coating of sample aged for 2000 hours at 850°C, including the coating, interdiffusion zone and the substrate

The Al-rich oxide scale formed on the surface of the coating presented similar characteristics to those observed in the sample aged for 190 hours. The average thickness of the oxide scale has increased with the length of exposure, from 1.5 μm observed at 190 hours to 9 μm at 2000 hours. At the coating surface a depletion of precipitates was observed, which resulted in a continuous layer of the γ matrix approximately 5 - 7 μm in thickness. Adjacent to the γ layer a layer of γ' precipitates was present, consequently the β phase with an average size of 2 - 3 μm is present at an average distance of 19.5 μm into the coating, as shown in Figure 5.22 a). This confirms that β depletion has occurred within this area due to the diffusion of Al from the coating out towards the protective oxide layer. The results of the EDX analysis carried out on the phases present in the bulk of the coating are reported in Table 5.5.

The γ'/γ domains present within the bulk of the coating have decreased in size, with the fine γ' precipitates increasing in size due to coarsening with increased thermal exposure time; this structure is illustrated in Figure 5.22 b). The large agglomerated γ' particles are once more present as a linear array through the centre of the coating, as observed in the sample aged for
190 hours indicating that the structure remains stable at the lower exposure times and temperatures.

Table 5.5 EDX analysis results of γ, γ' and β phases present within the bulk of the coating of sample aged for 2000 hours at 850°C (obtained using SEM)

<table>
<thead>
<tr>
<th>Phase</th>
<th>Elements (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ni</td>
</tr>
<tr>
<td>γ</td>
<td>26.0 - 29.4</td>
</tr>
<tr>
<td>γ'</td>
<td>51.8 - 57.2</td>
</tr>
<tr>
<td>β</td>
<td>55.4 - 57.2</td>
</tr>
</tbody>
</table>

Within the interdiffusion zone, globular Cr-rich precipitates similar to those present in samples aged at 190 hours were observed, as illustrated in Figure 5.22 d). Once more the SAED patterns and chemical analysis confirmed that these phases are M₂₃C₆ carbides, with a composition consistent with the MTDATA 'thought calculations' reported in Section 5.2.1. The continuous γ' layer which separates the coating from the substrate has increased in thickness with length of exposure, from 7.7 - 14.6 μm, indicating that the increase in diffusion of elements across the interdiffusion zone results in the transformation of γ to γ'. Figures 5.23 and 5.24 show that the TCP phases rich in Cr, Re and W present within the continuous γ' layer have also increased in size, ranging from 150 to 600 nm. The increase in size has resulted in the precipitates extending out of the γ' layer towards the substrate.

Table 5.6 EDX analysis results of M₂₃C₆ carbides and σ phase present within the interdiffusion zone of sample aged for 2000 hours at 850°C (obtained using TEM)

<table>
<thead>
<tr>
<th>Phase</th>
<th>Elements (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ni</td>
</tr>
<tr>
<td>M₂₃C₆</td>
<td>5.3 - 8.6</td>
</tr>
<tr>
<td>σ phase</td>
<td>7.2 - 21.0</td>
</tr>
</tbody>
</table>
Figure 5.22 SEM micrographs of NiCoCrAlY coated CMSX4 thermally exposed for 2000 hours at 850°C, showing a) coating surface including the oxide scale and β depletion layer, b) high magnification of the phases within the bulk of the coating, c) low magnification of the coating showing the agglomerated γ' particles and d) the coating adjacent to the interdiffusion layer.
Figure 5.23 SEM micrographs of NiCoCrAlY coated CMSX4 thermally exposed for 2000 hours at 850°C, showing a) the interdiffusion layer structure and b) high magnification image of the TCP phases within the γ’.

Figure 5.24 TEM micrographs in bright field mode showing a) and b) the morphology and sizes of the α phase within the γ’ layer of the IDZ.
Thermal Exposure at 850°C for 10,000 hours

The microstructure of the NiCoCrAlY coated CMSX4 coated system after thermal exposure at 850°C for 10,000 hours is illustrated in Figure 5.25.

The external scale present on the coating surface was again of similar structure to samples with shorter exposure lengths, comprising of an Al rich layer, thought to be Al₂O₃ with an average thickness of 6 µm. An outer layer on the oxide scale was identified, and chemical analysis showed it to contain elements present within the coating such as Ni, Cr and Co. It is suggested that this outer layer contains several transient oxides that initially develop due to the inward flux of oxygen at the coating surface. However, when a continuous oxide scale is formed, the oxygen pressure at the oxide/coating surface decreases allowing the stable Al₂O₃ to form. The result is a continuous Al₂O₃ scale on which remnants of the transient oxide phases remain. Fine precipitates, with a very bright appearance are also observed within the outer regions of the oxide scale. Chemical analysis of the precipitates showed them to be rich in Al, Ta and O, approximately 32.3, 38.2, and 15.8 wt.% respectively, indicating that outward diffusion of Ta from the coating has also occurred.

The continuous precipitate free γ layer and the adjacent γ’ precipitate layer, observed at the coating surface increased in thickness with thermal exposure, as shown in Figure 5.26 a). The
growth of these layers indicates an increase in the depletion of the β phase at the coating surface. Chemical analysis of the agglomerated γ’ precipitates present at the coating surface shows an increased amount of Al and Ta, 14.2 and 19.1 wt.% compared to the bulk of the coating, at 9.1 and 11.3 wt.% respectively. This once more supports the fact that there is outward diffusion of Al and Ta from the coating towards the surface, with the Ta partitioning to the γ’ phase, once it has transformed from the β phase. The bulk of the coating comprises of γ, γ’ and β phase. The majority of the fine γ’ precipitates observed are cuboidal in shape and as a result of coarsening with increased thermal exposure can be differentiated from the underlying γ matrix, as shown in Figure 5.26 b).

Figure 5.26 SEM micrographs of NiCoCrAlY coated CMSX4 thermally exposed for 10,000 hours at 850°C, showing a) coating surface including the oxide scale and β depletion layer and b) γ’ and β phases within the bulk of the coating.

Figure 5.27 shows the interdiffusion zone at the coating/substrate interface, which proves to have similar microstructural characteristics to those observed in the sample aged for 2000 hours. The Cr-rich M_{23}C_{6} carbides of globular morphology, present within the coating adjacent to the interdiffusion zone, have increased in size to approx 2 - 3 μm, as illustrated in Figure 5.27 b) and confirmed by the EDX elemental maps in Figure 5.28. The Re, W and Cr rich TCP phases present within the continuous γ’ layer have both rounded and needle-like morphologies, with the needle-like precipitates extending further into the substrate. Selected area diffraction and EDX analysis of the TCP phases indicated that the predominant phase present at 10,000 hours is once more the Cr-rich σ phase (a₀ = 9.3Å and c₀ = 4.86Å) with small
quantities of W/Re-rich \( \mu \) phase \((a_0 = 4.75\,\text{Å} \text{ and } c_0 = 25.8\,\text{Å})\) also being detected. The presence of the \( \sigma \) phase throughout the thermal exposures at 850°C verifies its low temperature stability. Typical SAED patterns for the \( \sigma \) phases are shown in Figure 5.29, and their compositions given in Table 5.7. Chemical analysis of the \( \sigma \) phase shows a decrease in W and Re, \( \sim 10 \) and \( \sim 13 \) wt.\%, compared to the precipitates present at 190 hours, \( \sim 13 \) and 22 wt.% respectively. This reduction indicates the possible diffusion of W and Re from the \( \sigma \) phase which re-precipitates as the \( \mu \) phase within the \( \gamma' \) layer.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Elements (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ni</td>
</tr>
<tr>
<td>( M_{23}C_6 )</td>
<td>2.7 - 3.8</td>
</tr>
<tr>
<td>( \Sigma ) phase</td>
<td>7.2 - 10.1</td>
</tr>
<tr>
<td>( M ) phase</td>
<td>8.4 - 15.5</td>
</tr>
</tbody>
</table>

*Table 5.7* EDX analysis results of \( M_{23}C_6 \) carbides, \( \sigma \) and \( \mu \) phase present within the interdiffusion zone of sample aged for 10,000 hours at 850°C (obtained using TEM)
Figure 5.27 SEM micrographs of NiCoCrAlY coated CMSX4 thermally exposed for 10,000 hours at 850°C, showing a) the interdiffusion layer structure, b) TCP phases extending out of the $\gamma'$ layer into substrate and c) the coating structure adjacent to the IDZ.

Figure 5.28 SEM micrographs of NiCoCrAlY coated CMSX4 thermally exposed for 10,000 hours at 850°C, showing a) the precipitates within the interdiffusion zone; EDX elemental maps of area illustrating the concentration of b) Cr and c) Al.
Figure 5.29 Micrographs and selected area diffraction patterns (SADP) of the α phase within the γ' layer of the IDZ: a) Micrograph highlighting area of interest, b) bright field image (BF); SADP of c) α phase. Zone axes are labelled.
5.3.3 Microstructure of NiCoCrAlY Coated CMSX4 Thermally Exposed at 950°C

The coating thickness of the samples aged at 950°C is approximately 230 µm, which is a significant reduction to the 360 µm measured for the samples aged at 850°C and 1050°C. The smaller coating thickness could have significant implications on the diffusion kinetics of the system and consequently the microstructural evolution. Care should therefore be taken when observing the microstructural changes that occur within these samples.

Thermal Exposure at 950°C for 190 hours

The microstructure of the NiCoCrAlY coated CMSX4 system after thermal exposure at 950°C for 190 hours is illustrated in Figure 5.30.

![Figure 5.30 SEM micrograph illustrating the overall structure of the substrate and coating of sample aged for 190 hours at 950°C, including the coating, interdiffusion zone and the substrate](image)

A continuous precipitate free γ layer of 5 - 6 µm was observed within the oxidation affected area at the coating surface, as illustrated in Figure 5.31. This is in contrast to the sample aged at 850°C for 190 hours where no precipitate free layer had formed. The depletion of γ’ and β precipitates at the coating surface indicates that with exposure to higher temperatures there is an increase of outward diffusion of the Al from the coating towards the oxide layer. The continuous precipitate free γ layer is followed by a layer of γ’ precipitates as observed in previous samples. These γ’ particles are present with sizes ranging from 0.4 - 0.8 µm. The β
precipitates are present within the bulk of the coating, starting at a distance of 24.5 µm from the coating surface which is significantly larger than in the sample aged at 850°C.

Figure 5.31 SEM micrograph of NiCoCrAlY coated CMSX4 thermally exposed for 190 hours at 950°C, showing the coating surface

Large agglomerated γ' particles are once more present, as shown in Figure 5.32. However, these γ' particles are scattered throughout the top half of the coating as opposed to forming a linear array through the central area, as in the case of those observed in the samples aged at lower temperatures. This structure proves very similar to that observed in the as-received sample. The random distribution of the particles may be due to the reduction in coating thickness of these two samples. Consequently, the slight microstructural changes can be due to quicker initial cooling of the coating or similarly the increased diffusion of elements across the smaller thickness.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Elements (wt.%%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ni</td>
</tr>
<tr>
<td>γ</td>
<td>37.9 - 38.4</td>
</tr>
<tr>
<td>γ'</td>
<td>45.8 - 53.8</td>
</tr>
<tr>
<td>β</td>
<td>53.5 - 56.0</td>
</tr>
</tbody>
</table>

Table 5.8 EDX analysis results of γ, γ' and β phases present within the bulk of the coating of sample aged for 190 hours at 950°C

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Figure 5.32 SEM micrograph of NiCoCrAlY coated CMSX4 thermally exposed for 190 hours at 950°C, showing the bulk of the coating.

The interdiffusion zone observed, has increased in thickness to ~ 24.5 μm but possesses similar microstructural features to those encountered in the samples exposed at 850°C. The Cr-rich M23C6 carbides of globular morphology were once more observed within the coating section of the interdiffusion zone, demonstrating their stability at increased temperatures. These carbides are shown in Figure 5.33 c) and confirmed by the EDX elemental maps in Figure 5.34. Ta, Hf and Ti rich particles are observed precipitating parallel to the coating/substrate interface, as illustrated in Figures 5.33 a) and c). Due to the high proportions of Ta (~ 50.8 wt.%) and the presence of C, the particles were identified as MC carbides. The presence of these carbides indicates the outwards diffusion of Ti and Hf from the substrate into the coating. The occurrence of both MC and M23C6 carbides within the same location of the interdiffusion zone is likely to be because the aging temperature of 950°C is close to the temperature of stability for both phases.

The area fraction and size of the acicular W, Re and Cr rich TCP phases present within the continuous γ’ layer have increased compared to the 850°C sample. The increase in size has resulted in the extension of the precipitates out of the γ’ layer towards the substrate, as illustrated in Figures 5.33 a) and b). As in the sample aged at 850°C, the majority of the TCP phases identified using SAED patterns and EDX analysis were the Cr-rich σ phase. However, in contrast to the sample aged at 850°C for 190 hours the rhombohedral μ phase was also
identified within the γ’ layer. The existence of this phase indicates an increased diffusion of refractory elements such as W and Re from the substrate towards the coating with increased temperature. Compositions of the TCP phases are reported in Table 5.9. Chemical analysis of the σ phase indicates that there was an increase in Re and a decrease in Cr compared to that observed within the samples aged at 850°C. It has been suggested that within TCP phases Re substitutes for Cr at higher temperatures. Furthermore this observation is also consistent with the thermodynamic equilibrium calculations for σ phase discussed in Section 5.2.1.

![Figure 5.33 SEM micrographs of NiCoCrAlY coated CMSX4 thermally exposed for 190 hours at 950°C, showing: a) interdiffusion layer structure, b) TCP phases extending from the γ’ layer into substrate and c) coating structure adjacent to the IDZ including carbide phases](image)

Figure 5.33 SEM micrographs of NiCoCrAlY coated CMSX4 thermally exposed for 190 hours at 950°C, showing, a) interdiffusion layer structure, b) TCP phases extending from the γ’ layer into substrate and c) coating structure adjacent to the IDZ including carbide phases
**Figure 5.34** SEM micrographs of NiCoCrAlY coated CMSX4 thermally exposed for 190 hours at 950°C, showing a) the precipitates within the interdiffusion zone; EDX elemental maps of area illustrating the concentration of b) Cr and c) Al.

**Figure 5.35** Micrographs and selected area diffraction patterns (SADP) of the α phase within the γ' layer of the IDZ: a) Micrograph highlighting area of interest, b) bright field image (BF); SADP of c) α phase, zone axes are labelled.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Ni</th>
<th>Ti</th>
<th>Cr</th>
<th>Co</th>
<th>Mo</th>
<th>W</th>
<th>Re</th>
</tr>
</thead>
<tbody>
<tr>
<td>σ Phase</td>
<td>8.65 - 17.5</td>
<td>0.0 - 0.23</td>
<td>24.7 - 30.1</td>
<td>13.1 - 15.6</td>
<td>1.7 - 3.12</td>
<td>13.7 - 16.1</td>
<td>22.7 - 28.7</td>
</tr>
<tr>
<td>μ phase</td>
<td>5.7 - 10.8</td>
<td>0.0 - 0.8</td>
<td>12.2 - 16.6</td>
<td>10.9 - 11.5</td>
<td>1.8 - 3.4</td>
<td>21.9 - 30.8</td>
<td>21.1 - 30.3</td>
</tr>
</tbody>
</table>

**Table 5.9** EDX analysis results of the σ and μ TCP phases present in the γ’ layer within the interdiffusion zone of sample aged for 190 hours at 950°C (obtained using TEM).
<table>
<thead>
<tr>
<th>Phase</th>
<th>Ti</th>
<th>Cr</th>
<th>Co</th>
<th>Ta</th>
<th>W</th>
<th>Re</th>
<th>Hf</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>MC</td>
<td>1.8 - 2.4</td>
<td>2.0 - 3.9</td>
<td>5.5 - 7.6</td>
<td>42.5 - 51.2</td>
<td>-</td>
<td>0.0 - 1.5</td>
<td>5.8 - 7.8</td>
<td>4.5 - 5.1</td>
</tr>
<tr>
<td>M_23C_6</td>
<td>-</td>
<td>59.4 - 75.2</td>
<td>2.0 - 4.1</td>
<td>-</td>
<td>6.2 - 12.3</td>
<td>9.6 - 14.7</td>
<td>0.9 - 1.8</td>
<td>4.6 - 5.5</td>
</tr>
</tbody>
</table>

Table 5.10 EDX analysis results of MC carbides and M_23C_6 carbides present within the coating adjacent to the interdiffusion zone of sample aged for 190 hours at 950°C (obtained using SEM)
Thermal Exposure at 950°C for 2000 hours

The microstructure of the NiCoCrAlY coated CMSX4 coated system after thermal exposure at 950°C for 2000 hours is illustrated in Figure 5.36.

Figure 5.36  SEM micrograph illustrating the overall structure of the substrate and coating of sample aged for 2000 hours at 950°C, including the coating, interdiffusion zone and the substrate

The microstructural features observed within the sample were very similar to those encountered in the sample exposed at 950°C for 190 hours. The main phases present within the bulk of the coating were $\gamma$, $\gamma'$ and $\beta$. The continuous $\gamma$ layer and adjacent $\gamma'$ layer present at the coating surface have increased with exposure time from $\sim 5.6$ μm and 24 μm, to 10 μm and 39 μm respectively. The size of the $\gamma'$ precipitates within the bulk of the coating, as shown in Figure 5.37 b), have increased in comparison to 190 hours.

As observed throughout the samples, the interdiffusion of elements between the coating and substrate has resulted in the formation of a continuous $\gamma'$ layer. This layer has increased in thickness from 10.5 μm observed at 190 hours to 21 μm, indicating the increased diffusion of Al into the substrate and Ni into the coating. A layer of large agglomerated $\gamma'$ particles are observed parallel to the coating/substrate interface. This layer has replaced the ‘vein’ and ‘finger-like’ protrusions of $\gamma'$ observed in previous samples. The increase in diffusion activity across the coating/substrate interface has resulted in the coarsening and coalescence of
adjacent \(\gamma'\) particles. As observed at 190 hours, the Cr-rich \(\text{M}_{23}\text{C}_6\) carbides of globular morphology (\(\text{M}_{23}\text{C}_6(\text{g})\)) are present within the coating section of the interdiffusion zone. These \(\text{M}_{23}\text{C}_6\) carbides were observed in all of the samples investigated and increased in area fraction with temperature and exposure time. Light grey phases with a geometric morphology were observed within the continuous \(\gamma'\) layer, as shown in Figure 5.38. Chemical analysis showed that these precipitates were once more rich in Cr and Re and also contained C, initially indicating that they were \(\text{M}_{23}\text{C}_6\) carbides (\(\text{M}_{23}\text{C}_6(\text{g})\)). Subsequently, these particles were positively identified as \(\text{M}_{23}\text{C}_6\) using the combination of SAED patterns and EDX analysis. Typical SAED patterns are illustrated in Figure 5.40. The difference in Cr and Re content between the globular and geometric morphology reported in Table 5.12, implies that the composition of the \(\text{M}_{23}\text{C}_6\) carbide is dependent on position within the interdiffusion zone. Furthermore, the high coherency between \(\text{M}_{23}\text{C}_6\) carbides and \(\sigma\) phase has been well documented\(^{[1,10,22,103,106]}\). This suggests that the \(\sigma\) phase present in the \(\gamma'\) layer at the lower temperatures can act as nucleation sites for other phases with similar crystallography and chemistry, such as \(\text{M}_{23}\text{C}_6\) carbides.

Figure 5.37 d), shows the Re, W and Cr rich acicular phases present within the \(\gamma'\) layer as observed at shorter exposure times. These precipitates have once more increased in size with an extension of \(\sim 20\ \mu\text{m}\) into the substrate at various angles to the interface. With the use of SAED patterns and EDX analysis, the TCP phases present within the interdiffusion zone were identified as \(\sigma\) (\(a_0 = 9.3\ \text{Å}\) and \(c_0 = 4.86\ \text{Å}\)), \(\mu\) (\(a_0 = 4.75\ \text{Å}\) and \(c_0 = 25.8\ \text{Å}\)) and \(\text{P}\) (\(a_0 = 17.2,\ b_0 = 4.86\) and \(c_0 = 9.2\ \text{Å}\)) phase; where \(\sigma\) is tetragonal, \(\mu\) is Rhombohedral and \(\text{P}\) is Orthorhombic. The predominant phases observed at 2000 hours were the W/Re-rich \(\mu\) and \(\text{P}\) phases, compositions of which are reported in Table 5.13. The increase in area fraction of these phases reinforces the statement that in MCrAlY coated systems with high Cr and Co contents \(\sigma\) phase are stable at lower temperatures.
Figure 5.37 SEM micrographs of NiCoCrAlY coated CMSX4 thermally exposed for 2000 hours at 950°C, showing a) the coating surface including the oxide scale and β depletion layer, b) phases within the bulk of the coating, c) the coating structure adjacent to the interdiffusion layer and d) interdiffusion layer structure.

Figure 5.38 a) SEM micrograph and b) ion beam micrograph of NiCoCrAlY coated CMSX4, thermally exposed for 2000 hours at 950°C, showing the γ' layer within the interdiffusion zone containing TCP phases and M23C6 carbides.
Figure 5.39 SEM micrographs of NiCoCrAlY coated CMSX4 thermally exposed for 2000 hours at 950°C, showing a) the precipitates within the interdiffusion zone; EDX elemental maps of area illustrating the concentration of b) Cr and c) Al

<table>
<thead>
<tr>
<th>Phase</th>
<th>Elements (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ni</td>
</tr>
<tr>
<td>( \gamma )</td>
<td>36.7 - 45.7</td>
</tr>
<tr>
<td>( \gamma' )</td>
<td>56.5 - 58.1</td>
</tr>
<tr>
<td>( \beta )</td>
<td>57.4 - 59.2</td>
</tr>
</tbody>
</table>

Table 5.11 EDX analysis results of \( \gamma, \gamma' \) and \( \beta \) phases present within the bulk of the coating of sample aged for 2000 hours at 950°C (obtained using SEM)

<table>
<thead>
<tr>
<th>Phase</th>
<th>Elements (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ni</td>
</tr>
<tr>
<td>( M_{23}C_6(\theta) )</td>
<td>2.4 - 3.2</td>
</tr>
<tr>
<td>( M_{23}C_6(\theta) )</td>
<td>3.2 - 3.7</td>
</tr>
</tbody>
</table>

\( M_{23}C_6(\theta) \) - \( M_{23}C_6 \) with globular morphology
\( M_{23}C_6(\theta) \) - \( M_{23}C_6 \) With geometric morphology

Table 5.12 EDX analysis results of the \( M_{23}C_6 \) carbides present within the interdiffusion zone of sample aged for 2000 hours at 950°C (obtained using TEM)
Figure 5.40 TEM micrograph and selected area diffraction pattern (SADP) of phases within the γ' layer of the IDZ of sample aged for 2000 hours at 950°C: a) bright field image (BF); SADP for b) $M_2C_6$ carbide, c) μ phase, d) P phase, in which the relevant zone axes are labelled.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Ni</th>
<th>Cr</th>
<th>Co</th>
<th>Mo</th>
<th>W</th>
<th>Re</th>
</tr>
</thead>
<tbody>
<tr>
<td>σ phase</td>
<td>7.5 - 9.9</td>
<td>38.2 - 43.4</td>
<td>16.2 - 24.4</td>
<td>1.5 - 4.2</td>
<td>9.6 - 12.1</td>
<td>13.4 - 18.1</td>
</tr>
<tr>
<td>μ phase</td>
<td>4.9 - 7.4</td>
<td>9.7 - 12.1</td>
<td>9.2 - 12.0</td>
<td>0.0 - 4.5</td>
<td>33.8 - 37.8</td>
<td>29.2 - 33.8</td>
</tr>
<tr>
<td>P phase</td>
<td>5.7 - 8.5</td>
<td>12.4 - 14.5</td>
<td>12.5 - 13.8</td>
<td>3.2 - 5.7</td>
<td>33.6 - 37.4</td>
<td>25.6 - 28.2</td>
</tr>
</tbody>
</table>

Table 5.13 EDX analysis results of the TCP phases present within the interdiffusion zone of sample aged for 2000 hours at 950°C (obtained using TEM)
Thermal Exposure at 950°C for 10,000 hours

The microstructure of the NiCoCrAlY coated CMSX4 coated system after thermal exposure at 950°C for 10,000 hours is illustrated in Figure 5.41.

![Figure 5.41](image)

Figure 5.41 SEM micrograph illustrating the overall structure of the substrate and coating of sample aged for 10,000 hours at 950°C, including the coating, interdiffusion zone and the substrate

The Al-rich oxide, presumed to be Al₂O₃ present on the coating surface presented similar characteristics to those discussed previously. However, the average thickness of the oxide scale has increased from 6 µm observed at 850°C to ~9 µm at 950°C. Figure 5.42 a) shows that the precipitates present within the oxide scale have increased in size and quantity compared to that observed at 850°C. Chemical analysis of these precipitates showed they were rich in Al, Ta, Y and O with concentrations of 29.2, 25.8, 19.6 and 20.1 wt.% respectively, as opposed to just Al, Ta and O, therefore suggesting that diffusion of the Y from the coating out towards the oxide scale had occurred. The diffusion of Y out towards the oxide scale is known to occur during high temperature exposure, in order to assist in the adherence of the oxide scale to the coating surface. [65,66,107]
Figure 5.42 SEM micrographs of NiCoCrAlY coated CMSX4 thermally exposed for 10,000 hours at 950°C, showing a) the coating surface including the oxide scale and β depletion layer, b) phases within the bulk of the coating, c) the coating structure adjacent to the interdiffusion layer and d) interdiffusion layer structure including the β depletion layer.
The \( \gamma \) layer adjacent to the oxide scale, known as the depletion layer, illustrated in Figure 5.42 a) has increased in thickness from \( \sim 10 \) \( \mu \)m observed at 2000 hours to 12.9 \( \mu \)m. As a consequence the \( \beta \) phase particles with an average size of 3.4 \( \mu \)m are present at an average distance of 60 \( \mu \)m into the coating. This distance into the coating has increased significantly compared to \( \sim 15 \) \( \mu \)m observed in the sample aged at 850°C for 10,000 hours, indicating a considerable increase in Al diffusion from the coating out towards the protective oxide scale and resulting in the depletion of the Al-rich \( \beta \) phase. In addition a \( \beta \) depletion layer was evident within the coating near to the coating/substrate interface, which is confirmed by the Al EDX map shown in Figure 5.45. The \( \gamma' \) precipitates present in the bulk of the coating were previously observed with a cuboidal structure. However, as illustrated in Figure 5.42 b) and c) an increase in size ranging from 3 - 5 \( \mu \)m together with a rounding effect has occurred. This change in size and morphology is due to the exposure at increased temperatures giving rise to an Ostwald ripening process. The process allows large precipitates to grow at the expense of smaller ones, with the rounding effect being the minimisation of the interfacial energy of the system\(^{[10,34]}\).

As observed in the samples aged at lower temperatures, \( M_{23}C_6 \) carbides of globular morphology (\( M_{23}C_6 (g) \)) are present within the coating section of the interdiffusion zone. The \( M_{23}C_6 \) carbides with geometric morphology (\( M_{23}C_6 (I) \)) observed within the continuous \( \gamma' \) layer have increased in area fraction compared to the sample aged at 2000 hours, as shown in Figure 5.43. The increase in area fraction of the carbides indicates an increase in Cr diffusion across the coating/substrate interface. Additionally, the increase in carbides within the \( \gamma' \) layer can be a result of the increased nucleation of the \( M_{23}C_6 \) carbides on the preceding \( \sigma \) phase observed at 850°C. It was evident that the small Cr, Re and W-rich TCP phases, observed within the interdiffusion zone at shorter exposure lengths, have significantly increased in size to form elongated and segmented needle-like structures. These precipitates were seen to initiate from within the interdiffusion zone and extend \( \sim 12 \) \( \mu \)m into the substrate at various angles to the interface, as shown in Figure 5.43 b). The TCP phases that have extended into the substrate are surrounded by bands on \( \gamma' \). These areas of \( \gamma' \) form as the TCP phases grow and deplete the refractory solid solution strengthening elements such as Re and W from the surrounding \( \gamma \) matrix. An indication of the presence of these TCP phases can be seen within the EDX elemental maps shown in Figure 5.45. Chemical analysis indicated that the TCP phases within the interdiffusion zone possess very similar compositions. Consequently, conclusive
Identification of the phases required the determination of their crystal structures. As in the sample aged for 2000 hours, the majority of the TCP phases identified using a combination of SAED patterns and EDX analysis are that of the W/Re-rich μ and P phase, illustrated in Figure 5.44, with compositions reported in Table 5.15. Increased precipitation and coarsening of the μ and P phase was observed with increasing diffusion of refractory elements such as W, Re and Mo from the substrate into the coating. The γ' rafting behaviour is still clearly observable beneath the coating/substrate interface.

![Figure 5.43](image)

**Figure 5.43** a) SEM micrograph and b) ion beam micrograph of NiCoCrAlY coated CMSX4, thermally exposed for 10,000 hours at 950°C, showing the γ' layer within the interdiffusion zone containing TCP phases and M23C6 carbides.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Cr</th>
<th>Co</th>
<th>Ta</th>
<th>W</th>
<th>Re</th>
<th>Ni</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>M23C6(1)</td>
<td>52.8 - 59.5</td>
<td>2.6 - 3.7</td>
<td>0.0 - 1.8</td>
<td>6.7 - 9.3</td>
<td>13.7 - 17.3</td>
<td>6.3 - 9.6</td>
<td>5.6 - 8.3</td>
</tr>
<tr>
<td>M23C6(2)</td>
<td>62.9 - 74.7</td>
<td>3.5 - 6.5</td>
<td>0.3 - 2.1</td>
<td>5.7 - 9.6</td>
<td>5.1 - 10.7</td>
<td>4.3 - 9.7</td>
<td></td>
</tr>
</tbody>
</table>

**Table 5.14** EDX analysis results of M23C6 carbides present within the interdiffusion zone of sample aged for 10,000 hours at 950°C (obtained using SEM)
Figure 5.44  a) and b) TEM bright field image (BF) of the $\mu$, P phase and $M_23C_6$ carbide within the $\gamma'$ layer of the IDZ; c) SADP of $\mu$ phase, zone axes are labelled.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Ni (wt.%)</th>
<th>Cr (wt.%)</th>
<th>Co (wt.%)</th>
<th>Mo (wt.%)</th>
<th>W (wt.%)</th>
<th>Re (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\mu$ phase</td>
<td>5.8 - 7.7</td>
<td>12.2 - 13.6</td>
<td>11.4 - 13.0</td>
<td>0.0 - 2.9</td>
<td>33.2 - 35.8</td>
<td>32.2 - 33.4</td>
</tr>
<tr>
<td>P phase</td>
<td>5.2 - 8.4</td>
<td>10.9 - 13.8</td>
<td>9.6 - 13.6</td>
<td>4.4 - 6.9</td>
<td>36.9 - 39.5</td>
<td>22.6 - 30.3</td>
</tr>
</tbody>
</table>

Table 5.15 EDX analysis results of the TCP phases present within the interdiffusion zone of sample aged for 2000 hours at 950°C (obtained using TEM)
Figure 5.45 SEM micrographs of NiCoCrAlY coated CMSX4 thermally exposed for 10,000 hours at 950°C, showing a) the phases within the interdiffusion zone; EDX elemental maps of area illustrating the concentration of b) Al, c) Cr, d) Re and e) W.
5.3.4 Microstructure of NiCoCrAlY Coated CMSX4 Thermally Exposed at 1050°C

Thermal Exposure at 1050°C for 190 hours

The microstructure of the NiCoCrAlY coated CMSX4 coated system after thermal exposure at 1050°C for 190 hours is illustrated in Figure 5.46.

![Figure 5.46 SEM micrograph illustrating the overall structure of the substrate and coating of sample aged for 190 hours at 1050°C, including the coating, interdiffusion zone and the substrate](image)

The continuous precipitate free γ layer observed adjacent to the external oxide scale has significantly increased in thickness from 5.6 μm observed at 950°C to ~ 43 μm. β precipitates of various sizes and morphologies were dispersed in the γ matrix, within which no γ' precipitates were detected, as illustrated in Figure 5.47 b). The absence of γ' within the coating is different from the other samples examined. Thermodynamic equilibrium calculations conducted on the coating indicate that at 1050°C, the γ' phase is not thermodynamically stable. The low exposure time of 190 hours suggests a limited amount of diffusion has occurred within the system. It can therefore be assumed that the coating at this stage is similar to the as coated composition, allowing a close comparison to calculated data. Chemical analysis of the γ matrix throughout the coating indicated an increase in Al content of ~ 6.2 wt.% compared to the samples aged at 850°C and 950°C for 190 hours, which had ~ 3.4 and 3.9 wt.% respectively. This increase in Al content within the γ matrix was a consequence of the instability of the γ' phase and was confirmed by the thermodynamic calculations.
reported in Section 5.2.1. A $\beta$ depletion layer of 14 $\mu$m was present within the coating adjacent to the coating/substrate interface. The location of the depletion layer emphasises that there has been an increase in outward diffusion of the Al from the coating towards the substrate alloy, with exposure to higher temperatures.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Elements (wt.%): Ni</th>
<th>Al</th>
<th>Ti</th>
<th>Cr</th>
<th>Co</th>
<th>Ta</th>
<th>Hf</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\gamma$</td>
<td>42.2 - 46.0</td>
<td>5.8 - 6.9</td>
<td>0.0 - 0.1</td>
<td>10.8 - 15.9</td>
<td>13.9 - 22.1</td>
<td>6.4 - 10.4</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$\beta$</td>
<td>51.2 - 58.1</td>
<td>14.1 - 14.9</td>
<td>0.0 - 0.2</td>
<td>6.4 - 7.3</td>
<td>14.3 - 16.8</td>
<td>2.6 - 5.3</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>MC</td>
<td>2.0 - 3.5</td>
<td>0.9 - 1.1</td>
<td>3.5 - 6.4</td>
<td>0.8 - 1.0</td>
<td>1.3 - 1.6</td>
<td>70.2 - 72.5</td>
<td>11.8 - 12.6</td>
<td>5.2 - 6.2</td>
</tr>
</tbody>
</table>

Table 5.16 EDX analysis results of $\gamma$, $\beta$ phases and MC carbides present within the bulk of the coating of sample aged for 190 hours at 1050°C (obtained using SEM)

Ta, Hf and Ti rich particles with high atomic contrast were observed precipitating in a linear array parallel to the coating/substrate interface. The existence of these particles was confirmed in the EDX elemental maps shown in Figure 5.48. Due to the high proportions of Ta $\approx$ 71 wt.% and the presence of C, the particles were identified as MC carbides. These carbides were observed in a similar location to the $M_{23}C_6$ carbides of globular morphology present in the samples exposed to lower temperatures. The change in carbide type confirms the low temperature and high temperature stability of the $M_{23}C_6$ carbides and MC carbides respectively, indicated by the thermodynamic calculations discussed in Chapter 4. The presence of the MC carbides adjacent to the coating/substrate interface also confirms Ta’s role as a barrier agent. The Ta inhibits the diffusion of Ti into the coating by trapping a substantial amount in the form of MC carbides. The diffusional transport of Ti through the coating is undesirable as it promotes the formation of $Cr_2O_3$ which would in turn inhibit the protective action of the $Al_2O_3$ scale$^{[1,103,108]}$.

The continuous $\gamma'$ layer that separates the coating and substrate appears to have become segmented in nature. The coarse and irregular finger-like precipitates have extended further into the coating, suggesting an increase in diffusion activity across this boundary, resulting in the dissolution and growth of the $\gamma$ and $\gamma'$ respectively. Within the interdiffusion zone the segmented needle-like phases extending out into the substrate were once again present. It is apparent the precipitates are longer and thicker compared to those in the samples aged at 850°C and 950°C. Significant coarsening of the TCP phases has therefore occurred with the
increase in temperature, as illustrated in Figure 5.47 d). Chemical analysis of these precipitates shows they are rich in Re and W, initially indicating the presence of μ and/or P phase. As indicated previously these two TCP phases within this coating system possess very similar compositions. This required the combined use of SAED patterns and chemical analysis to conclusively identify the presence of μ phase (rhombohedral) and P phase (orthorhombic) within the interdiffusion zone, the compositions of which are reported in Table 5.17. The existence of μ and P phase within the interdiffusion zone at 1050°C is in contrast to the samples aged at 850°C and 950°C for 190 hours, where the predominant TCP phase present was the Cr-rich σ phase (tetragonal). This change in phase within the interdiffusion zone demonstrates the high temperature stability of the TCP phases containing a greater percentage of refractory elements such as W, Re and Mo. The occurrence of μ and P phase within the interdiffusion zone contradicts the predictions made by the thermodynamic equilibrium calculations reported in Section 5.2.1. The discrepancy between the experimental data and calculated data lies in the complex nature of the interdiffusion zone, demonstrating the need to predict phases present within the coated superalloy system as a whole.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Ni</th>
<th>Cr</th>
<th>Co</th>
<th>Mo</th>
<th>W</th>
<th>Re</th>
</tr>
</thead>
<tbody>
<tr>
<td>M phase</td>
<td>5.9 - 7.6</td>
<td>11.6 - 13.3</td>
<td>10.7 - 12.1</td>
<td>0.0 - 2.2</td>
<td>33.1 - 37.2</td>
<td>31.6 - 34.7</td>
</tr>
<tr>
<td>P phase</td>
<td>6.3 - 6.6</td>
<td>11.5 - 12.9</td>
<td>10.6 - 12.7</td>
<td>2.5 - 3.7</td>
<td>35.6 - 38.8</td>
<td>29.8 - 30.6</td>
</tr>
</tbody>
</table>

Table 5.17 EDX analysis results of the TCP phases present within the interdiffusion zone of sample aged for 190 hours at 1050°C (obtained using TEM)
Figure 5.47 SEM micrographs of the NiCoCrAlY coated CMSX4 thermally exposed for 190 hours at 1050°C, showing a) the coating surface including the oxide scale and β depletion layer, b) β and γ phases within the bulk of the coating, c) the coating adjacent to the interdiffusion layer showing MC carbides and d) interdiffusion layer.
Figure 5.48 SEM micrographs of NiCoCrAlY coated CMSX4 thermally exposed for 190 hours at 1050°C, showing a) the phases within the interdiffusion zone; EDX elemental maps of area illustrating the concentration of b) Al, c) Ta, d) Ti, e) Cr and f) Re
Thermal Exposure at 1050°C for 2000 hours

The microstructure of the NiCoCrAlY coated CMSX4 coated system after thermal exposure at 1050°C for 2000 hours is illustrated in Figure 5.49.

![SEM micrograph illustrating the overall structure of the substrate and coating of sample aged for 2000 hours at 1050°C, including the coating, interdiffusion zone and the substrate](image)

The Al-rich oxide present on the coating surface presents similar characteristics to those discussed for shorter exposure lengths. However, cracks breaking up the thickness of the oxide scale were observed within some areas of the sample, and in some instances separating the oxide scale completely from the coating, as shown in Figure 5.50 a). The cracking/spalling of the oxide scale may have occurred on ageing, or during cooling from the ageing temperature. Similarly it is possible these cracks were formed during metallographic preparation of the sample. The continuous precipitate free γ layer observed at the coating surface had a similar thickness to that observed at 190 hours, indicating possible similarities in diffusion rates of the Al from the β phase. The bulk of the coating consisted mainly of β in a γ matrix with small quantities of the γ' phase. The reduction of γ' within the coating was similar to observations made at 190 hours, as expected due to its lack of thermodynamic stability at this temperature. Small amounts of γ' precipitates approximately 12 μm in size were scattered throughout the central section of the coating. These large γ' precipitates were of similar size and shape to that of the surrounding β phases, as shown in Figure 5.50 b). The similarity between these two phases suggests that diffusion of Al from the Al-rich β phase has resulted in the transformation
from β to γ' phase in several of the particles. As observed at 190 hours, a β depletion layer was observed within the coating adjacent to the coating/substrate interface, as confirmed by the EDX elemental maps shown in Figure 5.51. In contrast to the sample aged at 190 hours, smaller more rounded γ' precipitates (γ'_IDZ) were observed within the β depletion layer. The precipitates are illustrated in Figure 5.50 c) and their compositions are reported in Table 5.18.

The presence of the γ' precipitates adjacent to the interdiffusion zone suggests that the diffusion of the Al from the coating into the substrate is slower than that for the Al to the coating surface, therefore allowing the γ' to remain within this area.

MC carbides rich in Ta, Hf and Ti are observed within the lower section of the coating and precipitating in a linear array parallel to the coating/substrate interface similar to those observed in the sample aged at 190 hours. Chemical analysis of the carbides indicated a substantial increase in Hf content compared to the sample aged at 190 hours; 17.4 and 12.2 wt.% respectively. This increase in Hf in the MC carbides indicates the substantial increase in diffusion rates of this active element at 1050°C within the system. The increase in area fraction of these MC carbides was consistent with the reduction of γ' phase. As the γ' phase depletes, the γ' stabilising element Ta can combine with the reactive carbon present within this area. The microstructural features observed within the interdiffusion zone of the sample were very similar to those encountered in the sample exposed for 190 hours, with a continued increase in dissolution of the continuous γ' layer that separates the coating and substrate. The morphological development of the TCP needles within the interdiffusion zone shows that they are becoming increasingly coarser and more segmented with the increase in exposure length, as shown in Figures 5.50 e) and f).
Figure 5.50 SEM micrographs of NiCoCrAlY coated CMSX4 thermally exposed for 2000 hours at 1050°C, showing a) coating surface including a fractured oxide scale and β depletion layer, b) β and γ within the bulk of the coating, c) β depletion in the coating adjacent to the IDZ, d), e) and f) TCP phases within the interdiffusion zone.
<table>
<thead>
<tr>
<th>Phase</th>
<th>Elements (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ni</td>
</tr>
<tr>
<td></td>
<td>37.3</td>
</tr>
<tr>
<td></td>
<td>41.5</td>
</tr>
<tr>
<td>$\gamma'$</td>
<td>49.1</td>
</tr>
<tr>
<td>$\gamma'$</td>
<td>54.3</td>
</tr>
<tr>
<td>$\beta$</td>
<td>49.4</td>
</tr>
<tr>
<td>$\gamma'$</td>
<td>57.3</td>
</tr>
<tr>
<td>$\gamma'$</td>
<td>53.5</td>
</tr>
<tr>
<td>$\gamma'$</td>
<td>55.3</td>
</tr>
</tbody>
</table>

$\gamma'$ _tdz_ - $\gamma'$ adjacent to interdiffusion layer

*Table 5.18* EDX analysis results of $\gamma$, $\gamma'$ and $\beta$ phases present within the bulk of the coating of sample aged for 2000 hours at 1050°C (obtained using SEM)
Figure 5.51 SEM micrographs of NiCoCrAlY coated CMSX4 thermally exposed for 2000 hours at 1050°C, showing a) the phases within the interdiffusion zone; EDX elemental maps of area illustrating the concentration of b) Al, c) Cr, d) Ta, e) Ti, f) W and g) Re.
Thermal Exposure at 1050°C for 10,000 hours

The microstructure of the NiCoCrAlY coated CMSX4 coated system after thermal exposure at 1050°C for 10,000 hours is illustrated in Figure 5.52.

![Figure 5.52 SEM micrograph illustrating the overall structure of the substrate and coating of sample aged for 10,000 hours at 1050°C, including the coating, interdiffusion zone and the substrate](image)

The Al-rich oxide present on the coating surface appeared more linear, as opposed to following the contours of the coating observed in the samples aged at 850°C and 950°C. The average thickness of the oxide scale has increased, ranging in value from 16 - 25 μm, with additional fingers of oxide that protrude into the coating. It is unclear whether these values represent the full thickness of the oxide scale or are subsequent to spallation that was observed in the sample aged at 2000 hours. Particles of similar contrast to that of the coating were also observed within the oxide scale. Chemical analysis of these particles confirmed them to have similar compositions to that of the γ matrix adjacent to the coating/oxide interface. This entrapment of γ particles within the oxide scale can be due to the inward growth of the oxide scale into the coating with increased time and temperature. This growth results in the isolation of γ phase areas that continue to move further into the oxide scale, as illustrated in Figure 5.53. Precipitates with a bright appearance ranging in size of 5 - 10 μm were distributed throughout the oxide scale. Chemical analysis showed the precipitates to be rich in Ta, Ti and Hf, approximately 57.5, 18.4 and 12.1 wt.% respectively, and coupled with the presence of C, these particles were identified as MC carbides. The precipitation of these carbides within the
oxide scale indicates that Ti and Hf have diffused from the substrate, through the thickness of the coating, into the oxide scale. As stated previously, the diffusional transport of Ti through the coating is undesirable as it promotes the formation of Cr₂O₃ and consequently preventing the protective action of the Al₂O₃ scale. However, Cr₂O₃ oxide was not observed within this sample. Light grey precipitates were observed on both sides of the oxide/coating interface. These precipitates were present with various morphologies, random, coarse and blocky, as well as 'vein-like'. The 'vein-like' structures are seen to extend into the oxide scale and in some instances form a layer between the oxide scale and the coating. Chemical analysis showed these particles to comprise mainly of Al, Y and O with approximately 37.2, 43.7 and 18.9 wt.% respectively. Similar precipitates have been reported to occur within the oxide scale in samples aged within similar temperature ranges. The morphologies are such as they are known to segregate to the grain boundaries of the Al₂O₃ together with coating/oxide interface in the aid to increase scale adherence.

The overall observations made of the general coating structure at 1050°C, show a substantial reduction in second phases. The dissolution of the phases has occurred due to the increased diffusion of elements out towards the coating surface and across the substrate coating interface into the substrate. It is once again evident that the continuous γ layer at the coating surface had increased in thickness with increasing ageing temperatures and exposure times, as shown in Figure 5.54 a). The average thickness of the depletion layer is approximately 220 μm, which is a significant increase from the 10μm observed at 950°C after 10,000 hours. There was an absence of β precipitates observed within the coating, confirming that β acts as the initial Al reservoir in the coating for the production and sustainability of the protective oxide scale. The dissolution of the β has resulted in a thin layer of γ' particles remaining within the central bulk of the coating, as shown in Figure 5.54 b). Chemical analysis conducted on the γ' precipitates adjacent to the depletion layer indicated a lower Al content than that of the γ matrix, approximately 1.5 and 6.2 wt.% respectively. Ta, which is known to stabilise γ', is present in substantial quantities within the Al depleted γ' particles, increasing from ~13 to 31 wt.%, therefore allowing the phase to continue to precipitate within the coating. The decrease in Al content together with the consistent growth of the oxide scale suggests that the γ' phase observed was the remaining source of Al within the coating. Thus, suggesting that the γ' phase is sustaining the protective nature of the oxide scale once the β phase has fully depleted. The protection that the coating still provides can also explain why is has been suggested that
the coating life of MCrAlY systems is related to the critical Al content of the coating rather than the volume fraction of the β phase.

![Coating](image)

(a)

<table>
<thead>
<tr>
<th>Phase</th>
<th>Elements (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ni</td>
</tr>
<tr>
<td>A</td>
<td>42.9</td>
</tr>
<tr>
<td>B</td>
<td>41.78</td>
</tr>
</tbody>
</table>

Figure 5.53 SEM micrograph illustrating the oxide scale structure of sample aged for 10,000 hours at 1050°C, showing a) overall oxide structure, b) and c) precipitates within oxide scale, including EDX results obtained using the SEM of the areas labelled.
Figure 5.54 SEM micrographs of the NiCoCrAlY coated CMSX4 thermally exposed for 10,000 hours at 1050°C, showing a) the depletion layer at the coating surface, b) \( \gamma \) and \( \gamma' \) phases within the bulk of the coating, c) interdiffusion layer structure, d) MC carbides of varying contrast, e) and f) interdiffusion layer showing the TCP phase extending into the substrate.
Ta, Ti and Hf rich MC carbides were again observed to precipitate in a linear array parallel to the coating/substrate interface, as shown in Figures 5.54 c) and d). Chemical analysis of the carbides indicated that there were different areas within the particle characterised by varying ratios of Ta to Ti, Ta being the main constituent with Hf remaining fairly constant at ~ 12.1 wt.%. The areas with a brighter appearance in the backscattered electron mode proved to have a higher ratio of Ta to Ti, compositions of which are reported in Table 5.20. Voids were present within the coating at the coating/substrate interface, similar such voids have been observed within MCrAlY coating systems\[106\]. It has been stated that these are most likely Kirkendall voids and generally develop at the coating/substrate interface due to the combination of elements diffusing out towards the coating surface and in towards the substrate alloy. The area in which they are located tends to have a high concentration of incoherent phase boundaries in the matrix that favours condensation of vacancies.

The interdiffusion zone observed shows a significant increase in thickness compared to the samples aged at 850°C and 950°C; with a continued dissolution of the continuous $\gamma'$ layer that separates the coating and the substrate. The area fraction of acicular W, Re and Cr rich TCP phases present within the interdiffusion zone has significantly increased compared to that of the 2000 hour sample. As in the sample aged at 950°C, the morphology of the TCP needles are coarse and segmented. The W/Re-rich needles are seen to initiate within the interdiffusion zone and extend significantly into the substrate distances of up to 425 μm together with the formation of clusters. The relative orientation of the TCP phases and their morphology requires further investigation. Chemical analysis of these precipitates showed them to be rich in W and Re which would indicate the presence of $\mu$ and P phase, however, due to their large size conclusive diffraction patterns were unable to be obtained.

Table 5.19 EDX analysis results of $\gamma$, $\gamma'$ and $\beta$ phases present within the bulk of the coating of sample aged for 10,000 hours at 1050°C (obtained using SEM)
<table>
<thead>
<tr>
<th>Phase</th>
<th>Ni</th>
<th>Al</th>
<th>Ti</th>
<th>Cr</th>
<th>Ta</th>
<th>Hf</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>MC_{OX}</strong></td>
<td>1.2 - 1.9</td>
<td>0.3 - 7.9</td>
<td>8.3 - 33.7</td>
<td>-</td>
<td>46.3 - 67.9</td>
<td>10.0 - 14.9</td>
<td>4.3 - 6.6</td>
</tr>
<tr>
<td><strong>MC_{IDZ}</strong></td>
<td>1.4 - 8.4</td>
<td>0.0 - 1.1</td>
<td>7.9 - 35.1</td>
<td>0.0 - 3.7</td>
<td>42.9 - 64.9</td>
<td>9.9 - 15.4</td>
<td>7.1 - 9.5</td>
</tr>
</tbody>
</table>

MC_{OX} - MC carbides within the oxide  
MC_{IDZ} - MC carbides within the IDZ

**Table 5.20** EDX analysis results of MC carbides present within the oxide scale and the interdiffusion zone of sample aged for 10,000 hours at 1050°C (obtained using SEM)
5.4 Discussion

This section discusses the main microstructural changes that occur within the coating and interdiffusion zone with increasing temperature and exposure time.

5.4.1 Elemental Profiles

Elemental profiles were constructed across the coating, interdiffusion zone and substrate. The profiles demonstrate the distribution of elements within these areas over increasing exposure with time at temperature. This was achieved by defining a matrix of points across the coating and interdiffusion zone, and collecting quantitative chemical data at each point. An average value from the various points at the same position in respect to the coating surface was then used to smooth the effect of the individual phases present.

Figure 5.55 a) illustrates the elemental profile of the sample aged for 190 hours at 850°C. Within the coating section, the Al, Cr, Co and Ta, fluctuate between values of 8 - 15, 8 - 17, 18 - 27 and 5 - 10 wt.% respectively, thus indicating the presence of several second phases throughout this area. The fluctuations continue through the coating into the interdiffusion zone until fairly constant values are indicated through the substrate. For the samples aged at 850°C the majority of the elemental profiles were similar due to the relatively small changes observed within the microstructure with increasing exposure times, however, Figures 5.55 b) and 5.56 illustrate elemental profiles with slight differences due to the precipitation and dissolution of certain phases. The elemental profile of the sample exposed for 10,000 hours at 850°C is shown in Figure 5.55 b) and illustrates similar characteristics, with the addition of a noticeable decrease in Ni levels within the interdiffusion zone as a result of Cr precipitating out as various phases within this area, such as the M23C6 carbides observed within the microstructure. An increase in Re and W is also indicated within the latter stages of the interdiffusion zone, thus illustrating an agreement with the TCP phases observed within the microstructure. Figure 5.56 a) shows the elemental profile of the sample aged for 190 hours at 1050°C. The initial 29 μm from the coating surface illustrates reasonably constant values, hence indicating the lack of second phase particles within this area, which represents the depletion layer present within the microstructure. Figure 5.56 b) shows that this depletion layer increases with exposure time until a second set of constant values is observed adjacent to the interdiffusion zone. Once more this was consistent with the microstructure observed at 1050°C for 10,000 hours. The depletion layer is subsequently followed by the fluctuations
present in the profiles of previous samples. Once more the increase in refractory elements was observed within the interdiffusion zone, confirming the presence of carbides and intermetallic such as TCP phases, with a significant increase in Ta adjacent to the interdiffusion zone coinciding with the precipitation of MC carbides within this area.

These elemental profiles are compared with the predictions of a combined thermodynamic and kinetic model in the following chapter.
Figure 5.55 Elemental profiles across the coating, interdiffusion layer and substrate of sample aged at 850°C for a) 190 and b) 10,000 hours

Figure 5.56 Elemental profiles across the coating, interdiffusion layer and substrate of sample aged at 1050°C for a) 190 and b) 10,000 hours
5.4.2 Microstructural Changes Observed at 850°C

The main phases observed within the bulk of the coating of the isothermally aged samples were \( \beta \) and \( \gamma' \) in a \( \gamma \) matrix. The majority of the \( \gamma' \) phase present within the sample aged for 190 hours was present as very fine spherical precipitates, of the order of 100 nm in diameter. These were dispersed over areas of \( \gamma \) matrix and are referred to here as \( \gamma' \gamma' \) domains. With increased thermal exposure, these domains are seen to decrease in area fraction, with the fine \( \gamma' \) precipitates increasing in size to approximately 1 - 2 \( \mu \text{m} \) enabling them to be differentiated from the underlying \( \gamma \) matrix, as illustrated in Figure 5.57.

![Figure 5.57](image)

**Figure 5.57** SEM micrographs of NiCoCrAlY coated CMSX4 thermally exposed at 850°C showing the size and morphology of the phases present within the bulk of the coating for a) 190, b) 2000 and C) 10,000 hours

Figure 5.58 shows that after 2000 hours, a depletion of precipitates was observed at the coating surface, which results in a continuous layer of the \( \gamma \) matrix approximately 5 - 7 \( \mu \text{m} \) in thickness. Adjacent to the \( \gamma \) layer, a layer of \( \gamma' \) precipitates are present. Consequently the \( \beta \) phase with an average size of 2 - 3 \( \mu \text{m} \) is present at an average distance of 19.5 \( \mu \text{m} \) into the coating, hence confirming that \( \beta \) depletion within this area has occurred due to the diffusion of Al from the coating out towards the protective oxide layer. The depletion of the \( \beta \) phase continues with increased exposure times up to 10,000 hours.
Interdiffusion of elements between the coating and the substrate during aging has formed an interdiffusion zone (IDZ). A continuous $\gamma'$ layer separating the coating from the substrate can be observed within the interdiffusion zone at all aging times. It has been suggested that this layer forms due to the net increase of Al in the substrate and Ni in the coating. This results in the transformation of the $\gamma$ phase in the substrate adjacent to the coating into the $\gamma'$ layer. At 850°C this layer was seen to increase in thickness with length of exposure from 7.7 - 18.3 $\mu$m, indicating the increase in diffusion of elements across the interdiffusion zone, resulting in the dissolution of $\gamma$, and the formation of $\gamma'$.

In addition to the $\gamma'$ layer, the interdiffusion of elements such as Cr, Re and W across the coating/substrate interface has encouraged the formation of several intermetallic phases. Cr-rich phases of globular morphology are observed within the coating adjacent to the interface, throughout the exposure lengths at 850°C. These precipitates were identified as $\text{M}_2\text{C}_6$. 
carbides \( (a_o = 10.638\AA) \) using a combination of selected area electron diffraction (SAED) patterns and EDX analysis. Precipitates rich in W, Re and Cr are observed within the \( \gamma' \) layer; the high levels of refractory elements and the needle-like structure suggests these are topologically closed packed (TCP) phases. With increased diffusion across the interdiffusion zone with increased exposure time these precipitates are seen to increase in area fraction and size resulting in their extension out into the substrate, as shown in Figure 5.60. Selected area diffraction and EDX analysis enabled the identification of the TCP phases as the Cr-rich \( \sigma \) phases \( (a_o = 9.3\AA \text{ and } c_o = 4.86\AA) \) and the W/Re rich \( \mu \) phase \( (a_o = 4.75\AA \text{ and } c_o = 25.8\AA) \). From TEM studies, it was observed that at the lower exposure times up to approximately 1000 hours the predominant precipitates that have formed are \( \sigma \) phase, whereas after prolonged exposure up to 10,000 hours both \( \sigma \) and \( \mu \) are present within the interdiffusion zone and are difficult to distinguish on morphology alone.

![Figure 5.60 SEM micrographs of NiCoCrAlY coated CMSX4 thermally exposed at 850°C showing the growth of the TCP phases observed in the \( \gamma' \) layer within the IDZ for a) 190, b) 2000 and C) 10,000 hours](image.png)

**5.4.3 Microstructural Changes Observed at 950°C**

As observed at 850°C, the main phases present within the bulk of the coating of the isothermally aged samples were \( \beta \), \( \gamma' \) and \( \gamma \). A continuous precipitate-free \( \gamma \) layer of 5 - 6 \( \mu m \) was observed at the coating surface of the sample aged at 950°C. This is in contrast to the sample aged at 850°C for 190 hours where no precipitate free layer had formed. This depletion of \( \gamma' \) and \( \beta \) precipitates at the coating surface indicated that with exposure to higher temperatures there was an increase in outward diffusion of Al from the coating towards the oxide layer. Similar to observations at 850°C, the precipitate free \( \gamma \) layer increased in thickness with longer exposure times, although at a faster rate, as illustrated in Figure 5.61. In addition, at 950°C a \( \beta \) depletion layer was becoming evident within the coating close to the
coating/substrate interface. Once more, the result of the outward diffusion of Al from the coating towards the substrate alloy.

Figure 5.61 SEM micrographs of NiCoCrAlY coated CMSX4 thermally exposed at 850°C showing the depletion of phases at the coating surface of samples aged at a) 190, b) 2000 and C) 10,000 hours

The γ' precipitates within the bulk of the coating have remained cuboidal in shape at the shorter exposure times, but have increased in size when compared to those in the 190 hour samples. The increase in size continues with increased exposure eventually giving rise to rounding of the precipitates at 10,000 hours, shown in Figure 5.62.

Figure 5.62 SEM micrographs of NiCoCrAlY coated CMSX4 thermally exposed at 850°C showing the size and morphology of the phases within the bulk of the coating for samples aged at a) 190, b) 2000 and C) 10,000 hours

The interdiffusion zone observed at 950°C had similar microstructural features to those encountered in samples aged at lower temperatures. The continuous γ' layer within the interdiffusion zone increased in thickness with exposure length from approximately 25 to 54 μm. The Cr-rich M_{23}C_{6} particles of globular morphology were once more observed within the coating section of the interdiffusion zone; this proved consistent with increased exposure
times. In addition, at 950°C light grey phases with a geometric morphology are observed within the γ' layer, increasing in area fraction with thermal exposures of 190 to 10,000 hours, as shown in Figure 5.63. Chemical analysis showed that these precipitates are rich in Cr and Re, with ~ 5 wt.% C, once more indicating M23C6 carbides. Subsequently, the phase was positively identified using the combination of SAED patterns and EDX analysis. The difference in Cr and Re content between the globular and geometric morphology indicates the composition of the M23C6 carbide is dependent on position within the interdiffusion zone. The volume fraction and size of the needle-like W, Re and Cr rich TCP phases within the continuous γ' layer have increased in comparison to the sample aged at 850°C. This growth results in the extension of the TCP phases out into the substrate at various angles to the interface, together with becoming more segmented as the exposure time increases. From TEM studies using SAED patterns and EDX analysis, the TCP phases present within the IDZ at 950°C have been identified as σ, μ and P phase. The predominant phases observed within the higher exposure times of 2000 to 10,000 hours are W/Re rich μ and P phase.
Figure 5.63 SEM micrographs of NiCoCrAlY coated CMSX4 thermally exposed at 950°C showing the growth of the carbides and TCP phases observed within the IDZ for a) 190, b) 2000 and c) 10,000 hours: d) and e) higher magnifications of areas located within a); f) higher magnification of γ' layer in b); g) and h) higher magnifications of areas located within c)
5.4.4 Microstructural Changes Observed at 1050°C

At the shorter exposure times of 190 and 2000 hours $\beta$ and the $\gamma$ matrix were the predominant phases present within the coating, which is different from the other samples investigated. At 190 hours, $\beta$ precipitates of various sizes and morphologies were observed in the coating, within which no $\gamma'$ precipitates were detected. Thermodynamic equilibrium calculations conducted on the coating indicate that at 1050°C, $\gamma'$ is not thermodynamically stable. Similar observations were made at 2000 hours, except for the presence of large $\gamma'$ precipitates scattered throughout the central section of the coating as shown in Figure 5.65. The large $\gamma'$ precipitates observed at 2000 hours were of similar size and shape to those of the surrounding $\beta$ phase. The diffusion of Al out towards the coating surface and substrate has resulted in transformations from $\beta$ to $\gamma'$ in several of the particles. Exposure for 10,000 hours resulted in a substantial reduction in second phases within the coating. Dissolution of the phases had occurred due to the increased diffusion of elements out towards the coating surface and across the substrate/coating interface into the substrate. It is again evident that the continuous $\gamma$ layer produced on the outer edge of the coating had increased in thickness substantially to $\sim$ 220 $\mu$m with increasing exposure lengths. The absence of $\beta$ precipitates within the coating confirms that $\beta$ acts as the initial Al reservoir in the coating for the production and sustainability of the protective oxide scale. This dissolution of the $\beta$ results in a thin layer of $\gamma'$ particles remaining within the central bulk of the coating.

![Figure 5.64](image)

**Figure 5.64** SEM micrographs of NiCoCrAlY coated CMSX4 thermally exposed at 1050°C showing the depletion of phases at the coating surface for samples aged at a) 190, b) 2000 and C) 10,000 hours
The microstructure of the interdiffusion zone within the samples aged at 1050°C shows a substantial reduction in second phases in the coating, as shown in Figure 5.66. The continuous $\gamma'$ layer separating the coating and substrate appears to have become segmented in nature. Coarse and irregular finger-like precipitates extend into the coating suggesting increased diffusion activity across the boundary with temperature. At the shorter exposure times of 190 and 2000 hours, small particles rich in Ta, Hf and Ti were observed within the lower section of the coating and precipitating in a linear array parallel to the coating/substrate interface. Due to the high proportions of Ta and the presence of C, these particles were identified as MC carbides. The location of these carbides was similar to that of the $M_{23}C_6$ observed at lower temperatures, verifying the low and high temperature stability of the $M_{23}C_6$ and MC carbides respectively. The MC carbides are again observed at 10,000 hours, and chemical analysis showed that they contain differing areas within the particle that were characterised by varying ratios of Ta to Ti. The TCP phases observed at 1050°C have coarsened significantly with temperature, resulting in segmented needle and blocky type structures. These structures at shorter exposure times were observed to extend out from the $\gamma'$ layer into the substrate a distance of approx 12 μm; this increases considerably with exposure extending the interdiffusion zone 425 μm into the substrate. Chemical analysis of these precipitates suggested them to be the W/Re-rich $\mu$ and P phase, verifying the high temperature stability of these phases.
5.4.5 Overview of Microstructural Evolution

This chapter has presented and discussed the results of the detailed microstructural investigations carried out on NiCoCrAlY coated CMSX4 samples, isothermally exposed at different temperatures for different times. Thermodynamic equilibrium calculations were carried out on the NiCoCrAlY coating in order to predict the amount and chemical composition of the phases occurring at equilibrium as a function of temperature, which in turn assisted in phase identification. Thermodynamic ‘thought’ calculations were performed across the coating/substrate interface to provide an indication of the effect that interdiffusion has on the amount and type of phase predicted.

It has been well documented that the Al in the coating is consumed by both oxide formation at the surface and by interdiffusion at the substrate/coating interface, producing Al depletion zones that increase with time and temperature\[^{1,11,116}\]. These Al depleted zones correspond to the depletion of β-NiAl within these areas which increases with time and temperature. The increase in the β depletion and the increased growth of the oxide scale, as shown in Figures 5.67 a) and b) confirm that the β-NiAl acts as the initial Al reservoir within the coating. It can also be seen from Figure 5.67 that both the oxide thickness and the β depletion layer increases with increasing thermal exposure as expected.
Figure 5.67 Plots showing a) the thickness of the oxide scale on the coating surface and b) β depletion layer thickness at the coating surface of the NiCoCrAlY coated CMSX4 samples as a function of temperature for different exposure times.

It has been indicated in literature that the end of life for a coating is the dissolution of all the β-NiAl precipitates\[113\]. The investigation has shown that the transformation of β-NiAl to γ′-Ni₃Al within the bulk of the coating was observed within the sample aged at 1050°C for 2000 hours, and continued to occur until all of the β was consumed. The coating present at 1050°C was still intact indicating that, although no β remained, the Al content within the coating was greater than the critical value needed to sustain the protective nature of the oxide. The stability
of the $\gamma'$ phase at the higher temperatures illustrated the effect that alloying elements such as Ta within the coating can have on the relative stability of phases.

The continuous $\gamma'$ layer observed at the coating/substrate interface has been suggested to form due to the net increase of Al in the substrate and Ni in the coating. This flux of elements leads to the transformation of the $\gamma$ phase from the substrate adjacent to the coating into the $\gamma'$ layer. The growth of this layer into the substrate was observed as a result of increased temperature and length of exposure, indicating the increase in diffusion of elements across the interdiffusion zone, resulting in the dissolution of $\gamma$ to $\gamma'$. The $\gamma'$ phase has a lower solubility for certain elements such as Cr, Co and W resulting in the precipitation of phases rich in these elements.

Interdiffusion of elements occurs at the coating/substrate interface during high temperature service; this can be due to the differences in chemical composition between the two thus promoting chemically driven diffusion of certain elements. The diffusion of Cr from the coating towards the substrate has encouraged the formation of Cr-rich $M_{23}C_6$ carbides of globular morphology adjacent to the interdiffusion zone in all the samples thermally exposed at 850 and 950°C. Additionally Cr-rich $M_{23}C_6$ carbides of geometric morphology were only observed within the $\gamma'$ layer of samples exposed at 950°C. However, due to these latter geometric $M_{23}C_6$ precipitates having a higher Re content, it was suggested that these evolved from the pre-existing $\sigma$ phases observed at lower temperatures\textsuperscript{10,22,27}.

With increasing temperature the formation of MC carbides became evident; these are rich in Ti and Ta and were observed precipitating in a linear array parallel to the coating/substrate interface, the location of which proved very similar to that of the $M_{23}C_6$ observed at lower temperatures, thus verifying that there is a phase transformation from the high temperature stable MC to that of the lower temperature stable $M_{23}C_6$ carbides. The presence of these MC carbides confirms Ta's role as a barrier agent to inhibit the Ti diffusion into the coating hence trapping the majority of the Ti in the form of carbides at the coating/substrate interface. The diffusional transport of Ti through the coating is undesirable as it promotes the formation of Cr$_2$O$_3$, hence preventing the protective action of the Al$_2$O$_3$ scale\textsuperscript{103}. With increased temperatures up to 1050°C chemical analysis of the MC carbide particles showed that the
majority contain differing areas characterised by the varying ratios of Ta to Ti. The areas with a brighter appearance in the BSE mode proved have a higher wt.% of Ta.

The diffusion of refractory elements across the coating/substrate interface has led to the formation of complex plate-like TCP phases, rich in Re and W. These are seen to initiate within the interdiffusion zone and extend significantly into the substrate at an angle of ~ 45 degrees. It is apparent from this investigation that there is an increase in quantity and size of the TCP phases as aging temperature and exposure length of the sample is increased, resulting in significantly coarsened segmented needle and blocky type structures. Figure 5.68 shows the increase in interdiffusion zone thickness with time and temperature, which was mainly affected by the growth in TCP length. TEM studies have allowed the identification of the complex TCP phases formed within the interdiffusion zone using SAED patterns and EDX analysis. Within the samples exposed at the lower temperatures and lower exposure times up to approximately 1000 hours the predominant precipitates that have formed are $\sigma$ phase, whereas after prolonged exposure up to 10,000 hours both $\sigma$ and $\mu$ are present within the IDZ. With increase in temperature the phases identified were $\sigma$, $\mu$ and P phase; the predominant phases observed at longer exposure times being the W and Re rich $\mu$ and P phase, indicating the high temperature stability of these phases.

![Figure 5.68](image)

**Figure 5.68** Plot showing the thickness of the interdiffusion zone at the coating/substrate of the NiCoCrAlY coated CMSX4 samples as a function of temperature for different exposure times
5.5 Summary

This chapter has presented and discussed the results of the detailed microstructural investigations carried out on the NiCoCrAIY coated CMSX4 samples. Examination of the samples and determination of phase stability as a function of temperature, time and position relative to the coating/substrate interface was carried out using a variety of microscopy techniques. These experimental observations are compared with theoretical predictions using a coupled thermodynamic and kinetic model, of the chemical composition and phase stability as a function of temperature in the following chapter.
Chapter 6
Microstructural Modelling of MCrAlY Coated Ni-based Superalloys

6.1 Introduction

Operating temperatures within gas turbine engines are constantly being increased to keep pace with the desire for increased efficiency. The combination of these high temperatures and aggressive environments leads to increased rates of oxidation and hot corrosion attack upon the gas turbine components, which can significantly reduce their mechanical properties. It is therefore necessary to have sufficient oxidation and corrosion resistance at high temperatures in order to provide a satisfactory component life. In most modern situations, Ni-based superalloy components such as turbine blades and vanes are typically protected by MCrAlY coating systems (M being Ni and/or Co) as discussed in the previous chapter. Coatings attain their protective action from the interaction/reaction with oxygen present in the working environment. This interaction with oxygen forms dense, adherent oxide scales on the surface of the coating, which as a result inhibits the diffusion of damaging elements into the substrate material. To form this dense oxide layer the coating needs to be rich in elements that readily form protective oxide scales such as Al and Cr, and therefore the life of the coating is related to its ability to form the protective scales and/or replace the scale as and when required. The oxide scale may suffer periodic damage (spallation) due to the stresses induced by thermal cycling; however, the scale can be restored by further oxidation as long as there are sufficient scale forming elements remaining in the coating. The efficiency of this 'healing' process diminishes as the reservoir of protective scale formers, mainly Al in the coating, depletes over time due to its consumption by the oxide scale and interdiffusion with the substrate and as a result the rapid nucleation and growth of base metal oxides can occur. A critical Al content in the coating can be defined to indicate the useful life of the coating. This critical Al content could indicate the time at which less protective oxides form on the surface or indeed a time at which the coating should be stripped from the component and a new coating applied.

The differences in chemical composition between the coating and substrate promote chemically driven diffusion of certain elements across the coating/substrate interface. Modern
single crystal superalloys contain a multitude of heavy elements such as Co, Ta, Hf, W, Re and Mo, and because their compositions are optimised primarily for high creep strength, the Al and Cr concentrations are kept lower than the desirable levels for prolonged oxidation resistance. The overlay coatings on the other hand have higher levels of these elements, and since their major function is surface protection, they contain a smaller number of heavy elements compared to base metals. Consequently, these large differences in compositions between the coating and base metal cause significant interdiffusion across the coating/substrate interface.

MCrAlY coatings can typically consist of a mixture of $\beta$ (NiAl), $\gamma$' (Ni$_3$Al) and $\gamma$ (Ni) phases, depending on the chemical composition and temperature. The depletion of Al (and also Cr) from the coating by the formation and growth of the oxide scale at the coating surface and the interdiffusion with the substrate, results in the depletion of $\beta$ NiAl phase, which gradually transforms to a less Al-rich $\gamma$'-Ni$_3$Al and finally to a $\gamma$-Ni solid solution. On the other hand, single crystal Ni-based superalloys are characterised by a two phase microstructure consisting of a $\gamma$ matrix and high volume fractions of the $\gamma$' phase, as shown in Chapter 4. However, the interdiffusion of elements across the coating/substrate interface can result in a interdiffusion zone which is characterised by the area at the interface affected by the interdiffusion of elements, resulting in a distinct microstructure unlike that of the coating and/or substrate, which can also contain intermetallic TCP phases such as $\sigma$, $\mu$ and P phase, together with numerous carbides including MC and M$_{23}$C$_6$ carbides.

A complete understanding of the diffusion assisted degradation processes and the microstructural changes that take place within the coating, interdiffusion zone and substrate material is crucial in order to develop more accurate life prediction procedures for coatings and coated Ni-based superalloys. Modelling of these diffusion processes which occur during service can be an important tool to predict coating and substrate degradation as a function of time and operating temperature. This can be a significant advantage for the estimation of long term component performance, and also for the selection of optimum coating/substrate combinations.

It is important for any model dealing with microstructure evolution in coated superalloy systems to be able to simulate the oxidation, interdiffusion and phase stability simultaneously.
because these phenomena are all interlinked. Previous modelling efforts have been concentrated on limited systems. For example the work by Nesbitt\textsuperscript{[17]} was on the ternary system Ni-Cr-Al, and the models did not take either the phase constitution or diffusion in precipitate phases into account. A recent paper\textsuperscript{[18]} which utilizes the software package DICTRA\textsuperscript{[19]} takes multicomponent diffusion into account but it deals with oxidation in a limited manner, and does not explicitly treat diffusion in phases other than the $\gamma$ matrix.

The first part of this Chapter presents the details of the modelling approach, and the second part of the chapter compares the predictions of the model with the experimental observations presented in Chapter 5. Simulations were carried out at 850, 950 and 1050$^\circ$C for times up to 10,000 hours for the NiCoCrAlY overlay coating Amdry 997 on a CMSX4 substrate using their nominal chemical compositions.

### 6.2 Combined Thermodynamic and Kinetic Coupled Model\textsuperscript{1}

Within this investigation the aim was to develop a one-dimensional model to predict the concentration profiles associated with the oxidation and interdiffusion that occurs in coated superalloys. This model can therefore act as a time temperature recorder, to allow the prediction of the effective operating temperature of a component and as a result (in combination with other information such as operating stress) estimate its remaining life in service. Due to the complexities of the problem, a numerical solution scheme employing finite difference (F-D) techniques was implemented.

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\textsuperscript{1} The development of the model discussed in this chapter has been carried out by Dr Mudith Karunaratne in a parallel project which is part of the same overall research programme. A description of the model is provided here for completeness; however, the main aim of this research was to compare the predictions of the model with the experimental observations discussed in the previous chapter, with the view both to validation of the model and to make suggestions as to further improvement.
6.2.1 Diffusion Model

For a multicomponent system with \( n \) elements, the diffusion of a species can be mathematically described by means of Fick’s First Law of diffusion:\(^{120,121}\):

\[
J_i = -\sum_{j=1}^{n-1} \tilde{D}^n_{ij} \frac{\partial C_j}{\partial x}
\]  

[6.1]

where \( i \) and \( j \) are diffusing components and \( J_i \) is the flux of diffusing element \( i \). \( \tilde{D}^n_{ij} \) is the interdiffusion coefficient matrix and is expressed in relation to solvent \( n \), in this case the substrate element is Ni and \( C_j \) is the concentration of element \( j \). Furthermore, the time dependent concentration of a species is given by Fick’s second law of diffusion:

\[
\frac{\partial C_j}{\partial t} = -\sum_{j=1}^{n-1} \frac{\partial}{\partial x} \tilde{D}^n_{ij} \frac{\partial C_j}{\partial x}
\]  

[6.2]

where \( x \) and \( t \) are distance and diffusion time respectively. This equation can be expanded when concentration dependent coefficients \( \tilde{D}_{i,j}^{Ni} \) are taken into account:

\[
\frac{\partial C_i}{\partial t} = \sum_{j=1}^{n-1} \left\{ \tilde{D}^n_{ij} \frac{\partial^2 C_j}{\partial x^2} + \left( \sum_{k=1}^{n-1} \frac{\partial}{\partial C_k} \tilde{D}^n_{ik} \frac{\partial C_k}{\partial x} \right) \frac{\partial C_j}{\partial x} \right\}
\]  

[6.3]

However, if the diffusion coefficients are constant, the following simplification is possible:

\[
\frac{\partial C_i}{\partial t} = \sum_{j=1}^{n-1} \tilde{D}^n_{ij} \frac{\partial^2 C_j}{\partial x^2}
\]  

[6.4]

The numerical model used to solve the Equation 6.3 was based on a finite difference (F-D) method, with the differential terms being replaced by F-D equivalents derived from Taylor series expansions\(^{122}\). The F-D method requires the use of a nodal grid across the regions of the material over which the diffusion processes occur. For each node, the unknown values are calculated, replacing the differential equations by difference equations. In such a system, the solution is derived for small concentration differences (\( \Delta C \)) at finite locations identified by a
grid-spacing ($\Delta X$) and time intervals ($\Delta t$). The concentration profile at a time $t$ is found by solving the F-D equations for small time increments ($\Delta t$) iteratively. These iterations are applied until the increments sum to the desired total ageing time $t$. Figure 6.1 shows a schematic representation of a diffusion zone at time $t$ and the new concentrations at time $t + \Delta t$.

![Figure 6.1 Schematic representation of the diffusion zone for time t and time t + \Delta t](image)

The F-D equivalent to Fick's second law can be given by either an explicit or implicit representation. The explicit F-D method enables the determination of an unknown value at one node within a grid to be expressed directly in terms of a subsequent known value at node $n-1$ at each time step. This method is most commonly used within diffusion based models for high temperature oxidation when there is a strong time dependent boundary condition, which requires the use of fairly small time increments.

In the explicit solution, the first and second derivatives of the concentration gradients in respect to distance are represented by central difference formulae as:

$$\frac{\partial C_i}{\partial x} = \frac{C_{J,N+1}^i - C_{J,N-1}^i}{2\Delta X} \quad [6.5]$$

$$\frac{\partial^2 C_i}{\partial x^2} = \frac{C_{J,N+1}^i - 2C_{J,N}^i + C_{J,N-1}^i}{\Delta X^2} \quad [6.6]$$

where $i$ refers to the diffusing element, $N$ is the node number and $J$ is the current iteration at time $t$. These equations apply to all nodes $n$, where the adjacent nodes $n-1$ and $n+1$ exist.
forward difference expression was used for the time derivative in the left hand side of Equation 6.3:

$$\frac{\partial C_j}{\partial t} = \frac{C_{j+1,N}^i - C_{j,N}^i}{\Delta t}$$ \[6.7\]

where $J+1$ is the next iteration at time $t + \Delta t$. The first derivatives of the diffusion coefficients were also represented by:

$$\frac{\partial \bar{D}_{ij}^n}{\partial x} = \frac{\bar{D}_{ij(N+1)}^n - \bar{D}_{ij(N-1)}^n}{2\Delta X}$$ \[6.8\]

Substitution of Equations 6.5 - 6.8 into 6.3 would provide a formula for the unknown concentrations at $J+1$ time step $C_{j+1,N}^i$, in terms of known concentrations, diffusion coefficients and boundary conditions at step $J$, explicitly. Such an explicit solution has the advantage of being able to account for variable diffusion coefficients. However, the explicit F-D method can suffer from instabilities and therefore the size of the time increment $\Delta t$ must be restricted by a stability criterion, typically given as:

$$\Delta t \leq 0.25 \frac{\Delta X^2}{\bar{D}_{ij}^n}$$ \[6.9\]

where $X$ is the grid spacing. A consequence of this stability criterion is that there are limitations on having comparatively large diffusion coefficients within the system.

The implicit F-D method proposed by Crank and Nicolson\cite{123} implies that the solution of a set of $N$ simultaneous equations at each time step, for a number of unknown values is related to the number of nodes within a grid as a function of the initial values and boundary values. Therefore, this method involves a significantly greater amount of computational work at each time step when compared to the explicit method. However, the advantage is that this method is stable for all values of $\frac{\Delta X^2}{\bar{D}_{ij}^n}$ in Equation 6.9. The implicit solution is derived by replacing the
second derivative of Equation 6.4 by the average of its F-D representations on the $J+1$ and $J$th iterations as:

$$\frac{\partial^2 C_i}{\partial x^2} = \frac{1}{2} \left\{ \frac{C_{j+1,N+1} - 2C_{j+1,N} + C_{j+1,N-1}}{\Delta X^2} + \frac{C_{j,N+1} - 2C_{j,N} + C_{j,N-1}}{\Delta X^2} \right\} \quad [6.10]$$

Substitution of Equations 6.7 and 6.10 in 6.4 produces a system of linear equations which, after applying appropriate boundary conditions, can be solved efficiently for $C_{J,N}$ by a tridiagonal matrix algorithm\(^{124}\).

### 6.2.2 Oxidation Model

There have only been a few studies into the oxidation kinetics of bond coat materials, and in the absence of a model and data specific for the coating being investigated, the model proposed by Meier et al. for a Ni-Co-Cr based bond coat was used\(^{125}\). The model assumes that Al and Cr are being oxidised at the coating surface. However, no experimental and/or physically based models for Cr oxidation were available, therefore an arbitrary factor of 0.4 (the ratio of Cr flux to Al flux at the oxidation interface) was introduced, although in general the oxidation behaviour of Cr was assumed to be similar to that of Al. The diffusion of elements within the oxide are not considered in the current model. For isothermal oxidation, the boundary condition at the oxide/coating interface is given as the rate of Al and Cr consumption, where the thickness $\delta$ of the oxide scale in $\mu$m is given by

$$\delta = \left[ \exp \left\{ Q \left( \frac{1}{T_0} - \frac{1}{T} \right) \right\} \right]^{nt} \quad [6.11]$$

where $Q$ is a constant and equal to 27777.4, $T$ is the temperature in Kelvin, $T_0$ is 2423.7 K, $t$ is time and $n$ is equal to 0.332. For the rate of change of oxide thickness, $\dot{\delta}$ the first derivative of Equation 6.11 was taken:

$$\dot{\delta} = n \left[ \exp \left\{ Q \left( \frac{1}{T_0} - \frac{1}{T} \right) \right\} \right]^{nt-1} \times \left[ \exp \left\{ Q \left( \frac{1}{T_0} - \frac{1}{T} \right) \right\} \right] \quad [6.12]$$
Following a similar approach proposed by Nesbitt et al.\cite{117} and Lee et al.\cite{126} the rate of change of oxide scale thickness in Equation 6.12 can be used to calculate the Al atomic flux in the coating, which was used as a boundary condition in the diffusion model. The Al flux away from the oxide/coating interface can be determined by the following equation:

$$J_{Al} \bigg|_{x=\psi^-} = \hat{\delta} \rho_{ax} \dot{r}$$ \hspace{1cm} [6.13]$$

where \(\psi\) represents the position of the interface, \(\dot{\delta}\) is the rate at which the oxide grows, \(\rho_{ax}\) is the density of the oxide and \(r\) is the ratio of atomic weight which for \(\text{Al}_2\text{O}_3\) is equal to \(2a_{Al}/3a_O = 1.1242708\). This flux of Al is equal to the diffusional flux of Al in the coating towards the interface. However, as the interface between the oxide and the coating is moving, the flux away from the interface into the oxide is related to the flux towards the interface by the following equation:

$$J_{Al} \bigg|_{x=\psi^+} = \alpha J_{Al} \bigg|_{x=\psi^-}.$$ \hspace{1cm} [6.14]$$

where \(\psi^-\) and \(\psi^+\) refer to the oxide and coating sides of the interface respectively, with \(\alpha\) given by:

$$\alpha = \frac{1}{1 - V_{Al} C_{Al,O}}$$ \hspace{1cm} [6.15]$$

where \(V_i\) is the partial molar volume of Al and \(C_{Al,O}\) is the concentration of Al at the oxide/coating interface.

The Al flux towards the coating surface can also be represented by:

$$J_{Al} \bigg|_{x=\psi^+} = -\sum_{j=1}^{n-1} \tilde{D}_j \frac{\partial C_j}{\partial x}$$ \hspace{1cm} [6.16]$$

For which the concentration gradients at the interface have to be determined using second order forward difference equations as follows:
Equation 6.17 is then used in conjunction with Equations 6.11 - 6.16 to calculate the concentrations at the oxidation boundary.

6.2.3 Thermodynamic Model

The thermodynamic equilibrium calculations were performed using the Application Interface\(^{[127]}\) of MTDATA\(^{[128]}\). The MTDATA program consists of a numerical technique for the minimisation of Gibbs energy, and was used in conjunction with a thermodynamic database for Ni-based superalloys, Ni-DATA as discussed in Chapter 3\(^{[101]}\). Assuming that the local equilibrium hypothesis is valid for the calculation, the code calls the MTDATA application interface at each time-step, with the concentration at each node in the diffusion grid sequentially. It should be noted that the system temperature and pressure are assumed to remain constant during each simulations, with the pressure set to be one atmosphere and the temperature chosen as the isothermal ageing temperature. MTDATA in turn returns a description of equilibrium phases which are likely to be present at each node. This description includes the fractional phase composition and the composition within each of the phases. These data are used by the diffusion code to calculate an ‘effective’ diffusion coefficient for each element at each node.

It should be noted that diffusion within these systems is a non-equilibrium process, however, the results provided by thermodynamic calculations are obtained under the hypothesis that thermodynamic equilibrium conditions exist at a given temperature and concentration. Although the non equilibrium conditions exist in reality, the thermodynamic calculations provide a good indication of the phases present as a function of time, temperature and composition.

Due to the incorporation of a large number of elements, alloy phases and grid-points, the equilibrium calculations become computationally expensive, especially as a result of the presence of phases with miscibility gaps. In order to minimise computational speed, the simulation code, including the MTDATA program, was run in parallel on a computer cluster at the High Performance Computer Facility at Loughborough University. The simulation was
run using 16 processors with the grid points equi-partitioned between the processors. The code was written in the C language, with Message-Passing-Interface (MPI) code extensions to facilitate parallel computing.

6.3 Implementation

6.3.1 Zone Division

In the initial stages of the simulation, the diffusion was modelled only at two separate locations, as independent phenomena. These are depicted as zone 1 and zone 2, where concentration gradients are steepest as shown in Figure 6.2. Zone 1 is at the surface of the coating, near the oxide/coating interface and related to the diffusional transport due to oxidation. Zone 2 covers the coating/substrate interface which is related to the interdiffusion between the two materials. Regions outside these zones were assumed to have zero concentration gradients and hence no interdiffusion fluxes should exist in these regions initially. Considering interdiffusion at the two zones as independent problems initially allowed computational resources to be concentrated more efficiently.

![Schematic diagram of the initial concentration profiles across zone 1 and zone 2](image)

Figure 6.2 Schematic diagram of the initial concentration profiles across zone 1 and zone 2

The oxidation of the coating (Zone 1) can be treated as the oxidation of a semi-infinite material which only affects the immediate area underneath the surface of the coating. In a similar manner, coating/substrate interdiffusion (Zone 2) can be treated as a case of interdiffusion between two semi-infinite materials, the coating and substrate.
The initial grid layout used in the simulations at different temperatures, including the number of nodes defined for each zone are presented in Table 6.1. The coating thickness and grid spacing inputted were chosen to provide the best comparison with the experimental data obtained.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Coating thickness (μm)</th>
<th>Zone</th>
<th>Nodes</th>
<th>Spacing (μm)</th>
<th>Range (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>850</td>
<td>350</td>
<td>Zone 1</td>
<td>40</td>
<td>0.2</td>
<td>0.0 - 7.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Zone 2</td>
<td>40</td>
<td>0.2</td>
<td>346.0 - 353.0</td>
</tr>
<tr>
<td>950</td>
<td>215</td>
<td>Zone 1</td>
<td>40</td>
<td>0.5</td>
<td>0.0 - 19.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Zone 2</td>
<td>40</td>
<td>0.5</td>
<td>205.0 - 224.5</td>
</tr>
<tr>
<td>1050</td>
<td>350</td>
<td>Zone 1</td>
<td>40</td>
<td>1.20</td>
<td>0.0 - 46.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Zone 2</td>
<td>40</td>
<td>1.20</td>
<td>326.0 - 372.8</td>
</tr>
</tbody>
</table>

Table 6.1 Initial grid layout for the simulations

6.3.2 Initial Concentration Distribution

An error function solution was used to initially assign the coating and substrate compositions to the nodes in order to provide a smooth transition between the coating and substrate compositions. The nodes in zone 2 are assigned concentrations, with the initial concentration distribution given by:

$$C_j = C_j^C + \left[ \frac{C_j^S - C_j^C}{2} \left( 1 + \text{erf} \left( \frac{x - x_T}{x_{Z2}} \right) \right) \right]$$  \[6.18\]

where $C_j^C$ and $C_j^S$ are the initial concentrations of element $j$ in the coating and substrate respectively, $x_T$ is the thickness of the coating and $x_{Z2}$ is the length of zone 2. The constant $k$ determines the sharpness of the distribution variation; for this work $k = 0.33$ was used.

The compositions of the coating and substrate used in these simulations are given in Table 6.2. The substrate and coating composition is based on the standard single crystal CMSX-4...
material and on the Amdry-997 coating. These are similar to the full chemical compositions given in Chapter 3. However, the presence of Y was neglected in the model as it is not allowed for within the thermodynamic database. However, Y is generally thought to form oxides within such coatings and does not take part in the formation of any of the main coating phases; therefore, the predictions of the phases within the bulk of the coating are likely to be a reasonable representation.

<table>
<thead>
<tr>
<th>Element</th>
<th>Coating Amdry-997</th>
<th>Substrate Standard CMSX4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>Bal Bal</td>
<td>Bal Bal</td>
</tr>
<tr>
<td>Al</td>
<td>8.5 16.84</td>
<td>5.6 12.56</td>
</tr>
<tr>
<td>Ti</td>
<td>1.0 1.26</td>
<td>1.0 1.26</td>
</tr>
<tr>
<td>Cr</td>
<td>20.0 20.56</td>
<td>6.5 7.56</td>
</tr>
<tr>
<td>Co</td>
<td>23.0 20.87</td>
<td>9.5 9.75</td>
</tr>
<tr>
<td>Mo</td>
<td>- 0.6</td>
<td>0.6 0.38</td>
</tr>
<tr>
<td>Ta</td>
<td>4.0 1.18</td>
<td>6.25 2.09</td>
</tr>
<tr>
<td>W</td>
<td>- 6.0</td>
<td>1.97</td>
</tr>
<tr>
<td>Re</td>
<td>- 3.0</td>
<td>0.97</td>
</tr>
<tr>
<td>C</td>
<td>0.0024 0.0107</td>
<td>0.0024 0.0121</td>
</tr>
</tbody>
</table>

Table 6.2 Initial coating and substrate compositions used within the model

6.3.3 Zone Expansion and Merger

A flexible grid scheme was used and a diffusion zone was initially defined which would expand or contract to match the position of the moving boundaries. As the simulation progresses, the concentration profiles calculated extend further into the coating, in case of zone 1, and both into the substrate and coating in the case of zone 2. As a result the boundaries of the zones are extended accordingly. The difference in concentration ($|dC|$) of an element between the two outermost nodes of a zone was taken as the criterion for expansion. If $|dC| < 0.0005$ at.%, the zone expanded by a distance equivalent to the current node spacing, in the relevant direction. The expansion process involved relocation of the nodes and interpolating the concentrations onto the new grid locations using a spline-interpolation
process, similar to the one outlined in \cite{124}. The expansion process continues until the diffusion fields of the two zones overlap (soft impingement) and from that stage, the diffusion zones are combined together to form a single zone. The merging process involves the relocation of the nodes in zones 1 and 2 so that they form a continuous, equal spaced zone.

6.3.4 Treatment of Moving Boundaries

The interface between the oxide-scale and coating represents a moving phase boundary, which moves at a rate given by

\[
\frac{d\psi}{dt} = -V_i J_{OX} \tag{6.19}
\]

and as such was treated numerically according to the grid-point motion technique suggested by Murray and Landis \cite{129}. The main features of this method are that (i) the number of grid points is kept constant, and (ii) the moving phase boundary is always located on a node. This makes the grid either shrink or expand at each time step, depending on the direction of the expansion. It also requires redistribution of grid points at each time step. Application of this method to Zone 1, which is the zone affected by the moving oxidation/bond coat phase boundary, makes the grid-spacing in the zone to be reduced by a distance \(\Delta\psi/(N_{Z1} - 1)\), where \(\Delta\psi\) is the finite distance the oxidation interface moves during a time step, calculated by integrating Equation 6.19, and \(N_{Z1}\) is the number of nodes in Zone 1. As a result of the relocation of nodes in the zone, the concentration of each element \(i\) at each node \(N\) of the zone has to incremented at each timestep \(J\) by a factor \(\Delta C_{J,N}^i\) given by

\[
\Delta C_{J,N}^i = \frac{d\psi}{dt} \frac{(N_{Z1} - N) \left( C_{J,N+1}^i - C_{J,N-1}^i \right)}{(N_{Z1} - 1) 2\Delta X_{Z1}} \tag{6.20}
\]

where \(\Delta X_{Z1}\) is the grid spacing of Zone 1.

6.3.5 Carbon Diffusion

In the case of C, the diffusion coefficient is several orders of magnitude larger than that of the rest of the elements. The large diffusion coefficient, severely limits the size of time step that can be used in an explicit solution scheme according to Equation 6.9 and therefore results in extremely long computation times. Consequently the diffusion of carbon was treated using the
Crank-Nicolson implicit scheme, outlined in Equation 6.10. A parallel, equi-spaced grid was implemented for C diffusion, independent of the two Zone grid used for the other elements. At each time step, the C diffusion profile was interpolated onto the main grid to allow phase equilibrium calculations to be performed at the main nodes with C concentrations incorporated.

6.3.6 Diffusion Coefficients

The diffusion model is based on the binary interdiffusion coefficient of each element with Ni. The cross interdiffusion coefficients are only available for a few ternary systems which are for limited concentration and temperature fields. However, these are generally an order of magnitude smaller than the major coefficients, and were therefore ignored in this work. Where reliable concentration dependent binary data were available, they were incorporated into the model in terms activation energies and frequency factors as polynomial functions of concentration. For the γ phase, binary interdiffusion data are available for all the elements used in the current simulations. However, when elements for which reliable data are unavailable for a certain phase (P), the diffusion coefficient was assumed to be a fraction $f$ of its coefficient in the γ phase,

$$D_p^* = fD_0^*$$  \[6.21\]

where $f = 0.05$ for these simulations.

**Diffusion in γ Phase**

The interdiffusion coefficient $\tilde{D}$ obeys the Arrhenius relationship as follows:

$$\tilde{D} = \tilde{D}_0 \exp\{Q/RT\}$$  \[6.22\]

where $Q, \tilde{D}_0, R$ and $T$ are the activation energy, frequency factor, universal gas constant and absolute temperature respectively.
When such data were available, the concentration dependence of $\tilde{D}$ in the $\gamma$-Ni phase was modelled by fitting a third degree polynomial derived from the Arrhenius relationship to the $\ln \tilde{D}_o$ and $Q$ terms:

$$
\tilde{D} = \exp(\ln \tilde{D}_o - \ln Q)
$$

[6.23]

The polynomial parameters representing $\ln \tilde{D}_o$ and $Q$ are given in Table 6.3, together with the source from which they were obtained; the polynomial parameters correspond to the following expressions:

$$
Q = A_Q + B_Q C_i + C_Q C_i^2 + D_Q C_i^3
$$

[6.24]

$$
\ln \tilde{D}_o = A_{D_o} + B_{D_o} C_i + C_{D_o} C_i^2 + D_{D_o} C_i^3
$$

[6.25]

where $C_i$ represents the concentration of element $i$ in atomic-fractions. It should be noted that for C and Cr, reliable concentration data do not exist for the temperature range considered in the simulations and therefore, concentration independent diffusion coefficients were used in these cases.
\[ Q = A_Q + B_Q C_i + C_Q C_i^2 + D_Q C_i^3 \]

<table>
<thead>
<tr>
<th>Element</th>
<th>( A_Q )</th>
<th>( B_Q )</th>
<th>( C_Q )</th>
<th>( D_Q )</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>264060.32</td>
<td>-185785.25</td>
<td>7876261</td>
<td>-43162718.89</td>
<td>[130]</td>
</tr>
<tr>
<td>Ti</td>
<td>235752.04</td>
<td>431062.85</td>
<td>-5619895.9</td>
<td>-15667534.3</td>
<td>[131]</td>
</tr>
<tr>
<td>Cr</td>
<td>256990.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>[132]</td>
</tr>
<tr>
<td>Co</td>
<td>277341.76</td>
<td>66459.557</td>
<td>-161296.20</td>
<td>103145.10</td>
<td>[133]</td>
</tr>
<tr>
<td>Mo</td>
<td>267943.98</td>
<td>401832.57</td>
<td>84552.276</td>
<td>3083.533129</td>
<td>[134]</td>
</tr>
<tr>
<td>Ta</td>
<td>245665.10</td>
<td>386576.60</td>
<td>82003.439</td>
<td>2842.274527</td>
<td>[135]</td>
</tr>
<tr>
<td>W</td>
<td>286096.55</td>
<td>-1486255.9</td>
<td>-2030.5180</td>
<td>-11.82006453</td>
<td>[135]</td>
</tr>
<tr>
<td>Re</td>
<td>259018.77</td>
<td>-518079.88</td>
<td>2606.3586</td>
<td>-251.9939130</td>
<td>[135]</td>
</tr>
<tr>
<td>C</td>
<td>138164.4</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>[136]</td>
</tr>
</tbody>
</table>

\[ \ln D_0 = A_{D_0} + B_{D_0} C_i + C_{D_0} C_i^2 + D_{D_0} C_i^3 \]

<table>
<thead>
<tr>
<th>Element</th>
<th>( A_{D_0} )</th>
<th>( B_{D_0} )</th>
<th>( C_{D_0} )</th>
<th>( D_{D_0} )</th>
<th>( C_{\text{Max}} ) (at. fraction)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>-8.9487099</td>
<td>-8.2237061</td>
<td>667.07525</td>
<td>-3519.5345</td>
<td>0.120</td>
</tr>
<tr>
<td>Ti</td>
<td>-11.326019</td>
<td>47.902887</td>
<td>-612.70667</td>
<td>34.973423</td>
<td>0.060</td>
</tr>
<tr>
<td>Cr</td>
<td>-9.7145214</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>-</td>
</tr>
<tr>
<td>Co</td>
<td>-8.3511690</td>
<td>-0.62406121</td>
<td>-0.99282309</td>
<td>-0.027067801</td>
<td>0.90</td>
</tr>
<tr>
<td>Mo</td>
<td>-10.325493</td>
<td>41.560840</td>
<td>-112.43721</td>
<td>366.25500</td>
<td>0.064</td>
</tr>
<tr>
<td>Ta</td>
<td>-11.356740</td>
<td>57.955144</td>
<td>-1432.0071</td>
<td>9964.6323</td>
<td>0.035</td>
</tr>
<tr>
<td>W</td>
<td>-10.495898</td>
<td>-81.674914</td>
<td>-1554.5447</td>
<td>14552.435</td>
<td>0.034</td>
</tr>
<tr>
<td>Re</td>
<td>-14.078119</td>
<td>1.9533470</td>
<td>-2057.9530</td>
<td>26267.299</td>
<td>0.034</td>
</tr>
<tr>
<td>C</td>
<td>-11.512926</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 6.3 Polynomial coefficients used to model \( \ln D_0 \) (m2/s) in Equation 6.18 for concentration \( C \) of each element given in atomic fraction. The parameters are valid only up to the maximum concentration \( C_{\text{Max}} \). For concentrations above \( C_{\text{Max}} \) the diffusion coefficient at \( C_{\text{Max}} \) was used.

**Diffusion in the \( \gamma' \) Phase**

For Al diffusion in the \( \gamma' \) phase, the Arrhenius coefficients were determined by fitting a second degree polynomial to Arrhenius parameters provided by Ikeda et al[137]. The
polynomial expressions for the frequency factor $D_0$ in m$^2$s$^{-1}$ and activation energy $Q$ in kJmol$^{-1}$ are given by the following expressions$^{[137]}$:

$$\log_{10} D_0 = -1000C^2 + 530C - 67.4 \quad [6.26]$$

$$Q = 5000C^2 - 3750C + 930 \quad [6.27]$$

The concentration independent Arrhenius parameters ($Q$ and $D_0$) for Co and Cr were taken from data by Minamino et al.$^{[138]}$, whereas for Ti, data published by St. Frank et. al were used$^{[139]}$. The values for the parameters used for Co, Cr and Ti are presented in Table 6.4.

<table>
<thead>
<tr>
<th>Element</th>
<th>Activation energy $Q$ (kJ mol$^{-1}$)</th>
<th>Frequency factor $D_0$ (m$^2$s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co</td>
<td>325.0</td>
<td>4.2 x 10$^3$</td>
</tr>
<tr>
<td>Cr</td>
<td>366.0</td>
<td>1.10 x 10$^{-1}$</td>
</tr>
<tr>
<td>Ti</td>
<td>424.6</td>
<td>8.59 x 10$^{-1}$</td>
</tr>
</tbody>
</table>

Table 6.4 The Arrhenius parameters $Q$ and $D_0$ for a number of diffusing elements in the $\gamma'$ phase.

**Diffusion in the $\beta$ Phase**

In the case of the $\beta$ phase, reliable data exist only for Al and at concentrations $C > 0.48$ at.%. The concentration dependence Arrhenius parameters for $C > 0.48$ at.% were therefore modelled by fitting a third order polynomial to the data reported by Wei et. al.$^{[140]}$ and these are given by the following pair of equations:

$$\ln D_0 = 248416C^3 - 380687C^2 + 194221C - 32999.7 \quad [6.28]$$

$$Q = (2.63889C^3 - 4.04333C^2 + 2.06112C - 0.349333) \times 10^6 \quad [6.29]$$

However, for Al concentrations $C < 0.48$ at.%, data published by Nakamura et al.$^{[141]}$ were applied with following expressions derived by polynomial regression:

$$\ln D_0 = -7890.25C^3 + 10962.7C^2 - 5032.65C + 759.432 \quad [6.30]$$
$Q = \left(-1.51515C^3 + 2.02987C^2 - 8.96807C - 0.13397 \right) \times 10^8 \quad [6.31]$

**Diffusion in TCP and Carbide Phases**

There is an absence of diffusion data for elements within TCP and carbide phases. Therefore, the interdiffusion coefficient of an element with these phases was assumed to be a constant fraction ($f_D$ in this case $f_D = 0.05$) of the same element in the $\gamma$ phase represented as:

$$\bar{D}_{i,\text{Carbides/TCP}} = f_D \bar{D}_{i,\gamma} \quad [6.32]$$

**Effective Diffusion Coefficient**

At each node in the grid, an effective diffusion coefficient $\bar{D}_{i,\text{eff}}$ for each element $i$ was calculated by weighting in the volume fraction $f_P^V$ of each phase $P$ at that node, and the interdiffusion coefficient of that element in each phase $\bar{D}_{i,P}$ according to Equation 6.*

$$\bar{D}_{i,\text{eff}} = \sum_P f_P^V \bar{D}_{i,P} \quad [6.33]$$

The volume fractions of each phase were determined from the mass fractions $f_P^M$ obtained from thermodynamic calculations using the following equation:

$$f_P^V = \frac{f_P^M / \rho_P}{\sum_P \left(f_P^M / \rho_P \right)} \quad [6.34]$$

where $\rho_P$ is the density in phase $P$. The values used for the density in $\gamma$, $\gamma'$, $\beta$ and TCP/carbide phases are presented in Table 6.5.

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6.4 Concentration Profiles

### 6.4.1 Surface Concentration

Figure 6.3 illustrates the predicted change in concentration at the oxide/coating interface of the elements Al, Cr, Co and Ta at temperatures of 850, 950 and 1050°C as a function of ageing time. Al is known to be one of the main oxide formers in MCrAlY coatings and therefore the depletion observed at the coating surface is a direct result of the oxidation process. However, Figure 6.3 a) also shows that the Al concentration at the oxide/coating interface is predicted to increase with temperature. After 2000 hours ageing at a particular temperature, all of the composition profiles indicate that a fairly constant value is achieved and sustained over the period up to 10,000 hours. This therefore indicates that the Al eventually achieves a steady state, whereby the consumption rate at the interface is matched by the supply of Al via diffusion through the coating. Figure 6.3 b) illustrates that Cr is predicted to behave in a similar manner to Al at ageing times below 1000 hours. At 950 and 1050°C the Cr concentration decreases slightly with ageing time, therefore indicating that the consumption of Cr at the oxide/coating interface is faster than its supply through the coating by diffusion.

Within the model it was assumed that Co and Ta are not consumed by the oxidation process and therefore they can be seen to accumulate at the oxide/coating interface as a result of the receding surface. The concentration of Co at the oxide/coating interface is predicted to decrease slightly as a function of ageing time. As the temperature is increased to 1050°C, the Co is predicted to decrease at a greater rate until it falls below the original concentration of 23 wt.% after 10,000 hours ageing, which suggests that the increase in diffusion into the coating at the higher temperatures rapidly removes any build up of Co at the receding interface. However, the diffusion rate of Ta is slower than that of Co, which results in an increase at the oxide/coating interface particularly at the higher temperatures.

### Table 6.5 Density values of the γ, γ', β and TCP/Carbide phases used in the model

<table>
<thead>
<tr>
<th>Phase</th>
<th>Density (kg m⁻³)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>γ</td>
<td>8908</td>
<td>[1]</td>
</tr>
<tr>
<td>γ'</td>
<td>7230</td>
<td>[142]</td>
</tr>
<tr>
<td>β</td>
<td>5900</td>
<td>[143]</td>
</tr>
<tr>
<td>TCPs/Carbides</td>
<td>7140</td>
<td></td>
</tr>
</tbody>
</table>
Figure 6.3 Predicted concentration values of a) Al, b) Cr, c) Co and d) Ta at the coating/oxide interface as a function of ageing time.

### 6.4.2 Bulk Concentration

Concentration profiles for all elements were calculated within the simulations in order to model the distribution of elements across the coating, interdiffusion zone and substrate. Figure 6.4 shows an example of the concentration profiles calculated from the model simulations for a number of elements present after 190 hours ageing at 850°C. It can be seen in the Figure that soft impingement has not yet occurred and that there are changes in the interfacial concentrations at the oxide/coating interface as expected.
Figure 6.4 Predicted concentration profiles across the coating and interdiffusion zone at 850°C for 190 hours ageing.

Figure 6.5 illustrates the changes in concentration profile of Al, Cr, Co and Ta after ageing at 850°C for increasing ageing times, as a direct result of both the oxidation which occurs at the coating surface and interdiffusion between the coating and substrate. The predicted Al profiles across the coating and substrate presented in Figure 6.5 a) show a decrease at the coating surface from the original concentration value of 8.5 wt.% to 2 wt.% after ageing for 190 hours. This initial decrease is due to the removal of Al from the coating surface as a result of oxidation. However after 10,000 hours ageing the concentration of Al at the coating surface increases to ~ 4 wt.% . Therefore, suggesting that the Al begins to diffuse from the bulk of the coating out towards the coating surface due to the composition difference between these areas. The depletion of Al at the coating surface increases with ageing time from ~ 30.5 µm after 190 hours to 95 µm after 2000 hours. A depletion in Al is also predicted at the coating/substrate interface as a result of interdiffusion between the two, which again increases with time. The original concentration of 8.5 wt.% Al within the bulk of the coating remains constant until 10,000 hours ageing, whereby it decreases slightly to 8.4 wt.%, and therefore has been affected by both the oxidation and coating/substrate interdiffusion. The predicted concentration profile for Cr at 850°C indicated a similar behaviour to that of the Al, including the depletion at the coating surface as a result of oxidation, and interdiffusion between the coating and substrate. Figure 6.5 b) shows the predicted composition profiles for Co and Ta across the coating and substrate. The Co profile illustrates similar interdiffusion across the coating/substrate interface to the Al and Cr, with a negative gradient indicating the diffusion
out of the coating towards the substrate. The opposite is true for the Ta, which has a positive gradient at the coating/substrate interface, indicating the inward diffusion from the substrate into the coating. With increasing ageing time the Co concentration within the central section of the coating (~ 150 - 200 μm from the coating surface) remains unaffected by the diffusion occurring at both the coating surface and the coating/substrate interface. At the coating surface the profiles of Co and Ta show opposite trends to those predicted for Al and Cr such that their concentrations are predicted to increase at the coating/oxide interface with increasing ageing time. There is a build up of these elements at the interface due to the receding surface, and the fact that they are not allowed to take part in the oxidation process within the model, resulting in a diffusional flux in towards the coating.

Figure 6.6 illustrates the changes in profile of Al, Cr, Co and Ta after ageing at 950°C with increasing exposure times. At 950°C the profiles appear similar to those predicted at 850°C, although an increased amount of diffusion has occurred at the higher temperature as expected. The profiles shown in Figure 6.6 a) illustrate an initial reduction in Al and Cr at the oxide/coating interface after ageing for 190 hours, which again changes slightly with increased exposure time due to the diffusion from the coating out towards the interface. Both the Al and Cr show a depletion zone at the coating surface of ~ 85 μm, after which they have their original bulk concentrations of 8.5 and 20 wt.% respectively. With increasing ageing time, soft impingement of the diffusion fields occurs and unlike the profiles at 850°C, the concentration of Al and Cr throughout the coating decreases overall to ~ 6 and 13 wt.% respectively. It should be noted that the coating thickness was reduced in the 950°C simulations to allow for direct comparison with experimental results which indicated that the coating at 950°C was approximately two thirds of the thickness at 850°C.

After 10,000 hours ageing the Al was predicted to have homogenised considerably across the system, resulting in a fairly constant value of ~ 6 wt.%. It is possible this increased homogenisation is a result of both increased diffusion rates at higher temperatures and the reduced thickness of the coating at 950°C compared to that at 850°C.
Figure 6.5 Simulated concentration profiles of a) Al and Cr and b) Co and Ta across the coating and substrate at 850°C after ageing at 0, 190, 1000, 2000 and 10,000 hours.

Figure 6.6 Simulated concentration profiles of a) Al and Cr and b) Co and Ta across the coating and substrate at 950°C after ageing at 0, 190, 1000, 2000 and 10,000 hours.
Elemental concentration profiles were constructed across the coating, interdiffusion zone and substrate in which the predicted values were compared with those determined experimentally using EDX in the SEM, and show the changing distribution of elements within these areas as a function of increasing exposure to time and temperature. The measured values are seen to fluctuate significantly throughout the coating, which is a direct result of the numerous second phases precipitating within this area, and which is particularly noticeable in the IDZ. Figures 6.7 and 6.8 show the comparison of the measured and simulated concentration profiles of Al, Co, Cr and Ta across the coating and substrate for the same time and temperature conditions. In general, there is a good agreement between the calculated and experimentally measured values of the concentration profiles across the coating and substrate.

The calculated and experimental values for Al and Co shown in Figure 6.7 follow similar profiles, therefore demonstrating good correlation between the model and the experimental data. However, at 850°C the simulations suggest a lower amount of Al was present at the coating surface after 190 hours ageing: ~ 2.5 wt.% compared to the 9 wt.% measured experimentally (although it should be noted that it is difficult to measure an exact surface concentration using EDX in the SEM due to the spot size). It is possible that the amount of Al consumed at the coating surface by oxidation is lower in reality than that predicted at 850°C. At 1050°C for 10,000 hours, the simulations predict a greater amount of homogenisation of Co across the system than measured experimentally. In comparison, the measured values remain fairly constant throughout the coating thickness at ~ 23 wt.%, decreasing through the interdiffusion zone finally to the substrate concentration of ~ 9.5 wt.%. This difference indicates that Co is predicted to diffuse at a faster rate than is being observed experimentally. This difference could be due to the features within the interdiffusion zone, such as the γ' layer discussed in Chapter 5, reducing the interdiffusion of certain elements across the coating/substrate interface.

At the lower temperatures of 850 and 950°C, the calculated values for the Cr concentration within the system display similar profiles to the experimentally measured data, as shown in Figures 6.8 a) and b). However, the simulations consistently overestimate the amount of Cr present within the coating. The model was based on a starting composition corresponding to the nominal Cr concentration in the coating of 20 wt.%. However, it would appear from the experimentally determined profiles at 850°C for only 190 hours, and indeed the profile in an
as-received sample prior to thermal ageing, that the actual composition achieved in the coating is lower than the nominal value by an amount equal to ~ 5 wt.%. Similarly, the initial Ta concentrations differ between the nominal value assumed in the model to be 4 wt.% and the experimentally determined value, which is ~ 6-8 wt.%. As for the case of the Co profile at 1050°C, the simulations predict a greater amount of homogenisation of Cr across the system than measured experimentally, indicating that the values used in the model for Cr diffusion are either too fast or are not fully accounting for diffusion across the γ' layer.
**Figure 6.7** Comparison of the simulated (calculated) and measured concentration profiles of Al and Co across the coating, interdiffusion zone and substrate for a) 190 hours at 850°C, b) 190 hours at 950°C and c) 10,000 hours at 1050°C.

**Figure 6.8** Comparison of the simulated (calculated) and measured concentration profiles of Cr and Ta across the coating, interdiffusion zone and substrate for a) 190 hours at 850°C, b) 190 hours at 950°C and c) 10,000 hours at 1050°C.
6.5 Phase Profiles

The starting point for the calculations was the nominal chemical composition for the coating and the substrate, and therefore before any diffusion occurred the calculated phase distribution across the coating was uniform. Figure 6.9 shows that the model initially predicted the coating to consist of $\gamma$, $\gamma'$, $\beta$ and the $\sigma$ phase, and the substrate to comprise $\gamma$ and $\gamma'$ together with small quantities of TCP phases at 850°C.

![Figure 6.9 Predicted initial phase profiles across the coating and the substrate for the NiCoCrAlY coated CMSX4 at 850°C](image)

The NiCoCrAlY coating in its as-received condition was experimentally found to contain $\beta$ (NiAl), $\gamma'$ (Ni$_3$Al) and $\gamma$ (Ni) as predicted by the simulations. However, the Cr-rich $\sigma$ phase was not observed within the samples as predicted. A relatively large amount of the $\sigma$ phase, ~20 wt.%, was predicted in the coating, however, it should be noted that the TCP phases typically form after long periods of ageing as the microstructure approaches equilibrium. Nevertheless, it would appear that this value is an overestimate. Cr-rich phases were present in the interdiffusion zone, rather than in the bulk of the coating, however, they were identified to be M$_{23}$C$_6$ carbides rather than the $\sigma$ phase, indicating that the presence of carbon within the coating has altered the stability of the phases present. It has been previously noted that there is a close relationship between M$_{23}$C$_6$ carbide and the $\sigma$ phase, and therefore it appears that if C is present in the system, it is more likely that Cr-rich carbides rather than TCP phases will be observed.
6.5.1 β Phase Depletion

As discussed in Chapter 5, the Al in the coating is consumed by both oxide formation at the surface and by interdiffusion at the substrate/coating interface, producing Al depletion zones that increase in extent with time and temperature. These Al depleted zones correspond to the depletion of β-NiAl within these areas, as shown in Figure 6.10. At all three temperatures, the simulation predicted that the thickness of the β phase would reduce with increasing time as a result of the formation of β depleted layers at both the oxidation interface and substrate sides, and also that the process is faster at higher temperatures, as illustrated in Figure 6.11.

![SEM micrographs showing the depletion of the β phase at the coating surface of the NiCoCrAlY coated CMSX4 samples thermally exposed for a) 190 hours at 850°C, b) 10,000 hours at 950°C and C) 2000 hours at 1050°C](image)

After 190 hours at 850°C, the simulation predicts the development of a β depleted layer of ~11 μm adjacent to the coating/oxide interface. This layer increases in thickness with time, with a similar β depleted zone developing near the coating/substrate interface, albeit at a slower rate. In comparison, a β depleted layer of 5.2 μm was observed, therefore indicating that the amount of Al consumed at the coating surface by oxidation is lower in reality than that predicted. Figure 6.12 shows the comparison of the predicted and experimental β depletion layer thicknesses. These graphs illustrate that at the lower exposure time of 190 hours, the model predictions correspond well with the experimental observations, however, with increasing exposure time the simulations and experimental measurements deviate, with the β depletion becoming progressively more overestimated. This overestimation of the β depletion was also seen at 1050°C, with the β phase only predicted to be present within the coating after 190 and 1,000 hours ageing. However, experimentally the β was only observed to become
unstable between 2,000 and 10,000 hours ageing. This comparison has highlighted the need for calibration of the model through examination of the initial concentrations used, and the diffusion kinetics, particularly across the coating/substrate interface.
6.5.2 $\gamma'$ Profile

Figure 6.14 illustrates how the $\gamma'$ phase is predicted to develop across the coated superalloy system at temperatures of 850, 950 and 1050°C. As the exposure time increases, the fraction of the $\gamma'$ phase adjacent to the oxide/coating interface increases as a direct result of the $\beta$ depletion. As the $\beta$ phase depletes from either side of the initial coating it is replaced by a layer of $\gamma'$ which increases with ageing time. This production of a $\gamma'$ layer at the coating surface was indeed observed experimentally, as shown in Figure 6.13.

![Figure 6.13](image)

Figure 6.13 SEM micrographs showing the depletion of the $\beta$ phase and the formation of a $\gamma'$ layer at the coating surface of the NiCoCrAlY coated CMSX4 samples thermally exposed for a) 2000 hours at 850°C and b) 10,000 hours at 950°C

The simulations also predict an increase in the $\gamma'$ phase at the coating/substrate interface at all temperatures, which increases in thickness towards the substrate with increasing ageing times. The prediction of a $\gamma'$ layer at the coating/substrate interface correlates very well with the experimental observations. A continuous $\gamma'$ layer was indeed observed at the coating/substrate interface. The diffusional flux of Al and Ni in particular leads to the transformation of the $\gamma$ phase from the substrate adjacent to the coating into the $\gamma'$ layer, and the growth of this layer into the substrate was observed as a result of increased temperature and exposure time, as shown in Figure 6.15. However, after ageing at 1050°C for 10,000 hours the simulation predicts a homogenisation of the $\gamma'$ phase across the coating and substrate which proved inconsistent with the experimental observations. Although the continuous $\gamma'$ layer observed experimentally does become segmented in nature, it was apparent that the increased amount of
with this localised area was still observed. The amount of $\gamma'$ predicted at the coating/substrate interface also requires investigation: maximum values of ~75-80 wt.% are predicted, yet in places the experimental observations indicate that the $\gamma'$ layer is virtually continuous, and therefore may be being underestimated in the simulations.

6.5.3 Topologically Closed Packed Phases

Different types of Topologically Close Packed (TCP) phases were predicted by the simulations for each of the temperatures considered. At 850°C, the substrate was initially predicted to contain ~ 2 wt.% of $\mu$ phase and ~ 1.5 wt.% $\sigma$ phase. The coating was predicted to contain high amounts at ~ 18 wt.% of $\sigma$ phase, however, as discussed previously $\sigma$ phase was not observed within the coating. However, with increase in temperature the $\sigma$ phase is indeed predicted within the interdiffusion zone which does correlate with the experimental observations.

At 950°C, no TCP phases are predicted to be present in the coating. With increasing ageing time, a thin layer of $\sigma$ is predicted to form at the coating/substrate interface, which gradually broadens toward the substrate. The simulations also predict that the $\mu$ phase is present at the coating/substrate interface, coexisting with the $\sigma$ phase, although more on the substrate side. The experimental observations were that all three phases, $\sigma$, $\mu$ and P, were present in the IDZ at the shorter ageing times, with $\mu$ and P dominating at the longer ageing times.

At 1050°C, no TCP phases are predicted to be present for the substrate or coating bulk compositions. However, a sharp peak of P phase is predicted to appear at the bondcoat interface with the substrate, which widens into the substrate and the peak position shifts towards the substrate. This is in broad agreement with experimental observations; the P phase was identified at the coating/substrate interface after increased ageing at 1050°C, however, the $\mu$ phase was also identified within the samples extracted for examination in the TEM. It was noted experimentally that the compositions of the $\mu$ and P phase were similar, and that it was difficult to discriminate between the phases on the basis of chemistry alone. It is perhaps therefore not surprising that there are differences in the prediction of the minor amounts of the TCP phases given their apparently close relationships with each other and small differences in their thermodynamic stability.
Figure 6.14 Simulated predictions of the $\gamma'$ phase profiles across the coating at a) 850°C, b) 950°C and c) 1050°C for increasing ageing times.

Figure 6.15 SEM micrographs showing the growth of the $\gamma'$ layer at the coating/substrate interface of the NiCoCrAlY coated CMSX4 samples thermally exposed for a) 190 hours at 850°C, b) 190 hours at 950°C and C) 2000 hours at 1050°C.
6.5.4 Carbide Phases

It has been observed experimentally that phase stabilities are very sensitive to C concentration, and that if there is C present in the system, then carbides tend to form, both Cr-rich $\text{M}_{23}\text{C}_6$ phases, and Ti/Ta-rich MC carbides. The model is capable of allowing for C diffusion and for predicting carbides to be present across the coated system. In the nominal concentration for the coating, there is no carbon, however, it seems likely that some carbon is introduced during processing, and also carbon is able to diffuse from the substrate, which does contain relatively small concentrations of C.

At 850°C, both $\text{M}_{23}\text{C}_6$ and MC carbides are predicted to occur and are sensitive to the amount of C present in the system, and can exist up to 10,000 hours of ageing. A peak in the amount of $\text{M}_{23}\text{C}_6$ is predicted to form at the coating/substrate interface. Simulations at 950°C, follow a similar pattern, with both carbides predicted to be stable and a peak in the amount of $\text{M}_{23}\text{C}_6$ forming at within the IDZ. The MC carbides, on the other hand, are predicted to form towards the oxidation end of the bond coat, rather than the experimental observations which show that they form in a line in the coating adjacent to the $\gamma'$ layer. At 1050°C, only the MC carbide is predicted to be stable initially, however, with increasing ageing time, again the peak in the amount of $\text{M}_{23}\text{C}_6$ appears within the IDZ.

It has been shown therefore, that there is broad agreement with the experimental observations and the predictions of the model in respect of carbide formation. However, the treatment of carbon diffusion requires closer examination because it appears that once the carbides form in a particular location through the combination of a particular element with the available C, they are very stable, and therefore possibly further C diffusion through the system should then be prevented.

6.6 Summary

This Chapter has outlined the principles behind a coupled thermodynamic and kinetic model which has been developed in a parallel project. The predictions of the model have then been compared extensively with the experimental observations detailed in Chapter 5. It is shown that in general there is broad agreement with the predictions of the major phases precipitating as a function of time at temperature. The model also has the capability to correctly predict the
occurrence of TCP and carbide phases, which are typically observed, associated with the IDZ between the coating and the substrate. Areas for future development of the model have been highlighted, which include in particular: the observation that the actual coating composition deviates from the nominal value; the rate of diffusion across the continuous \( \gamma' \) layer which forms between the coating and the substrate; the possibility of "locking" the C once it has formed carbides in a particular region; the importance of obtaining accurate, concentration dependent diffusion data for all elements and finally the need for physically-based, multicomponent alloy oxidation models.
Chapter 7
Microstructural Characterisation of PtAl Coated CMSX4

7.1 Introduction
Platinum modified aluminide diffusion coatings are produced by both inward and outward growth and each mechanism forms a distinctive coating microstructure. In this section, two commercial Pt modified aluminide diffusion coatings which had been applied to the single crystal Ni-based superalloy CMSX-4 are compared. The RT22 coatings were inward grown (high activity), whereas the CN91 coatings were outward grown (low activity). This section presents and discusses the results of the detailed microstructural investigations carried out on the RT22 coated CMSX4 system. The coating system was investigated in the as-received condition, in addition to after isothermal aging. Samples were isothermally aged in a controlled combustion gas environment at 850, 900, 950, 1000 and 1050°C each for 1000, 2000 and 4,000 hours. These temperatures were chosen to be representative of possible service conditions experience by gas turbine blades. The CN91 coated CMSX4 samples were investigated in the as-received condition and following isothermal exposure at 1000°C for 1000 hours, in order to make a comparison with the RT22 coated CMSX4 thermally exposed under the same conditions. A variety of experimental techniques have been used in the study of the coating system. These include field emission gun scanning electron microscopy (FEGSEM) and energy dispersive x-ray analysis (EDX). A dual FIB FEGSEM has also been utilised to make site specific samples for high resolution transmission electron microscopy (TEM) analysis.

7.2 Microstructure of the RT22 Coated CMSX4: As-Received
The microstructure of the RT22 coated CMSX4 system in the as-received condition taken using the SEM is shown in Figure 7.1.
Platinum aluminide coatings are known to form single phase $\beta$-NiAl or two phase $\beta$-NiAl and PtAl$_2$ structures. The RT22 coating in the as-received condition was found to consist of a single phase $\beta$ matrix, indicating that the Pt has enriched the $\beta$ phase, such that it becomes the $\beta$-(Ni,Pt)Al phase. Throughout this chapter $\beta$(Ni,Pt)Al will be referred to as ‘$\beta$’, even though this is not the pure $\beta$ binary (NiAl) phase. An external scale was present on the coating surface approximately 1.5 $\mu$m thick, which comprised mainly of Al/O-rich layer, thought to be Al$_2$O$_3$. The outer layer in the coating can be distinguished by a brighter appearance in backscattered electron mode; this is associated with higher Pt concentration levels within this area. The Pt levels within the $\beta$ phase were found to decrease from $\sim$ 44 wt.% with increasing distance from the coating surface to $\sim$ 12 wt.% in the interdiffusion zone (IDZ). The chemical compositions are given in Table 7.1. Concentration profiles were determined using the main alloying elements in the various regions were constructed across the coating, interdiffusion layer and substrate measured using multipoint EDX analysis, as shown in Figure 7.2. This illustrates the distribution of Pt throughout the coating, demonstrating the high concentrations at the coating surface followed by a significant decrease over a distance of 30 $\mu$m. Chemical analysis of the $\beta$ phase at the coating surface showed that only nominal values of refractory elements such as Ta, W and Re were present in solid solution. This therefore supports the claim that Pt excludes refractory elements such as W, Re Ta and Mo from the outer coating layers$^{[53,54]}$. Large dark precipitates were observed, to lie in a line about 15 $\mu$m into the coating surface, as shown in Figure 7.1. Chemical analysis showed high proportions of Al (53 wt.%)
and O (19 wt.%) indicating that they are alumina particles, probably entrapped from the grit blasting used to prepare the substrate surface in the coating process. RT22 is an inward grown (high activity) coating in which inward diffusion of Al into the substrate is greater than the outward diffusion of Ni from the substrate. This results in the Al-rich β layer containing slow diffusing elements from the substrate. Therefore the entrapped alumina particles and their proximity to the coating surface indicates the original surface of the substrate, and also that the majority of the coating has grown inwards through Al diffusion.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Elements (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ni</td>
</tr>
<tr>
<td>βCS</td>
<td>28.8 - 29.5</td>
</tr>
<tr>
<td>βBC</td>
<td>35.4 - 46.6</td>
</tr>
<tr>
<td>βIDZC</td>
<td>52.7 - 55.6</td>
</tr>
</tbody>
</table>

βCS - β phase at the coating surface
βBC - β phase within the bulk of the coating
βIDZC - β phase adjacent to the IDZ

Table 7.1 EDX analysis results of β phase present with increasing distance from the coating surface in RT22 coated CMSX4 in the as-received sample (obtained using SEM)

Figure 7.2 Compositional profile of main alloying elements across the coating, interdiffusion layer and substrate of RT22 coated CMSX4 sample in the as-received condition
Clusters of spherical precipitates of the order of 100 nm in diameter were observed throughout the bulk of the coating, as illustrated in Figure 7.3. The bright appearance of these precipitates in backscattered electron mode suggests that they contain high levels of refractory elements. It has been previously reported that these precipitates form primarily as a consequence of the inward diffusion of Al, which results in the entrapment of W, Re, Mo and Ta due to the low solubility of these refractory elements in β-NiAl grains\textsuperscript{[61,144]}. Figure 7.3 b) indicates that the majority of these precipitates are located along the β matrix grain boundaries. Chemical analysis showed the precipitates to be rich in W and Re (\~{}45 and 26 wt.\%) with smaller amounts of Ta and Mo. Similar precipitates have been reported in literature to be bcc α-W\textsuperscript{[52,144-146]} In this research, the precipitates were conclusively identified as α-W (a\textsubscript{o} = 3.16 Å), the Re-rich tetragonal σ phase (a\textsubscript{o} = 9.12 - 9.3 Å and c\textsubscript{o} = 4.72 - 4.86 Å) and the W-rich orthorhombic P phase (a\textsubscript{o} = 17.2, b\textsubscript{o} = 4.86 and c\textsubscript{o} = 9.2 Å), using a combination of selected area diffraction patterns and EDX analysis. Typical SAED patterns are shown in Figure 7.4, and their compositions given in Table 7.2. TEM analysis of the coating illustrates that the intermetallic phases are all precipitating together within the β matrix. The α-W precipitates can be clearly distinguished from the other intermetallic phases using high resolution as they appear to contain a high density of crystallographic faults. The relative amount of the σ and P phases is extremely difficult to determine due to the similarities in the morphology and composition of the two phases.

![Figure 7.3](image_url)

\textbf{Figure 7.3} a) SEM micrograph of RT22 coated CMSX4 in the as-received condition showing the clusters of precipitates within the bulk of the coating and b) Bright field TEM micrograph showing the precipitates forming on the β grain boundaries
During the commercial heat treatment following the coating process, diffusion of elements such as Cr, Re, W, Mo and Ta has occurred between the coating and substrate. This has created an interdiffusion zone with an average thickness ranging from 16 - 17 µm, as shown in Figure 7.5. This interdiffusion of elements across the coating/substrate interface has encouraged the formation of several intermetallic phases. These are observed as an abundance of large elongated precipitates approximately 10 µm in size, forming a band adjacent to the coating/substrate interface. The precipitates within the band appear to show some alignment in the diffusion direction, from the substrate towards the coating surface, therefore indicating the initial growth direction. Chemical analysis of these precipitates indicated that they are mainly composed of W, Re, Ta and Cr with additions of Mo. These precipitates are likely to be topologically closed packed (TCP) phases due to the small amounts of Ni and absence of Al. Selected area electron diffraction (SAED) and EDX analysis indicates that the precipitates are...
a mixture of W/Re-rich $\sigma$ phase ($a_0 = 9.12 - 9.3\,\text{Å}$ and $c_0 = 4.72 - 4.86\,\text{Å}$), $\mu$ phase ($a_0 = 4.73 - 4.75$ and $c_0 = 25.54 - 25.8\,\text{Å}$) and P phase ($a_0 = 17.2$, $b_0 = 4.86$ and $c_0 = 9.2\,\text{Å}$), the compositions of which are reported in Table 7.2. The precipitation of $\mu$ and $\sigma$ phase is in accordance with previous work conducted on this coating system\cite{61} however, the presence of P phase within the interdiffusion zone has yet to be reported. The morphology and composition of these TCP phases were found to be extremely similar; consequently the only method for phase identification is selected area electron diffraction of the individual particles as illustrated in Figure 7.6. It can therefore be assumed that the band of precipitates contains a mixture of $\sigma$, $\mu$ and P phase. It was not possible to determine the relative amounts of each of these three phases due to the relatively small number of particles conclusively identified using electron diffraction.

Figure 7.5 SEM micrographs of RT22 coated CMSX4 in the as-received condition, showing a) the interdiffusion layer, b) precipitates within coating adjacent to the IDZ and c) $\gamma'$ layer at the coating/substrate interface containing small TCP phases
Figure 7.6 TEM micrograph and selected area diffraction patterns (SADP) of the TCP phases within the coating adjacent to the IDZ of RT22 coated CMSX4 sample in the as-received condition: a) bright field image (BF); SADP for b) a phase, c) μ phase, d) P phase in which the relevant zone axes are labelled.

A continuous γ' layer with a thickness of approximately 4 μm was observed within the interdiffusion zone, separating the coating from the substrate. This γ' layer has been suggested within literature to form due to the net increase of aluminium in the substrate and nickel in the coating\textsuperscript{[89]}. This results in the transformation of the γ phase from the substrate adjacent to the coating, into the γ' layer. Small precipitates rich in Cr, Re and W (approximately 39, 16 and 18 wt.% respectively) are also observed within this γ' layer; once again the high amount of refractory elements suggests that these precipitates are TCP phases. These phases are known to accommodate the excess chromium and rhenium produced as a result of the phase transformation from γ to γ', due to their reduced solubility in γ' compared to γ\textsuperscript{[11,52,61,89,144,147]}. SAED and EDX analysis across the continuous γ' layer enabled the identification of the small TCP phases as the Cr-rich σ phase. There is a difference in composition of the σ phases.
identified within the interdiffusion zone. Therefore, suggesting a possible dependence on location and the differences in solubility of elements within the different matrix phases that the TCP phases precipitate within. The $\beta$ phase has a low solubility of W therefore it promotes the precipitation of W-rich $\sigma$, $\mu$ and P; whereas $\gamma'$ has a low solubility for Cr and Re resulting in the Cr-rich $\sigma$ phase.

The $\gamma / \gamma'$ structure within the substrate near to the coating/substrate interface has a similar microstructure to that of the bulk of the substrate of the uncoated CMSX4 discussed in Chapter 4. The $\gamma'$ particles still retain their regular cuboidal morphology, with sizes ranging from approximately 0.4 - 0.6 $\mu$m.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Elements (wt.%)</th>
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<tbody>
<tr>
<td></td>
<td>Ni</td>
</tr>
<tr>
<td>$\alpha$ - W</td>
<td>0.0 - 6.5</td>
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<tr>
<td>$\sigma_{C}$</td>
<td>0.0 - 4.7</td>
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<tr>
<td>$\sigma_{IDZ/C}$</td>
<td>6.2 - 7.6</td>
</tr>
<tr>
<td>$\sigma_{IDZ/S}$</td>
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<tr>
<td>$\mu_{IDZ/C}$</td>
<td>6.8 - 8.6</td>
</tr>
<tr>
<td>$P_{C}$</td>
<td>4.7 - 6.6</td>
</tr>
<tr>
<td>$P_{IDZ/C}$</td>
<td>6.9 - 7.1</td>
</tr>
</tbody>
</table>

$X_{C}$ - Precipitates in bulk of coating
$X_{IDZ/C}$ - Precipitates present within the coating section of the IDZ
$X_{IDZ/S}$ - Precipitates present within the substrate section of the IDZ ($\gamma'$ band)

Table 7.2 EDX analysis results of the intermetallic and TCP phases present within the coating and interdiffusion zone of the RT22 coated CMSX4 sample in the as-received sample (obtained using analysis of thin foil samples within the TEM)
7.3 Microstructure of RT22 Coated CMSX4 Thermally Exposed at 850°C

7.3.1 Thermal Exposure at 850°C for 1000 hours

The microstructure of the RT22 coated CMSX4 system after thermal aging at 850°C for 1000 hours is illustrated in Figure 7.7.

![Figure 7.7 SEM micrograph illustrating the overall structure of the substrate and coating of the sample aged for 1000 hours at 850°C, including the coating, interdiffusion zone and substrate](image)

Following thermal exposure at 850°C for 1000 hours the overall coating and substrate microstructure appears very similar to that of the as-received sample. The Al-rich oxide scale, presumably Al₂O₃, was present on the coating surface and was approximately 0.9 μm thick, as shown in Figure 7.8 a). There was no significant increase in thickness observed in comparison to the as-received sample. It can be therefore assumed that the diffusion of Al from the coating out towards the scale was not large enough to considerably affect the growth of the protective oxide scale under these conditions. After 1000 hours at 850°C, the two contrasting layers of the coating (the outer layer having the brighter appearance) observed in the as-received sample have become less distinct. The diffusion of Pt from the higher concentration at the coating surface towards the substrate has occurred. Chemical analysis of the β matrix in which the Pt partitions, confirms this increase in diffusion of the Pt. An initial decrease in Pt content from the as-received sample ~ 44 to 33 wt.% was observed, which again decreases with increasing distance from the coating surface. The compositions of the β phase across the coating are
reported in Table 7.3. The small W, Re and Ta rich precipitates observed throughout the bulk of the coating have coarsened very slightly with thermal aging, owing to the reduction of the sub-micron clusters observed in the as-received sample, as shown in Figure 7.8 b). Once again the majority of these precipitates are located along the β matrix grain boundaries. The high solubility of Ta within these phases is associated with the lack of Ta stabilising phases such as γ′ (Ni3Al) within the coating.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Ni</th>
<th>Al</th>
<th>Cr</th>
<th>Co</th>
<th>Ta</th>
<th>W</th>
<th>Re</th>
<th>Pt</th>
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<tbody>
<tr>
<td>βCS</td>
<td>37.0 - 38.2</td>
<td>17.3 - 17.6</td>
<td>1.9 - 2.2</td>
<td>4.4 - 4.6</td>
<td>1.4 - 2.2</td>
<td>1.0 - 3.2</td>
<td>0.2 - 0.6</td>
<td>32.6 - 34.6</td>
</tr>
<tr>
<td>βBC</td>
<td>41.7 - 44.5</td>
<td>18.0 - 18.7</td>
<td>1.9 - 2.2</td>
<td>5.0 - 5.6</td>
<td>2.0 - 2.6</td>
<td>1.1 - 1.9</td>
<td>-</td>
<td>24.8 - 29.7</td>
</tr>
<tr>
<td>βIDZ/C</td>
<td>49.4 - 51.5</td>
<td>19.8 - 20.2</td>
<td>2.4 - 2.6</td>
<td>6.6 - 7.1</td>
<td>1.5 - 2.3</td>
<td>1.1 - 1.9</td>
<td>-</td>
<td>14.1 - 17.8</td>
</tr>
</tbody>
</table>

βCS - β phase at the coating surface
βBC - β phase within the bulk of the coating
βIDZ/C - β phase adjacent to the IDZ

Table 7.3 EDX analysis results of β phase present with increasing distance from the coating surface in sample aged for 1000 hours at 850°C (obtained using SEM)

The interdiffusion zone after 1000 hours at 850°C has increased in thickness from 17 to 24 μm. This is not a large change in thickness; however, it does indicate an increase in diffusion activity of elements across the coating/substrate interface. Similar to the as-received sample, a large area fraction of TCP phases with sizes ranging from 0.2 - 1.1 μm were observed within the coating section of the interdiffusion zone; the larger size quoted is a result of agglomeration of the smaller particles. The precipitates appear to demonstrate a reduction in alignment in regards to the diffusion direction, as a result their morphology is more rounded indicating the onset of coarsening, as shown in Figure 7.8 d). Chemical analysis indicated these precipitates are mainly composed of W, Re, Ta and Cr with additions of Mo as reported previously, therefore it is feasible that the same phases are present. Particles rich in Ta, Hf and Ti, ~ 51, 8.5 and 4.9 wt.% respectively are observed scattered throughout the band of TCP phases adjacent to the coating/substrate interface. Due to the high proportions of Ta and Hf and the presence of C, these particles were likely to be MC carbides. The presence of these carbides indicates the outwards diffusion of Hf together with reactive C from the substrate into the coating. These carbides have been observed within the interdiffusion zone of similar
coating systems\textsuperscript{[144,148]}. The only distinguishing feature of the carbides compared to the surrounding TCP phases is their slight increase in size at $\sim 1 - 1.5 \text{ \mu m}$.

The continuous $\gamma'$ enriched layer that separates the coating from the substrate has increased in thickness with aging from 4 to 11 $\mu$m. This again indicates the increase in diffusion of elements across the interdiffusion zone, resulting in the dissolution of $\gamma$ to $\gamma'$. Islands of $\beta$ phase were observed within the $\gamma'$ enriched layer, as illustrated in Figure 7.8e), therefore suggesting this layer extends/grows into the coating in addition to towards the substrate. However, it has been stated that the interdiffusion process does not involve the growth of the $\gamma'$ layer from the substrate into the coating but instead new $\gamma'$ is nucleated within the coating and subsequently grows upwards into the $\gamma'$ layer\textsuperscript{[149]}. In contrast it has been reported that the initial high interdiffusional flux of Al and Ni within the interdiffusion zone causes local phase transformations from $\gamma'$ to $\beta$\textsuperscript{[145]}. As a consequence of the $\gamma'$ layer increasing in thickness and the reduced solubility of Cr and Re has allowed the TCP phases present within the continuous $\gamma'$ layer to increase in size and begin to develop a needle-like structure.

The $\gamma/\gamma'$ structure within the substrate near to the coating/substrate interface is observed to have a similar microstructure to that of the as-received sample, as shown in Figure 7.8 f). The $\gamma'$ particles have retained their cuboidal morphology, although they have begun to show signs of directionality, indicating the onset of rafting.
Figure 7.8 SEM micrographs of RT22 coated CMSX4 thermally exposed for 1000 hours at 850°C, showing a) coating surface including the oxide scale, b) the sub-micron sized precipitates within bulk of the coating, c) Complex interdiffusion zone (IDZ) structure, d) Band of W-rich precipitates observed within the coating section of the IDZ e) γ' layer in the IDZ and f) the substrate adjacent to the IDZ
7.3.2 Thermal Exposure at 850°C for 2000 hours

The microstructure of the RT22 coated CMSX4 system after thermal aging at 850°C for 2000 hours is illustrated in Figure 7.9.

![Image](image.jpg)

**Figure 7.9** SEM micrograph illustrating the overall structure of the substrate and coating of sample aged for 2000 hours at 850°C, including the coating, interdiffusion zone and substrate.

The contrast variation related to the Pt concentrations observed within the coating of the sample aged for 1000 hours was no longer present. This therefore suggests that the Pt has diffused in towards the substrate with increased exposure length, and is confirmed by the concentration profile illustrated in Figure 7.10.
Figure 7.10  Profile of Pt concentration with increasing distance from the coating surface in the RT22 coated samples in the as-received condition and after aging at 850°C for 1000 and 2000 hours

The interdiffusion zone illustrated in Figure 7.11 has increased in thickness from 24 to 32 µm, indicating an increase in diffusion activity of elements across the coating/substrate interface. The increase in thickness has occurred mainly through the growth of the γ' layer, which is in turn mainly affected by the net increase of Al in the substrate and Ni in the coating. The concentration profiles of Al and Ni represented in Figure 7.12 show an increase in the amount of Ni and a decrease in the amount of Al within the interdiffusion zone after 2000 hours compared to 1000 hours. This confirms the increase in diffusion of Ni from the substrate into the coating and Al from the coating into the substrate with increased ageing time.
Figure 7.11 SEM micrographs of RT22 coated CMSX4 thermally exposed for 2000 hours at 850°C, showing the interdiffusion layer structure including the band of precipitates and $\gamma'$ layer.

Figure 7.12 Profile of Al and Ni concentrations with increasing distance from the coating surface in the RT22 coated samples aged at 850°C for 1000 and 2000 hours.

Light grey phases of blocky morphology with sizes ranging from ~0.6 - 1.2 μm were observed within the high density band of precipitates adjacent to the coating/substrate interface. Chemical analysis showed these particles contained a lower Al and higher Ta concentration that that of the surrounding $\beta$ matrix as reported in Table 7.4, and were therefore thought to be $\gamma'$ - Ni$_3$Al. The phase transformation from $\beta \rightarrow \gamma'$ indicated an increased
diffusion of Al from the coating in towards the substrate alloy. Cr-rich phases with lath-like morphologies were observed within the \( \gamma' \) layer at the coating/substrate interface. These particles proved difficult to identify at first due to their similar contrast to the entrapped \( \beta \) phase also present, as shown in Figure 7.13. Chemical analysis conducted in the SEM showed these particles contained high concentrations of Cr ~ 37 wt.% with similar amounts of W and Re ~ 8 and 7 wt.% respectively. The ratios of Cr, W and Re are similar to those observed for the \( \sigma \) phase present in the interdiffusion zone of the sample in the as-received condition, although it should be noted that chemical analysis will vary between the SEM and TEM due to differing activation volumes. It is also possible these particles are \( \text{M}_{23}\text{C}_6 \) particles; however, conclusive identification requires determination of their crystal structure.

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<th>Ni (wt.%)</th>
<th>Al (wt.%)</th>
<th>Cr (wt.%)</th>
<th>Co (wt.%)</th>
<th>Ta (wt.%)</th>
<th>W (wt.%)</th>
<th>Re (wt.%)</th>
<th>Pt (wt.%)</th>
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<td>6.8 - 7.6</td>
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<td>3.9 - 4.4</td>
<td>2.1 - 2.8</td>
<td>17.6 - 18.9</td>
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<tr>
<td>( \gamma' )</td>
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<td>4.1 - 6.0</td>
<td>1.4 - 2.6</td>
<td>8.6 - 8.8</td>
</tr>
</tbody>
</table>

Table 7.4 EDX analysis results of \( \beta \) and \( \gamma' \) phase present within the band of precipitates of the IDZ of RT22 coated CMSX4 sample aged for 2000 hours at 850°C (obtained using SEM)

Figure 7.13 SEM micrographs of RT22 coated CMSX4 thermally exposed for 2000 hours at 850°C, showing a) band of precipitates adjacent to the coating/substrate interface, containing small \( \gamma' \) particles, and b) Cr-rich phases observed within the \( \gamma' \) layer of the IDZ
The needle-like TCP phases identified as σ phase in the as-received sample have increased in length with thermal exposure. Consequently the precipitates have begun to extend out of the γ' layer into the substrate, typically at angles close to 45° to the γ/γ' structure, as illustrated in Figure 7.14.

![SEM micrographs of RT22 coated CMSX4 thermally exposed for 2000 hours at 850°C, showing a) the extension of needle-like precipitates from the γ' layer in the IDZ into the substrate and b) higher magnification of the same area with 45° angle superimposed.](image)

**Figure 7.14** SEM micrographs of RT22 coated CMSX4 thermally exposed for 2000 hours at 850°C, showing a) the extension of needle-like precipitates from the γ' layer in the IDZ into the substrate and b) higher magnification of the same area with 45° angle superimposed.
7.3.3 Thermal Exposure at 850°C for 4000 hours

The microstructure of the RT22 coated CMSX4 system after thermal aging at 850°C for 4000 hours is illustrated in Figure 7.15.

![Microstructure Illustration](image)

**Figure 7.15** SEM micrograph illustrating the overall structure of the substrate and coating of sample aged for 4000 hours at 850°C, including the coating, interdiffusion zone and substrate

In contrast to the sample aged for 2000 hours, small particles of $\gamma'$ ($\text{Ni}_3\text{Al}$) with an average size of 2.1 $\mu$m were present throughout the bulk of the coating as well as dispersed within the high density band of precipitates, as shown in Figure 7.16. No $\gamma'$ particles were observed at the coating surface, indicating that the interdiffusion of Al across the coating/substrate interface is at a greater rate than the Al consumed at the surface due to oxidation. The increase in oxide thickness from 1.5 $\mu$m at 2000 hours to 2.3 $\mu$m, indicates that Al was diffusing from the coating towards the oxide scale. However, chemical analysis of the $\beta$ matrix reported in Table 7.5 showed similar compositions at the coating surface to that in the bulk of the coating, which suggests that consumption of Al at the coating surface as a result of oxidation is matched by the diffusion of Al towards the oxide scale, allowing the $\beta$ phase to remain stable within this area.
Figure 7.16 SEM micrographs of RT22 coated CMSX4 thermally exposed for 4000 hours at 850°C, showing a) low magnification image of the coating structure containing γ' particles, b) higher magnification of the γ' particles within the band of precipitates in the interdiffusion zone, c) higher magnification of the γ' particles in the bulk of the coating and d) coating surface showing no γ' particles at the oxide/coating interface.

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<tbody>
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<td>Al</td>
</tr>
<tr>
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<td>45.6 - 46.3</td>
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<tr>
<td>β_{BC}</td>
<td>45.6 - 46.6</td>
</tr>
</tbody>
</table>

β_{CS} - β phase at the coating surface
β_{BC} - β phase within the bulk of the coating

Table 7.5 EDX analysis results of β phase present with increasing distance from the coating surface in sample aged for 4000 hours at 850°C (obtained in the SEM)
As observed at shorter exposure times, the increases in thickness of the interdiffusion zone from 32 µm at 2000 hours to 38 µm results mainly from the growth of the γ' layer. The γ' layer appears to have grown outwards towards the substrate and in doing so has encased the needle-like TCP phases that at 2000 hours extended into the substrate, as shown in Figure 7.17.

![Figure 7.17](image)

Figure 7.17 SEM micrographs showing the structure of the interdiffusion zone in RT22 coated CMSX4 samples aged at 850°C for a) 2000 and b) 4000 hours.

Cr-rich phases with lath-like morphologies, as observed at 2000 hours, are present within the γ' layer at the coating/substrate interface, as shown in Figure 7.18. Once more these particles are located near to or on the entrapped β particles also present and are difficult to identify within the backscattered imaging mode as they have similar contrast to the β phase. Chemical analysis showed these particles to be rich in Cr ~ 49 wt.%, with similar amounts of W and Re at ~ 8 and 9 wt.% respectively. The presence of C up to ~ 3 wt.% indicated these particles were likely to be M23C6 carbides, as opposed to the σ phase discussed previously.

The γ/γ' structure observed within the substrate directly adjacent to the coating/substrate interface appears to show some alignment of the γ' precipitates, therefore indicating the onset of rafting, as shown in Figure 7.19. However, the thickness of the affected area observed was ~ 14 µm, possibly suggesting that this rafting is caused by biaxial compressive stresses induced due to the formation of the continuous γ' layer at the coating/substrate interface.
Figure 7.18  *SEM micrograph of RT22 coated CMSX4 thermally exposed for 4000 hours at 850°C, showing the Cr-rich phases observed within the γ' layer of the interdiffusion zone.*

Figure 7.19  *SEM micrograph of RT22 coated CMSX4 thermally exposed for 4000 hours at 850°C, showing the alignment of the γ' precipitates in the substrate adjacent to the coating/substrate interface.*
7.4 Microstructure of RT22 Coated CMSX4 Thermally Exposed at 900°C

7.4.1 Thermal Exposure at 900°C for 1000 hours

The microstructure of the RT22 coated CMSX4 system after thermal aging at 900°C for 1000 hours is illustrated in Figure 7.20.

![Figure 7.20](image)

**Figure 7.20** SEM micrograph illustrating the overall structure of the substrate and coating of sample aged for 1000 hours at 900°C, including the coating, interdiffusion zone and substrate

The general coating structure exhibits very little contrast variation across the coating compared to that observed in the sample aged at 850°C for 1000 hours. Chemical analysis of the β matrix shows a reasonably constant value of ~20 wt.% Pt with increasing distance from the coating surface, finally decreasing through the interdiffusion zone to an average value of ~10 wt.%, as shown in Figure 7.21. These results indicate that Pt diffusion in towards the substrate has increased with temperature, which has lead to an evening out of the concentration profile across the coating. The sub-micron sized intermetallic precipitates throughout the bulk of the coating remain located along the β matrix grain boundaries. However, they appear to have coarsened with temperature, with an increase in the average size to 0.5 μm; qualitatively it appears that the area fraction remained approximately constant. Chemical analysis showed the precipitates to be rich in W, Re, Ta and Mo; however, using a combination of SAED patterns and EDX analysis only the tetragonal σ phase and orthorhombic P phase were observed indicating that the α-W phase observed at 850°C was no longer present. Typical SAED patterns are shown in Figure 7.22. It has been suggested that Pt
in high concentrations may have a stabilising effect on the α-W phase. Consequently the redistribution of the Pt that has occurred with the increase in temperature to 900°C results in lower Pt concentrations, allowing the dissolution of the W-rich phase.\textsuperscript{52}

![Graph showing compositional profile of main alloying elements across the coating, interdiffusion layer and substrate of RT22 coated CMSX4 sample aged for 1000 hours at 900°C]

**Figure 7.21** Compositional profile of main alloying elements across the coating, interdiffusion layer and substrate of RT22 coated CMSX4 sample aged for 1000 hours at 900°C

![TEM micrograph of RT22 coated CMSX4 thermally exposed for 1000 hours at 900°C, showing a) bright field image (BF) of W-rich precipitates located on grain boundaries; SADP of b) α phase, c) P phase, in which the relevant zone axes are labelled]

**Figure 7.22** TEM micrograph of RT22 coated CMSX4 thermally exposed for 1000 hours at 900°C, showing a) bright field image (BF) of W-rich precipitates located on grain boundaries; SADP of b) α phase, c) P phase, in which the relevant zone axes are labelled
In contrast to the samples aged at 850°C, small isolated light grey phases with a blocky morphology were observed at the surface and central regions of the coating, illustrated in Figure 7.23. Chemical analysis of this phase using the SEM indicated it to have a lower Al and higher Ta concentration than that of the $\beta$ matrix, therefore was thought to be $\gamma'$ - Ni$_3$Al. Compositions measured using EDX in the SEM are reported in Table 7.6. It is likely that increased diffusion of Al both out of the coating towards the protective oxide scale and towards the substrate with increasing temperature has initiated the phase transformation of $\beta$ (Ni,Pt)Al into $\gamma'$ (Ni$_3$Al). The $\gamma'$ precipitates are predominately located at the coating surface, consistent with the diffusion of Al out towards the oxide scale.

![SEM micrographs](image)

**Figure 7.23** SEM micrographs of RT22 coated CMSX4 thermally exposed for 1000 hours at 900°C, showing a) the oxide scale, $\gamma'$ and W-rich precipitates at the coating surface and b) the $\gamma'$ and W-rich within the bulk of the coating
<table>
<thead>
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<th>Cr</th>
<th>Co</th>
<th>Ta</th>
<th>W</th>
<th>Re</th>
<th>Pt</th>
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<td>0.5 - 1.5</td>
<td>2.9 - 6.0</td>
<td>0.3 - 1.6</td>
<td>19.1 - 20.6</td>
</tr>
<tr>
<td>β\textsubscript{BC}</td>
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<td>2.8 - 3.0</td>
<td>6.1 - 6.4</td>
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<td>0.6 - 1.8</td>
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<tr>
<td>γ'</td>
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<td>1.0 - 1.3</td>
<td>6.4 - 6.5</td>
<td>14.3 - 16.8</td>
<td>3.3 - 4.7</td>
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<td></td>
</tr>
</tbody>
</table>

β\textsubscript{CS} - β phase at the coating surface
β\textsubscript{BC} - β phase within the bulk of the coating
β\textsubscript{IDZ/C} - β phase adjacent to the IDZ.

Table 7.6 EDX analysis results of β phase present with increasing distance from the coating surface in sample aged for 1000 hours at 900°C (obtained in the SEM)

Figure 7.24 illustrates the microstructure of the interdiffusion zone across the coating/substrate interface, which displayed similar characteristics to the sample aged at 850°C. The TCP phases that form a distinct band within the coating adjacent to the coating/substrate interface have grown slightly from ~ 0.4 to 0.8 μm. The increase in temperature has also led to an increase in diffusion across the interface, resulting in a higher concentration of refractory elements within the interdiffusion zone. With the use of SAED patterns and EDX analysis, the TCP phases present within this section of the interdiffusion zone have been identified as W-Re-rich σ, μ and P phase. Once more these phases display very similar compositions, with P and σ phase containing the greater amount of W and Re respectively, however, the distribution of each element within the phases indicates some overlap. The predominant phases observed are the μ and P phase, the compositions of which are reported in Table 7.7. Similar to sample aged at 850°C, particles rich in Ta, Hf and Ti were observed within the high density TCP band adjacent to the coating/substrate interface, which were conclusively identified as MC carbides (a₀ = 4.5 Å) with the use of SAED.
Figure 7.24 SEM micrographs of RT22 coated CMSX4 thermally exposed for 1000 hours at 900°C, showing a) the interdiffusion layer structure, b) TCP phases within the γ' layer extending into substrate and c) coating structure adjacent to the IDZ containing various TCP phases and carbides.

As observed in previous samples, the interdiffusion of elements between the coating and substrate has resulted in the formation of a continuous γ' enriched layer. This layer has increased substantially in thickness to 47 μm with increased temperature compared to the 11 μm observed at 850°C for 1000 hours, thus indicating the increased diffusion of Al into the substrate and Ni into the coating. As observed at 850°C, the entrapment of β particles within the γ' layer may well be due to the inward growth of the γ' layer into the coating with increased temperature. Small rounded particles of 0.5 μm, rich in W and Re were observed within this γ' and β phase region, in particular on the β/γ' grain boundaries, illustrated in Figure 7.24 c). This increase in formation of W-rich precipitates and their location on grain boundaries has been suggested to be a result of the increase in Al content within this section of the interdiffusion zone\textsuperscript{150}. As the Al content increases locally within the interdiffusion zone...
due to outward diffusion from the coating, the solubility of W within the \( \gamma' \) and \( \beta \) phases decreases allowing the precipitation of TCP phases. The area fraction of the needle-like Cr-rich \( \sigma \) phase observed within the continuous enriched \( \gamma' \) layer has increased compared to that of the sample aged for 1000 hours at 850°C. Additionally the growth of the \( \sigma \) precipitates has resulted in their extension out into the substrate at various angles to the interface, as illustrated in Figure 7.24 b). Typical SAED patterns of the various precipitates identified within the interdiffusion zone are shown in Figures 7.25 and 7.26, and their compositions are reported in Table 7.7. Composition analysis of the Cr-rich \( \sigma \) phase showed an increase in Re and a decrease in W content compared to that of the samples aged at 850°C; this observation is consistent with the increase in precipitation of W-rich phases within the \( \gamma' \) layer.

<table>
<thead>
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<th>Phase</th>
<th>Elements (wt.%)</th>
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<tr>
<td></td>
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<tr>
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<tr>
<td>( P_{C} )</td>
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<tr>
<td>( P_{IDZ/C} )</td>
<td>6.9 - 7.1</td>
</tr>
</tbody>
</table>

\( X_C \) - Precipitates in bulk of coating  
\( X_{IDZ/C} \) - Precipitates present within the coating section of the IDZ  
\( X_{IDZ/S} \) - Precipitates present within the substrate section of the IDZ (\( \gamma' \) band)  

Table 7.7 EDX analysis results of the intermetallic and TCP phases present within the coating and interdiffusion zone of sample aged for 1000 hours at 900°C (obtained using analysis of thin foil samples within the TEM)
Figure 7.25 Micrographs and selected area diffraction patterns (SADP) of phases within the coating adjacent to the IDZ: a) SEM micrograph highlighting area of interest, b) TEM bright field image (BF) showing rounded TCP phases; SADP of c) P phase, d) μ phase, zone axes are labelled.

Figure 7.26 Micrographs and selected area diffraction pattern (SADP) of the acicular σ phases within the γ' layer of the IDZ: a) micrograph highlighting area of interest, b) bright field image (BF); SADP zone axes are labelled c) σ phase.
7.4.2 Thermal Exposure at 900°C for 2000 hours

The microstructure of the RT22 coated CMSX4 system after thermal aging at 900°C for 2000 hours is illustrated in Figure 7.27.

![Figure 7.27 SEM micrograph illustrating the overall structure of the substrate and coating of sample aged for 2000 hours at 900°C, including the coating, the interdiffusion zone and substrate](image)

The external scale present on the coating surface was of similar structure to the sample exposed at 1000 hours, in that it mainly comprised of an Al-rich layer, thought to be Al₂O₃. The average thickness of the oxide scale was 3.2 μm, therefore it has increased with exposure length due to the diffusion of Al out towards the coating surface. A light grey band was observed throughout the central section of the oxide scale, as shown in Figure 7.28. Chemical analysis of the band showed it to be rich in Al, Ta and O (approximately 39.3, 35.4 and 19.8 wt.% respectively), confirming the tendency of Ta to diffuse from the substrate towards the outer surface of the coating.

The relative amount and size of the γ' (Ni₃Al) particles observed within the bulk of the coating have significantly increased compared to those observed at 1000 hours. The increase in phase transformation from β → γ' is a result of the increased diffusion of Al from the coating towards the oxide layer and in towards the substrate. The γ' phase was predominantly located along the β grain boundaries and in the interdiffusion zone[151]. However, in contrast to the sample aged at 1000 hours, very little γ' was observed at the coating surface. This initially
suggests that within this sample the Al is primarily diffusing from the coating into the substrate. Additionally it is possible that there are higher concentrations of γ' stabilising elements such as Ta towards the interdiffusion zone. On the other hand the β stability at the coating surface can possibly be attributed to the high concentration of Pt, as Pt is reported to lower the rate by which β transforms to γ' close to the oxide scale\[55,146,152,153\]. The W/Re rich precipitates within the bulk of the coating appear to be of similar size and area fraction to those observed within the sample aged for 1000 hours, indicating the slow diffusion of the refractory elements from the substrate into the bulk of the coating. However, chemical analysis showed a reduction in Ta content within the precipitates compared to those observed at 850°C; this can be readily associated with the development of γ' particles within the coating since Ta is a stabilising element of γ'.

Figure 7.29 shows the interdiffusion zone of two different areas around the cross-sectioned surface, indicating that in the case that there is a uniform surface and coating thickness, changes in the morphology of the phases can occur. The interdiffusion zone of both areas has an average thickness of ~49μm and contains a band with a high density of precipitates adjacent to the coating/substrate interface as observed in previous samples. These precipitates have sizes ranging from hundreds of nanometres to several microns, and are once more enriched in W, Re, Cr and Mo, with only very slight compositional differences between the different phases. Ta-rich MC carbides have again been observed intermingled amongst the W-rich precipitates within the interdiffusion zone, and as stated previously, the only distinguishing feature of the carbides is their slight increase in size compared to the surrounding TCP phases. The size of the interdiffusion is very similar to that observed within the sample aged for 1000 hours, however, the main difference is that the γ' layer has grown out towards the substrate alloy and, in doing so, has encased the needle-like σ phase particles that were extending out into the substrate. Figures 7.29 a) and b) show the needle-like TCP phases now encased within the γ' layer, precipitating at various angles to the interface, dependent on the position within the sample. Figure 7.29 c) illustrates an area within the sample in which the TCP phases are precipitating at an angle of ~45° to the γ'/γ substrate structure. In contrast, the second area shown in Figure 7.29 d) indicates that the TCP phases are once more precipitating at angles of ~45° to the interface, although in opposite directions creating 90° angles between intersecting precipitates. The γ' structure within the substrate near to the coating/substrate interface appeared rafted, unlike in the samples aged at shorter
times, with the direction of the rafts varying between the two different areas identified. It has previously been observed in the MCrAIY coated samples that the direction of the rafting can vary from sample to sample and also the position around the sample's surface. It is not fully understood why the differing alignments occur, but they could possibly be due to varying diffusion kinetics and slight microstructural differences within the interdiffusion zone around the samples surface. These may result in different values of stress, due to differing thermal expansion coefficients of the coating and substrate during aging, it is also possible that there are different amounts of residual stress around the circumference of the sample as a result of initial sample processing.
Figure 7.28  SEM micrographs of RT22 coated CMSX4 thermally exposed for 2000 hours at 900°C, showing a) coating surface including the oxide layer, b) and c) bulk of the coating showing the W-rich precipitates and γ’ phases, and d) coating adjacent to the interdiffusion layer showing the high density band of TCP phases
Figure 7.29 SEM micrographs of RT22 coated CMSX4 thermally exposed for 2000 hours at 900°C, showing a) and b) the interdiffusion zone at differing positions within the sample, including the γ' layer, the different alignments of the TCP phase and the corresponding rafting of the substrate; c) and d) are higher magnifications of the γ' layer within image a) and b) respectively.
7.4.3 Thermal Exposure at 900°C for 4000 hours

The microstructure of the RT22 coated CMSX4 system after thermal aging at 900°C for 4000 hours is illustrated in Figure 7.30.

![SEM micrograph illustrating the overall structure of the substrate and coating of sample aged for 4000 hours at 900°C, including the coating, the interdiffusion zone and substrate](image)

Figure 7.30 SEM micrograph illustrating the overall structure of the substrate and coating of sample aged for 4000 hours at 900°C, including the coating, the interdiffusion zone and substrate.

Figure 7.31 illustrates the general coating structure. The main changes in the microstructure with thermal exposure are the increase in the amount of $\gamma'$ particles within the bulk of the coating. The W-rich particles present within the coating appear to be surrounded by an area of brighter contrast, as illustrated in Figure 7.31 b). Chemical analysis of the particles indicated that they had similar compositions to those observed at 2000 hours, however, values of oxygen up to 4 wt.% were also detected. One possibility is that this is due to surface contamination, however, levels of ~ 0.3 wt.% were detected in the adjacent matrix (see Table 7.8) and therefore it is thought that this is a genuine result, and that the W-rich particles do contain oxygen.
Figure 7.31 SEM micrographs of RT22 coated CMSX4 thermally exposed for 4000 hours at 900°C, showing a) the distribution of the γ' and W-rich particles throughout the bulk of the coating and b) higher magnification indicating the area of brighter contrast surrounding the W-rich precipitates

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Table 7.8 EDX analysis results showing the compositions of the W-rich precipitates and the surrounding β phase in the samples aged at 900°C for 2000 and 4000 hours

The interdiffusion zone exhibited similar features to those observed in the sample aged for 2000 hours, as shown in Figure 7.32 a). Cr-rich phases were observed within the γ' layer, similar to those present in that sample aged at 850°C for 2000 hours. Once again the particles have lath-like morphologies and were located near the β particles also within the γ' layer, as
shown in Figure 7.32 b). Chemical analysis showed these particles to be rich in Cr ~ 54 wt.%, with similar amounts of W and Re at ~ 11 wt.%. The presence of C up to ~ 4 wt.% similar to those observed in the sample aged at 850°C for 4000 hours indicated these particles were likely to be $M_23C_6$ carbides. Large MC carbides rich in Ta and Ti, with sizes ranging from 1.5 - 3.6 μm were also observed within the $\gamma'$ layer, similar to 2000 hour sample. These MC carbides are surrounded by areas of $\beta$, as shown in Figure 7.32 c). It is possible that these MC carbides have nucleated and grown within the $\gamma'$ layer and in doing so have depleted the surrounding area of Ta and Ti, resulting in a phase transformation from $\gamma' \rightarrow \beta$. Figure 7.32 d) shows that the differing alignments of the needle-like TCP phases within the $\gamma'$ layer, as observed in the sample aged for 2000 hours have remained present after increase exposure time.
Figure 7.32 SEM micrographs of RT22 coated CMSX4 thermally exposed for 4000 hours at 900°C, showing a) the structure of the interdiffusion zone, b) higher magnification of the γ’ layer showing the Cr-rich lath-like phases, c) MC carbides surrounded by β within the γ’ layer and d) the different alignments of the needle-like TCP phases.
7.5 Microstructure of RT22 Coated CMSX4 Thermally Exposed at 950°C

7.5.1 Thermal Exposure at 950°C for 1000 hours

The microstructure of the RT22 coated CMSX4 system after thermal aging at 950°C for 1000 hours is illustrated in Figure 7.33.

![Figure 7.33](image)

**Figure 7.33** SEM micrograph illustrating the overall structure of the substrate and coating of sample aged for 1000 hours at 950°C, including the coating, interdiffusion zone and substrate.

The overall coating microstructure of the sample aged at 950°C for 1000 hours indicates a significant increase in the size and relative amount of the $\gamma'$ particles within the $\beta$ matrix compared to the sample aged for 1000 hours at 900°C. The size of the $\gamma'$ particles now ranges between 2 and 12 $\mu$m, showing both the growth of existing and precipitation of new particles. The increase in size of the $\gamma'$ particles indicates an increase in Al diffusion out towards the coating surface and in towards the substrate alloy. As observed in previous samples, these particles were located at the oxide/coating surface, within the bulk of the coating and towards the interdiffusion zone, as shown in Figure 7.35. The increased amount of $\gamma'$ within the bulk of the coating and the interdiffusion zone suggests that the Al is primarily diffusing from the coating into the substrate, although the Al concentration remained fairly constant throughout the coating, as illustrated in Table 7.9. This diffusion path is confirmed by the relatively small observed growth of the oxide scale to 2.7 $\mu$m from 2.1 $\mu$m observed in the sample aged at 900°C for 1000 hours. Chemical analysis of the $\beta$ matrix shows an overall decrease in Pt
content to ~ 16.5 wt.% compared to ~ 20 wt.% observed at 900°C, however, this value proves reasonably constant through the coating towards the interdiffusion zone, as shown in Figure 7.34. This constant value indicates a steady diffusion of the Pt from the coating into the substrate, increasing the content within the interdiffusion zone.

Figure 7.34  Compositional profile of main alloying elements across the coating, interdiffusion layer and substrate of RT22 coated CMSX4 sample aged for 1000 hours at 950°C

The W/Re-rich precipitates observed within the bulk of the coating have undergone significant growth and appear to have decreased in area fraction with the increase in temperature. The decrease in area fraction of the precipitates may be a result of the increase in $\gamma'$ within the coating, as $\gamma'$ is known to have a higher solubility for W than that of the $\beta$ phase$^{[146,147]}$. Identification of these precipitates with the combined use of SAED and EDX analysis showed that $\sigma$, $\mu$ and P phase were all precipitating together within the $\beta$ matrix. However, the relative fraction of each phase present is unknown due to the extreme similarities in their morphology and composition. There was a reduction in the Ta content of these W/Re-rich precipitates as observed at 900°C in comparison to ageing at 850°C; this is once more associated with the development and growth of the $\gamma'$ particles.
Figure 7.35 SEM micrographs of RT22 coated CMSX4 thermally exposed for 1000 hours at 950°C, showing a) the oxide scale, γ', and W-rich precipitates at the coating surface, b) these phases within the bulk of the coating and c) towards the interdiffusion zone.
Table 7.9 EDX analysis results of $\beta$ phase present with increasing distance from the coating surface in the sample aged for 1000 hours at 950°C (obtained using SEM)

X_{CS} - X phase at the coating surface
X_{BC} - X phase within the bulk of the coating
X_{IDZ/C} - X phase adjacent to the IDZ

Figure 7.36 shows the microstructure of the interdiffusion zone within the sample. As seen within the bulk of the coating, significant coarsening of the precipitates with the band adjacent to the coating/substrate interface was observed. Therefore, indicating an increase in diffusion of the refractory elements from the substrate into the coating. It is possible that exposure at increased temperatures has given rise to an Ostwald ripening process in which large precipitates grow at the expense of smaller ones \cite{34,37}. Chemical analysis of these precipitates once more showed them to be enriched in W, Re, Cr and Mo and they were conclusively identified as a mixture of W/Re-rich $\sigma$, $\mu$ and $P$ phase, with similar compositions to those observed at lower temperatures. Full chemical analysis of these phases is reported in Table 7.10. Ta-rich MC carbides with a globular morphology were present within the precipitate band; this has proved consistent throughout the samples investigated, increasing in size and relative fraction with increased temperature. Figure 7.36 c) illustrates that the TCP phases and the MC carbides have been observed to precipitate on each other, presumably due to the high concentration of refractory elements within this area.
Figure 7.36 SEM micrographs of RT22 coated CMSX4 thermally exposed for 1000 hours at 950°C, showing a) the interdiffusion layer structure, b) TCP phases extending from the γ' layer into substrate and c) coating structure adjacent to the IDZ.

As observed throughout the samples the interdiffusion of elements between the coating and substrate has resulted in the formation of a γ' layer. However, in contrast to the sample aged at 900°C the γ' layer is continuous throughout the thickness with no entrapment of β particles after ageing at 950°C. The diffusion of Cr from the substrate into the coating has encouraged the formation of Cr-rich phases of a globular morphology within the continuous γ' layer, illustrated in Figure 7.36 c). Chemical analysis of these precipitates indicated a significantly higher Cr content, similar Re and lower Co content compared to the σ phase observed in samples aged at lower temperatures. These precipitates were further identified as M₄₇C₆ carbides (a₀ = 10.638 Å) using a combination of selected area diffraction patterns and EDX analysis. These are illustrated in Figure 7.37, and their compositions are presented in Table 7.10. The Cr-rich M₄₇C₆ carbides were located within similar areas of the interdiffusion zone to that of the entrapped β phase observed at 900°C. Chemical analysis of the entrapped β phase
reported in Table 7.6 showed a significant increase in Cr and Re to that observed within the
bulk of the coating. This therefore suggests although these M$_{23}$C$_{6}$ carbides were unable to be
visually identified, they could have been present within or underlying the β phase in the
sample aged at 900°C for 1000 hours. In contrast to the interdiffusion zone observed in the
sample aged at 900°C, the γ' layer has grown out towards the substrate alloy and in doing so
has encased the coarsened needle-like TCP phases that were observed extending out towards
the substrate. Identification of these precipitates within the γ' layer using SAED patterns and
EDX analysis showed that the predominant phases present are the W and Re rich μ and P
phases, with similar compositions to those observed at lower temperatures, and reported in
Table 7.10. This agrees well with literature, and indeed the observations for the MCrAlY
coated samples which were reported in Chapter 5. The σ phase is stable within areas of high
Cr and Co content at lower temperatures, resulting in the dissolution and re-precipitation of
more stable TCP phases at higher temperatures$^{[102]}$.

With the exposure to increased temperatures the γ/γ' structure within the substrate adjacent to
the coating/substrate interface was observed to be rafted at an angle of ~ 45°, indicating that
the slight increase in temperature has induced enough stress within the system to initiate the
rafting.
Figure 7.37  a) bright field TEM image (BF) showing the various TCP phase and carbides within the coating adjacent to the IDZ and how they precipitate in respect to each other; SADP of b) σ phase, c) P phase, d) μ phase and e) M$_{23}$C$_6$ carbide; in which the relevant zone axes are labelled.
<table>
<thead>
<tr>
<th>Phase</th>
<th>Elements (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ni</td>
</tr>
<tr>
<td>(\sigma_c)</td>
<td>0.0 - 4.7</td>
</tr>
<tr>
<td>(\sigma_{IDZ})</td>
<td>6.2 - 7.6</td>
</tr>
<tr>
<td>(\mu_c)</td>
<td>5.7 - 9.6</td>
</tr>
<tr>
<td>(\mu_{IDZ})</td>
<td>6.8 - 8.6</td>
</tr>
<tr>
<td>(P_c)</td>
<td>4.7 - 6.6</td>
</tr>
<tr>
<td>(P_{IDZ})</td>
<td>6.9 - 7.1</td>
</tr>
</tbody>
</table>

\(X_c\) - Precipitates in bulk of coating

\(X_{IDZ/C}\) - Precipitates present within the coating section of the IDZ

\(X_{IDZ/S}\) - Precipitates present within the substrate section of the IDZ (\(\gamma^\prime\) band)

**Table 7.10** EDX analysis results of the intermetallic and TCP phases present within the coating and interdiffusion zone of sample aged for 1000 hours at 950°C (obtained using analysis of thin foil samples within the TEM)
7.5.2 Thermal Exposure at 950°C for 2000 hours

The microstructure of the RT22 coated CMSX4 system after thermal aging at 950°C for 2000 hours is illustrated in Figure 7.38. Initial observations of the coating structure show distinct differences to the sample aged at 950°C for 1000 hours and indeed the samples aged at lower temperatures.

![Figure 7.38 SEM micrograph illustrating the overall structure of the substrate and coating of sample aged for 1000 hours at 950°C, including the coating, the interdiffusion zone and the substrate](image!

The external oxide scale on the coating surface has an average thickness of 6.7 μm and comprises of two layers as shown in Figure 7.39. The thickness of the oxide scale has rapidly increased resulting in a growth of ~3.4 μm over 1000 hours. The different layers within the oxide scale have been observed in similar coating systems. The inner layer consists mainly of Al and O ~ 66 wt.% and 30 wt.% respectively, with small amounts of the solid solution elements, such as Ni, Cr and Ta, found within the substrate alloy. The outer layer contains areas rich in Ta and Hf with a similar structure to that observed in the sample aged at 900°C for 2000 hours. It has been suggested that this outer layer contains several transient oxides that initially develop due to the influx of oxygen at the coating surface. The oxygen pressure at the oxide/coating interface subsequently decreases allowing the stable Al₂O₃ to form. The result is a continuous Al₂O₃ scale on which remnants of the transient oxide phases remain\(^\text{[105]}\).
Table 7.1. EDX analysis of RT22 coated CMSX4 thermally exposed for 2000 hours at 950°C, showing the two layers of the oxide scale on the coating surface, including the EDX results obtained from the SEM of the different areas and precipitates observed.

<table>
<thead>
<tr>
<th>Area</th>
<th>Ni</th>
<th>Al</th>
<th>Ti</th>
<th>Cr</th>
<th>Ta</th>
<th>W</th>
<th>Hf</th>
<th>Fe</th>
<th>O</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>3.81</td>
<td>65.51</td>
<td>0.52</td>
<td>0.55</td>
<td>2.07</td>
<td>2.07</td>
<td>27.54</td>
<td>2.97</td>
<td>17.0</td>
</tr>
<tr>
<td>B</td>
<td>1.7</td>
<td>51.73</td>
<td>3.55</td>
<td>9.21</td>
<td>9.64</td>
<td>1.64</td>
<td>2.57</td>
<td>2.97</td>
<td>17.0</td>
</tr>
<tr>
<td>C</td>
<td>2.57</td>
<td>21.48</td>
<td>7.31</td>
<td>3.16</td>
<td>43.17</td>
<td>0.55</td>
<td>5.22</td>
<td>2.0</td>
<td>14.55</td>
</tr>
</tbody>
</table>

Figure 7.39 SEM micrographs of RT22 coated CMSX4 thermally exposed for 2000 hours at 950°C, showing the two layers of the oxide scale on the coating surface, including the EDX results obtained from the SEM of the different areas and precipitates observed.

The area fraction and size of the \( \gamma' \) particles throughout the bulk of the coating have increased significantly in comparison to those observed in the sample aged for 1000 hours. Figure 7.40 shows that the morphology of the \( \gamma' \) particles varies, ranging from rounded to blocky and are even observed in platelet form. The larger of the \( \gamma' \) particles are located at both the coating surface and the interdiffusion zone. The transformation of \( \beta \rightarrow \gamma' \) suggests an increase in diffusion of Al from the coating towards the oxide scale and in towards the substrate with exposure length. Chemical analysis of the \( \gamma' \) within the bulk of the coating shows a decrease in Ta and an increase in W content (~ 7 wt.% and 6.5 wt.% respectively) with thermal exposure. The precipitates rich in W and Re present within the bulk of the coating have coarsened with exposure time, increasing in average size from 0.8 \( \mu \)m observed at 1000 hours to 2.1 \( \mu \)m after 2000 hours. The area fraction of these precipitates has ultimately decreased, which can be directly associated with the increase in \( \gamma' \) within the coating; as \( \gamma' \) is known to have a higher solubility of W than that of the \( \beta \) phase. Therefore, the implication is that the W
is diffusing from the substrate into the coating and partitioning to the $\gamma'$ phase, preventing the precipitation and growth of these precipitates. Chemical analysis of these W-rich precipitates showed them to be mainly composed of W, Re, and Cr with additions of Co and Ni. Comparison of the compositions with the samples aged at lower temperatures suggests that the precipitates are a mixture of $\sigma$, $\mu$ and P phase, however, due to their similar compositions conclusive identification requires the determination of their crystal structure in addition to the quantitative chemical analysis.

Figure 7.40 SEM micrographs of RT22 coated CMSX4 thermally exposed for 2000 hours at 950°C, showing the varying sizes and morphologies of the $\gamma'$ and W/Re rich precipitates at a) the coating surface and b) in the bulk of the coating

The increase in diffusion of Cr and Re across the coating/substrate interface and their low solubility within $\gamma'$ and $\beta$ has resulted in the precipitation of Cr-rich phases within the coating. These precipitates are of a similar grey contrast to that of the $\gamma'$ phase, making them difficult to distinguish. However, they are mainly located on the $\gamma'$/ $\beta$ grain boundaries and range in size from 1 - 6 $\mu$m as illustrated in Figure 7.41. EDX analysis of the precipitates performed in the SEM indicated similar compositions to that of the $M_{23}C_6$ carbides observed within the interdiffusion zone at 1000 hours. It should be noted that the compositional analysis will vary between the SEM and TEM samples because of the differing activation volumes. However, it is likely that these particles are $M_{23}C_6$ carbides.
An interdiffusion zone is characterised as the area at the interface affected by the interdiffusion of elements, resulting in a distinct microstructure unlike that of the coating and/or substrate. The interdiffusion zone observed after 2000 hours falls into this classification, however, it has a very different microstructure to those observed in the samples aged at lower temperatures as illustrated in Figure 7.42. The interdiffusion zone has increased in thickness substantially from 40 μm at 1000 hours to 109 μm, indicating a significant increase in diffusion activity across the coating/substrate interface. The interdiffusion zone consisted of two distinct layers on either side of the interface.
A continuous $\gamma'$ layer was once again observed within the interdiffusion zone, however, this is present within the coating adjacent to the interface, as opposed to the substrate as seen in previous samples. The TCP phases, which form a distinct band within the coating section of the interdiffusion zone in samples aged at lower temperatures have increased significantly in size now ranging from 2.4 - 8.4 $\mu$m and are contained within the $\gamma'$ layer, as shown in Figure 7.43. Chemical analysis of the precipitates indicated that they contained high amounts of W, Re and Cr; ~ 38, 18 and 10 wt.% respectively, which are within the range of compositions of $\sigma$, $\mu$ and P phases. The $\gamma'$ layer also contains smaller precipitates with both rounded and acicular morphologies, all showing similar compositions to that of the larger W-rich precipitates. Figure 7.44 shows that in some cases the acicular precipitates are seen to extend out of the $\gamma'$ layer into the second layer of the interdiffusion zone, similar to observations at lower temperatures.
Figure 7.43 SEM micrograph of RT22 coated CMSX4 thermally exposed for 2000 hours at 950°C, showing the coarsened W/Re-rich precipitates forming a linear array within coating section of the interdiffusion zone.

Figure 7.44 SEM micrograph of RT22 coated CMSX4 thermally exposed for 2000 hours at 950°C, showing a) the W/Re-rich precipitate with rounded and acicular morphologies contained within the γ′ layer and b) the precipitates extending out of the γ′ layer into the substrate layer of the interdiffusion zone.

Adjacent to the γ′ layer was a layer of γ/γ′ which resembled a highly rafted substrate structure, as illustrated in Figure 7.45. The coalescence of adjacent γ′ particles has occurred within some areas of this layer, forming regions of continuous γ′. Very small precipitates with an acicular morphology were observed throughout this coarsened γ/γ′ layer, with sizes ranging from 0.3 - 1.5 μm. Due to the size of the particles, an accurate chemical analysis
proved hard to obtain. Therefore, compositions were taken of the larger precipitates which showed that they contained high amounts of W, Re and Cr ~ 28, 20 and 11 wt.% respectively.

Figure 7.45 SEM micrograph of RT22 coated CMSX4 thermally exposed for 2000 hours at 950°C, showing the coarsened γ' structure on the substrate section of the interdiffusion zone containing very small W and Re-rich precipitates.
7.5.3 Thermal Exposure at 950°C for 4000 hours

The microstructure of the RT22 coated CMSX4 system after thermal aging at 950°C for 4000 hours is illustrated in Figure 7.46. The general features within the microstructure are consistent with observations at earlier times at this temperature, and indicate that 950°C appears to be a 'special' temperature in respect to the kinetics of the various diffusional and oxidative processes for the coating system.

![Figure 7.46 SEM micrograph illustrating the overall structure of the substrate and coating of sample aged for 4000 hours at 950°C, including the coating, the interdiffusion zone and the substrate](image)

The oxide scale on the coating surface presents similar characteristics to those observed at 2000 hours, although the average thickness has slightly increased to ~ 7.1 μm. In contrast, cracks breaking up the two distinct oxide layers are observed within some areas of the sample, as shown in Figure 7.47. Cracking/spalling of the oxide scale may have occurred on aging, or during cooling from temperature. It is also possible that these cracks were formed during metallographic preparation of the sample, indicating a possible weakness between the transient oxides and the alumina layer.
After 4000 hours at 950°C the increase in γ' within the coating has resulted in virtually the complete dissolution of the W/Re rich precipitates, as shown in Figure 7.48. This has proved consistent with increasing exposure length. The few precipitates that remain are located in the central section of the coating and are of similar size and composition to those observed at 2000 hours. Narrow straight parallel bands are observed within several of the areas of β phase within the bulk of the coating, as shown in Figure 7.48 b). These bands have been observed within similar PtAl coating systems and have been reported to be the result of a martensitic transformation within β grains upon cooling. When the Al content falls below a critical level within the PtAl coating, the β will undergo the transformation from the B2 crystal structure to the martensitic L10. The critical cooling rate for the martensitic transformation has been shown to be low in NiAl alloys and therefore air cooling is sufficient for its formation. The martensitic start temperature Ms has a strong dependence on chemical composition therefore making it hard to predict, however the Ms is generally thought to be higher for (Ni,Pt)Al than for binary NiAl.
As observed in the sample aged for 2000 hours, Cr/Re rich phases are observed within the coating and interdiffusion zone. In the bulk of the coating these particles were located on the $\gamma'$/$\beta$ grain boundaries, due to the low solubility of these elements within these phases. The chemical composition of the Cr/Re-rich phases was similar to the compositions of particles identified as $\text{M}_{23}\text{C}_6$ carbides in the sample aged for 1000 hours. In addition these phases are found to precipitate on or surrounding the W/Re rich precipitates within the interdiffusion zone, confirmed by EDX maps shown in Figure 7.49. It is possible that these form due to the rejection of Cr from the W/Re-rich phases coupled with an increase in diffusion of Cr across the coating/substrate interface. A sample taken across the interdiffusion zone allowed their conclusive identification as $\text{M}_{23}\text{C}_6$ carbides with the use of SAED.
Figure 7.49 SEM micrographs of RT22 coated CMSX4 thermally exposed for 4000 hours at 950°C, showing a) the large precipitates within the interdiffusion zone; EDX elemental map of area illustrating the concentration of b) Re and c) Cr.

Figure 7.50 SEM micrograph of RT22 coated CMSX4 thermally exposed for 4000 hours at 950°C, showing a) the interdiffusion zone microstructure and b) the large W/Re-rich precipitates within coating section of the interdiffusion zone.
Large rounded W/Re-rich precipitates are present within the coating section of the interdiffusion zone, as shown in Figure 7.50. These are of similar size and shape to those observed at 2000 hours, however, they are seen to consist of three separate areas defined by variation in contrast. Figure 7.51 shows a line scan taken across the precipitates to illustrate the variation in composition of the different layers. The outer brighter layer has a similar composition to the precipitates observed in the interdiffusion zone at 2000 hours, containing high amounts of W (~35 wt.%) and Re (~26 wt.%). The W content is seen to increase within the darker band of the precipitate to an average value of 40 wt.%. This is coupled with a decrease in Re content from 25 to 16 wt.%. Oxygen has also been detected within this layer with values ranging from 5 to 10 wt.%. The W-rich oxide observed within the core of these precipitates suggests that it has formed initially and subsequently the W/Re-rich particles have precipitated around them. However, the W/Re-rich TCP phases are present within the interdiffusion zone at lower temperatures and exposure lengths were no oxygen has been detected. It is unclear at this point how the limited amount of oxygen has diffused into the coating and why it has reacted with the W to form W-rich oxides as opposed to elements such as Al and Cr present within the coating. One suggestion is that the oxygen has originated from the Al₂O₃ grit particles used in the coating process. The grit particles used can vary significantly in size with very fine particles being embedded as well as the large particles observed within the SEM micrographs. Although Al₂O₃ is a stable phase it is possible that it can be reduced within a nickel matrix under certain conditions, with oxygen combining with reactive elements within the interdiffusion zone. The oxygen would ideally travel to the free surface, however it becomes trapped resulting in a reaction with W, Re and Cr present in high concentrations within precipitates. Further investigation is required as to why the oxygen would partition to the W rather than with more reactive elements such as Cr.
Figure 7.51 Compositional profile across the large W/Re-rich precipitate within the interdiffusion zone of RT22 coated CMSX4 sample aged at 950°C for 4000 hours, measured by SEM-EDX.

The interdiffusion zone shown in Figure 7.52 demonstrates the two layer structure similar to that observed in the sample aged for 2000 hours. Light grey phases were observed intermingled with the smaller W/Re-rich phases of varying morphologies within the γ’ enriched layer. Chemical analysis of the particles showed them to be rich in Cr with similar compositions to the M23C6 carbides that preferentially surround the W/Re rich precipitates. The second layer has retained its highly rafted γ'/γ' structure and has increased in thickness from ~67 μm at 2000 hours to ~84 μm. The small precipitates of acicular morphology
observed throughout this second layer have coarsened with exposure length. Furthermore they were seen to increase size through the layer towards the γ'/γ' substrate and in some cases have extended out into the substrate at angles of ~45° to the γ'/γ' structure. Chemical analysis of the larger precipitates indicated that they contained equal amounts of W and Re ~ 35 wt.%

Figure 7.52 SEM micrograph of RT22 coated CMSX4 thermally exposed for 4000 hours at 950°C, showing a) the W/Re-rich precipitates and M23C6 carbides with rounded and acicular morphologies contained within the γ' layer and b) the second with a highly rafted γ' layer structure containing very small TCP phases, with the larger one extending out of the layer into the substrate.
7.6 Microstructure of RT22 Coated CMSX4 Thermally Exposed at 1000°C

7.6.1 Thermal Exposure at 1000°C for 1000 hours

The microstructure of the RT22 coated CMSX4 system after thermal aging at 1000°C for 1000 hours is illustrated in Figure 7.53.

![SEM micrograph illustrating the overall structure of the substrate and coating of sample aged for 1000 hours at 1000°C, including the coating, the interdiffusion zone and the substrate](image)

The amount of \(\gamma'\) particles within the coating was similar to that observed in the sample aged at 950°C. Their size, however, has increased with temperature and they are once more located at the coating surface, within the bulk of the coating and towards the interdiffusion zone as shown in Figure 7.55 a). The increase in size of the \(\gamma'\) particles initially indicates an increase in Al diffusion out towards the coating surface and substrate alloy, resulting in the phase transformation from \(\beta \rightarrow \gamma'\). In comparing the chemical compositions of both the \(\beta\) and \(\gamma'\) phase with those observed at 950°C, no significant changes in the Al concentrations were detected. Figure 7.54 shows that the Pt concentration within the coating has decreased within increasing temperature from 950°C to 1000°C, which indicates the increased diffusion of the Pt into the substrate. However, the Pt content within the \(\beta\) phase has increased from \(\sim 17\) wt.\% at 950°C to \(\sim 20\) wt.\%, therefore indicating that the majority of the Pt is located in the \(\beta\) phase within the coating.
The W/Re-rich precipitates within the bulk of the coating are of a similar size and shape to those observed at 950°C, but have decreased in area fraction. Once again this can be associated with the increase in size of the γ' and its higher solubility of W than that of the β phase. Chemical analysis of the precipitates showed them to consist mainly of W, Re and Cr (approximately 35, 19 and 11 wt.% respectively). Due to similarities in composition to samples aged at lower temperatures, it is possible that these particles are a combination of σ, μ and P phase.

Figure 7.55 SEM micrographs of RT22 coated CMSX4 thermally exposed for 1000 hours at 1000°C, showing the varying sizes and morphologies of the γ' and W/Re rich precipitates a) throughout the coating and b) higher magnification in the bulk of the coating.
<table>
<thead>
<tr>
<th>Element</th>
<th>950°C</th>
<th>1000°C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(\beta) (wt.%)</td>
<td>(\gamma') (wt.%)</td>
</tr>
<tr>
<td>Ni</td>
<td>47.4 - 49.0</td>
<td>50.7 - 54.1</td>
</tr>
<tr>
<td>Al</td>
<td>13.4 - 14.0</td>
<td>6.2 - 6.7</td>
</tr>
<tr>
<td>Cr</td>
<td>3.3 - 3.7</td>
<td>1.6 - 2.7</td>
</tr>
<tr>
<td>Co</td>
<td>6.5 - 7.0</td>
<td>6.8 - 7.4</td>
</tr>
<tr>
<td>Ta</td>
<td>4.5 - 4.9</td>
<td>15.6 - 17.6</td>
</tr>
<tr>
<td>W</td>
<td>0.2 - 1.2</td>
<td>0.0 - 3.4</td>
</tr>
<tr>
<td>Re</td>
<td>0.0 - 1.3</td>
<td>0.6 - 1.8</td>
</tr>
<tr>
<td>Pt</td>
<td>16.4 - 17.3</td>
<td>7.6 - 9.5</td>
</tr>
</tbody>
</table>

Table 7.11  EDX analysis results showing the compositions (wt.%) of \(\beta\) and \(\gamma'\) phases in the samples aged for 1000 hours at 950°C and 1000°C (obtained using SEM).

Figure 7.56 shows the microstructure of the interdiffusion zone. The distinct band of precipitates within the coating section of the interdiffusion zone is still present. As in the bulk of the coating, a combination of W/Re-rich \(\sigma\), \(\mu\) and P phase have been identified within this area of the interdiffusion zone in samples aged at lower temperatures.

Figure 7.56  SEM micrographs of RT22 coated CMSX4 thermally exposed for 1000 hours at 1000°C, showing a) the interdiffusion zone (IDZ) structure and b) higher magnification of the TCP phases that form a distinct band in the coating section of the IDZ.
Ta, Ti and Hf rich MC carbides are once more found mixed in within the band of TCP phase within the interdiffusion zone. The morphology and size of these carbides show little difference compared to the surrounding TCP phases, however, their existence is confirmed by the EDX elemental maps shown in Figure 7.57, in which the particles rich in Ta and Ti are clearly visible. At 950°C Cr-rich $\text{M}_{23}\text{C}_6$ carbides of globular morphology were observed around the same area, however, these are no longer observed at 1000°C. It is likely that this is a result of the decreased phase stability of $\text{M}_{23}\text{C}_6$ compared to MC at 1000°C, although it should be noted that observations at 950°C indicate differences in transformation kinetics at this temperature.

![Figure 7.57](image)

**Figure 7.57** SEM micrographs of RT22 coated CMSX4 thermally exposed for 1000 hours at 1000°C, showing a) the band of precipitates within the interdiffusion zone; EDX elemental map of area illustrating the concentration of b)Ta and c)Ti

The $\gamma'$ enriched layer at the coating/substrate interface has a thickness of ~ 32.5 μm and contains smaller precipitates with both rounded and geometric morphologies. The particles are seen to become more geometric towards the substrate, finally becoming acicular at the
interface, as illustrated in Figure 7.58. Chemical analysis showed these precipitates have very similar compositions to those observed within the band adjacent to the $\gamma'$ layer and the compositions are consistent throughout the $\gamma'$ layer. A slight increase in Re content of the precipitates within the $\gamma'$ layer was observed, which could be due to the high temperature allowing increased movement of the element from the substrate. Lighter grey particles were also observed within this layer as shown in Figure 7.58 b). These contained similar amounts of Cr and W, at ~25 wt.%, with smaller amounts of Re ~ 8 wt.%. The ratio of Cr to Re coupled with a low Co content of ~ 4 wt.% suggests the possibility of the particles being $M_2C_6$ carbides. Conclusive identification of these precipitates requires the determination of their crystal structure in addition to quantitative chemical analysis.

![SEM micrographs of RT22 coated CMSX4 thermally exposed for 10000 hours at 1000°C, showing a) the precipitates within the $\gamma'$ layer of the interdiffusion zone and b) higher magnification of the phases within the $\gamma'$ layer](image)

The growth of the acicular W, Re and Cr rich TCP phases present at the $\gamma'$ layer/substrate interface has resulted in their extension out of the $\gamma'$ layer into the substrate alloy. In some areas the precipitates are seen to extend up to 27 µm into the substrate at angles close to 45° to the $\gamma'$/$\gamma'$ structure, as shown in Figure 7.59. Bands of $\gamma'$ are seen to surround the phases which precipitate out into the substrate. As the TCP phases precipitate and grow, they deplete the surrounding $\gamma$ matrix of solid solution strengthening elements such as W, Re and Cr. This depletion of elements results in the phase transformation from $\gamma$ to $\gamma'$. 

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Figure 7.59 SEM micrographs of RT22 coated CMSX4 thermally exposed for 1000 hours at 1000°C, the extension of acicular precipitates from the $\gamma'$ layer in the IDZ into the substrate alloy.
7.6.2 Thermal Exposure at 1000°C for 2000 hours

The microstructure of the RT22 coated CMSX4 system after thermal aging at 1000°C for 2000 hours is illustrated in Figure 7.60.

![SEM micrograph illustrating the overall structure of the substrate and coating of sample aged for 2000 hours at 1000°C, including the coating, the interdiffusion zone and the substrate](image)

The oxide scale on the coating surface shows similar characteristics to the sample aged at 950°C, with the occurrence of two oxide layers, as shown in Figure 7.61. Once again the outer layer contained areas rich in Ta, Ti and Hf; with the inner layer consisting mainly of Al and O, presumably Al₂O₃. The oxide thickness has decreased from ~ 6.7 μm at 950°C to ~ 5.4 μm. The decrease in oxide thickness coupled with the decrease in relative fraction of γ' confirms that the diffusion kinetics of the coating system are altered at 950°C. The fraction of γ' precipitates at the coating surface has increased with exposure length, indicating an increase in Al diffusion primarily out towards the coating surface. A reduction in relative fraction of the W/Re-rich precipitates within the bulk of the coating was once more observed and can be associated with the increase in γ'. In addition the solubility of W within the β phase is known to increase with temperature. The size of the precipitates proved to be smaller than those observed at 950°C, again proving inconsistent with samples aged at 850°C and 900°C.
Figure 7.61 SEM micrographs of RT22 coated CMSX4 thermally exposed for 2000 hours at 1000°C, showing the varying sizes and morphologies of the γ' and W/Re rich precipitates (a) at the coating surface (b) higher magnification in the bulk of the coating.

Figure 7.62 shows the microstructure of the interdiffusion zone. This mainly consists of a γ' layer with an average thickness of 56.3 μm, which is a significant increase compared to the 29.2 μm observed at 1000 hours. The growth of the γ' layer is related to the diffusion of elements across the coating/substrate interface.

Figure 7.62 SEM micrographs of RT22 coated CMSX4 thermally exposed for 2000 hours at 1000°C, showing the interdiffusion zone (IDZ) structure.
Cavities were also observed throughout the coating section of the interdiffusion zone and the γ' layer, as shown in Figure 7.63. The larger of these cavities were located within the band of TCP phases observed within samples at lower temperatures and shorter exposure lengths. Chemical analysis of the holes showed them to be rich in Cr and Re \( \sim 48 \) wt.% and 20 wt.% respectively. The similar compositions of these holes suggest that preferential etching of the matrix has occurred revealing underlying Cr-rich precipitates. Site specific TEM samples taken across these precipitates allowed them to be identified as \( \text{M}_{23}\text{C}_6 \) carbides using a combination of SAED and EDX analysis. The existence of the \( \text{M}_{23}\text{C}_6 \) carbides throughout the interdiffusion zone is a result of the increase in Cr diffusion from the substrate into the coating with exposure length, although it is interesting to note that the \( \text{M}_{23}\text{C}_6 \) carbides appear to be stable at this temperature in this particular region. Typical SAED patterns are shown in Figure 7.64. High resolution analysis across the γ' layer indicates that the various TCP phases and carbides present are seen to precipitate on each other. The TCP phases remain W and Re rich with smaller amounts of Cr and Co. The majority of these precipitates were identified as \( \mu \) and \( \text{P} \) phase with the use of SAED. The reduction in fraction of \( \sigma \) phase identified could be related to the increase in \( \text{M}_{23}\text{C}_6 \), as it has been reported that the \( \sigma \) phase can act as nucleation sites for other phases with similar crystallography and chemistry, in particular \( \text{M}_{23}\text{C}_6 \) carbides\(^{[157]}\).

![Figure 7.63 SEM micrographs of RT22 coated CMSX4 thermally exposed for 2000 hours at 1000°C, showing a) and b) the TCP phases and the preferential etching of the matrix above \( \text{M}_{23}\text{C}_6 \) carbides within the interdiffusion zone](image-url)
Figure 7.64 TEM micrographs of RT22 coated CMSX4 thermally exposed for 2000 hours at 1000°C, showing bright field images a), b) and c) of the precipitation of various TCP phases and carbides present within the interdiffusion zone; SADP of d) $M_23C_6$ carbide, e) $\mu$ phase and f) P phase, in which the relevant zone axes are labelled.

Light grey areas surrounded by dark bands are observed close to or on the W/Re-rich $\mu$ and P phases within the interdiffusion zone, as shown in Figure 7.65 a). When imaged in secondary electron mode, these same areas were seen as particles that stood proud of the sample surface. The particles proved easier to identify within an ion induced secondary electron image (in the FIBSEM) as they appeared as black areas within the larger TCP phases, as illustrated in Figure 7.65 c). Chemical analysis within the SEM showed these particles to be richer in W and Ta, with lower amounts of Co and Re than that of the surrounding brighter particles. Oxygen was also found to be present within these particles, with values up to 9.5 wt.%, as observed at 950°C for 4000 hours. The TEM image of a FIB section taken across one of these particles is shown in Figure 7.66. The bright particle (labelled B) trapped between the
protective Pt layer and the dark W/Re rich precipitate (labelled A) was identified as the oxide. Several cross sections were taken, however, it proved difficult after thinning the sample to ~200 nm thick to retain the particles within the section. EDX analysis within the TEM shows the particle to be rich in W and O with smaller amounts of Cr, P and Ca.

Figure 7.65 SEM micrographs of RT22 coated CMSX4 thermally exposed for 2000 hours at 1000°C, showing a) backscattered electron image of the W-rich oxides within the interdiffusion zone (IDZ), b) Secondary electron image of the same area within the IDZ, and c) Ion induced secondary electron image of the W-rich oxide (appearing black)
<table>
<thead>
<tr>
<th>Elements (wt.%)</th>
<th>A</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>4.9</td>
<td>-</td>
</tr>
<tr>
<td>Cr</td>
<td>10.9</td>
<td>12.91</td>
</tr>
<tr>
<td>Co</td>
<td>9.2</td>
<td>-</td>
</tr>
<tr>
<td>Mo</td>
<td>2.4</td>
<td>-</td>
</tr>
<tr>
<td>W</td>
<td>47.4</td>
<td>49.2</td>
</tr>
<tr>
<td>Re</td>
<td>25.1</td>
<td>1.4</td>
</tr>
<tr>
<td>O</td>
<td>-</td>
<td>29.3</td>
</tr>
<tr>
<td>P</td>
<td>-</td>
<td>4.9</td>
</tr>
<tr>
<td>Ca</td>
<td>-</td>
<td>2.2</td>
</tr>
</tbody>
</table>

Figure 7.66 TEM micrograph of RT22 coated CMSX4 thermally exposed for 2000 hours at 1000°C, showing the W-rich oxide particle within the centre of a TCP precipitate situated within the interdiffusion zone, including the EDX results of the different precipitates obtained within the TEM.

It is evident that the acicular TCP phases observed at the shorter exposure times have significantly increased in size to form elongated, segmented structures. These precipitates are seen to extend up to 60 μm into the substrate alloy, as shown in Figure 7.67. There are several explanations for the segmented morphology of the TCP phases. Initially it was suggested that a basket weave morphology consisting of acicular precipitates overlapping at 90° angles can create this structure\[^{[1]}\]. The existence of a continuous precursor phase which becomes segmented and/or acts as a nucleation site for other precipitates, hence maintaining a common growth plane has also been reported. Another possibility is that the plates are connected in three dimensions, therefore representing the morphology within the habit plane\[^{[14]}\].
Figure 7.67 SEM micrographs of RT22 coated CMSX4 thermally exposed for 2000 hours at 1000°C, showing a) the extension of acicular precipitates from the γ' layer in the IDZ into the substrate alloy and b) higher magnification showing the segmented morphology of the TCP phases
7.6.3 Thermal Exposure at 1000°C for 4000 hours

The microstructure of the RT22 coated CMSX4 system after thermal aging at 1000°C for 4000 hours is illustrated in Figure 7.68.

Figure 7.68 SEM micrograph illustrating the overall structure of the substrate and coating of sample aged for 4000 hours at 1000°C, including the coating, the interdiffusion zone and the substrate

The general structure of the surface and bulk of the coating demonstrate similar characteristics to the samples aged both for 1000 and 2000 hours at 1000°C. An increase in size of the γ' precipitates has occurred with exposure time as a result of Al diffusion, as shown in Figure 7.69. The W/Re rich precipitates within the bulk of the coating have also coarsened with exposure time, with a small fraction being significantly larger than others. It is possible this is a result of an Ostwald ripening process, in which large precipitates grow at the expense of smaller ones. The continued dissolution of the W/Re rich precipitates again is linked with the increase in γ' within the coating. This is supported by the fact that the precipitates are mainly located in areas in low fractions of γ'. In contrast to the samples aged at shorter exposure lengths, light grey particles are seen to precipitate on the β/γ' grain boundaries, chemical analysis of which showed them to be rich in Cr and Re ~ 52 and 18 wt.%, similar to particles observed in the sample aged at 950°C for 2000 and 4000 hours. Once again these are suggested to form as a result of both the increased diffusion of Cr and Re across the coating/substrate interface and their low solubility within γ' and β. Due to the presence of
carbon within these particles, they were initially identified as $\text{M}_{23}\text{C}_6$ carbides. Conclusive identification, however, will require the examination of SAED patterns.

![Figure 7.69 SEM micrographs of RT22 coated CMSX4 thermally exposed for 4000 hours at 1000°C, showing the varying sizes and morphologies of the $\gamma'$, W/Re rich and Cr-rich precipitates a) at the coating surface and b) in the bulk of the coating](image)

The continuous $\gamma'$ layer observed within the interdiffusion zone has increased in thickness, which is consistent with increased thermal exposure. In contrast to the sample aged for 2000 hours, the $\gamma'$ layer is seen to fully contain the large W/Re rich precipitates, as illustrated in Figure 7.70. In samples aged at lower temperatures, these precipitates had formed a distinct band within the coating adjacent to the $\gamma'$ layer. The enclosed precipitates confirm that the $\gamma'$ enriched layer progresses both towards the substrate and in towards the coating. As discussed for the sample aged for 1000 hours at 850°C, there are differences in the way the $\gamma'$ layer grows into the coating. Light grey phases similar to those observed at 1000 and 2000 hours are present throughout the $\gamma'$ layer. However, these precipitates are not located within cavities, as observed at 2000 hours. This indicates that the holes were a result of preferential etching, most likely caused by slight changes in the etching voltage and/or the solution composition. EDX analysis of the precipitates performed in the SEM indicated that they had similar compositions to that of the $\text{M}_{23}\text{C}_6$ carbides identified within the interdiffusion zone at 2000 hours. However, it should be noted that the compositional analysis will vary between the SEM and TEM samples due to differing activation volumes. Therefore, conclusive identification of the phase could not be carried out. The occurrence of both MC and $\text{M}_{23}\text{C}_6$ carbides within the area of the interdiffusion zone suggests the temperatures range in which the two carbides are...
thermodynamically stable overlap. The morphology of the TCP phases and carbides are seen to change over the thickness of the γ' layer, being more rounded towards the coating and more geometric towards the substrate, as observed at shorter exposure times.

Figure 7.70 SEM micrographs of RT22 coated CMSX4 thermally exposed for 4000 hours at 1000°C, showing a) the interdiffusion layer structure, b) TCP phases and carbides of geometric morphology within the section of the γ' layer adjacent to the substrate and c) rounded morphology of phases within the section of the γ' layer adjacent to the coating.

Within the interdiffusion zone, segmented needle-like phases extending into the substrate are once again observed. Within Figure 7.71 it was apparent that that precipitates are longer and thicker than that of the samples aged at 2000 hours. The precipitates have also become more segmented with exposure length. The γ/γ' rafting behaviour is still clearly observable beneath the coating/substrate interface.
Figure 7.71 SEM micrographs of RT22 coated CMSX4 thermally exposed for 4000 hours at 1000°C, showing the extension of the segmented needle-like precipitates from the γ' layer in the IDZ into the substrate alloy.
7.7 Microstructure of RT22 Coated CMSX4 Thermally Exposed at 1050°C

7.7.1 Thermal Exposure at 1050°C for 1000 hours

The microstructure of the RT22 coated CMSX4 system after thermal aging at 1050°C for 1000 hours is illustrated in Figure 7.72.

![SEM micrograph illustrating the overall structure of the substrate and coating of sample aged for 1000 hours at 1050°C, including the coating, the interdiffusion zone and the substrate](image)

Figure 7.72  SEM micrograph illustrating the overall structure of the substrate and coating of sample aged for 1000 hours at 1050°C, including the coating, the interdiffusion zone and the substrate

The oxide scale of the coating surface has increased in thickness to ~ 7.4 μm and consists of two distinct layers. Once more the outer layer contains precipitates that are rich in Ta, Al, Hf and O ~ 46, 25, 8 and 12 wt.% respectively. This is confirmed by the EDX elemental maps shown in Figure 7.73. The overall coating structure shows a substantial reduction in second phases, compared to samples aged at lower temperatures, as shown in Figure 7.74. Chemical analysis of the β and γ' phase across the coating and their comparison with the sample aged at 1000°C are reported in Table 7.12. The slight decrease in Al content of the β and γ' phase indicates an increase in Al diffusion from the coating out towards the surface and in towards the substrate. This is supported by the increase in the β → γ' phase transformation together with the increase in thickness of the Al rich oxide scale. The increase in W content of the γ' within the coating corresponds to the dissolution of the W/Re-rich precipitates. As the diffusion of the W from the substrate into the coating increases with temperature, it results in the W preferentially partitioning to the γ' phase rather than the TCP precipitates. Small
amounts of Cr-rich particles were observed randomly on a few of the $\beta/\gamma'$ grain boundaries, similar to those observed at $1000^\circ C$ for 4000 hours. Due to the similarities in composition and the detection of carbon, these particles were once more assumed to be $\text{M}_2\text{C}_6$ carbides. The presence of these phases within the coating after aging for 1000 hours illustrates an increase in Cr diffusion from the substrate into the coating with increase in temperature.

Figure 7.73 SEM micrographs of RT22 coated CMSX4 thermally exposed for 1000 hours at $1050^\circ C$, showing a) the two layers of the oxide scale on the coating surface and the precipitates it contains; EDX elemental maps of the area illustrating the concentration of b) Al, c) O and d) Ta.
Figure 7.74 SEM micrographs of RT22 coated CMSX4 thermally exposed for 1000 hours at 1050°C, showing the γ', W/Re rich and Cr-rich precipitates in a) and b) throughout the coating structure.

<table>
<thead>
<tr>
<th>Element</th>
<th>Temperature (°C)</th>
<th>1000°C</th>
<th>1050°C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>β (wt.%)</td>
<td>γ' (wt.%)</td>
<td>β (wt.%)</td>
</tr>
<tr>
<td>Ni</td>
<td>47.9 - 49.5</td>
<td>54.4 - 55.6</td>
<td>48.8 - 50.9</td>
</tr>
<tr>
<td>Al</td>
<td>13.7 - 14.7</td>
<td>6.8 - 7.3</td>
<td>11.8 - 12.1</td>
</tr>
<tr>
<td>Cr</td>
<td>3.9 - 4.2</td>
<td>2.0 - 2.4</td>
<td>3.9 - 4.0</td>
</tr>
<tr>
<td>Co</td>
<td>6.5 - 6.7</td>
<td>6.9 - 7.5</td>
<td>6.3 - 6.9</td>
</tr>
<tr>
<td>Ta</td>
<td>2.3 - 3.8</td>
<td>11.1 - 13.9</td>
<td>1.7 - 2.9</td>
</tr>
<tr>
<td>W</td>
<td>0.1 - 0.5</td>
<td>1.1 - 2.6</td>
<td>1.2 - 2.4</td>
</tr>
<tr>
<td>Re</td>
<td>0.0 - 0.6</td>
<td>0.0 - 0.9</td>
<td>0.4 - 1.9</td>
</tr>
<tr>
<td>Pt</td>
<td>19.7 - 21.0</td>
<td>9.8 - 12.2</td>
<td>17.9 - 20.11</td>
</tr>
</tbody>
</table>

Table 7.12 EDX analysis results showing the compositions of β and γ' phases (wt.%) in the samples aged for 1000 hours at 1000°C and 1050°C (obtained using SEM).

Figure 7.75 is representative of the interdiffusion zone observed at 1050°C for 1000 hours. The large W/Re precipitates have increased in size but have reduced in area fraction in comparison to those observed at 1000°C. At lower temperatures the particles were seen to form a band within the coating adjacent to the γ' layer, therefore indicating the growth of this layer in towards the coating with the increased diffusion of elements across the interface. Once again MC carbides are found intermingled with the TCP precipitates within this area of the interdiffusion zone. Within this sample it proved possible to distinguish the MC carbides from
the surrounding phases in secondary electron mode. Figure 7.76 indicates that after etching of the sample, the MC carbides are slightly raised from the sample surface, whereas the TCP phases are slightly recessed.

![Figure 7.75 SEM micrographs of RT22 coated CMSX4 thermally exposed for 1000 hours at 1050°C, showing the interdiffusion layer structure](image)

![Figure 7.76 SEM micrographs of RT22 coated CMSX4 thermally exposed for 1000 hours at 1050°C, showing a) backscattered image of the TCP phases and carbides within the section of the γ' layer adjacent to the coating and b) secondary electron image of the same area](image)

High resolution analysis across the γ' layer within the interdiffusion zone confirmed the presence of σ, μ and P phase as illustrated in Figure 7.77. The μ and P phase remain similar in
composition to those observed in samples aged at lower temperature, with high amounts of W and Re with W being the principal element. However, the σ phases identified have become increasingly more Re based with temperature, which proves consistent across the interdiffusion zone. This increase in Re content could suggest an increase in diffusion of the element from the substrate across the interface, with it preferentially partitioning to the σ phase. Full compositions of the phases are reported in Table 7.13. M₂₃C₆ carbides observed at 1000°C proved no longer present within the interdiffusion zone. This indicates that the aging temperature of 1050°C lies outside the temperature range in which the M₂₃C₆ carbide is stable.

Figure 7.77 TEM micrographs of RT22 coated CMSX4 thermally exposed for 1000 hours at 1050°C, showing bright field images a) and b) of the precipitation of various TCP phases and carbides present within the interdiffusion zone; SADP of c) μ phase, d) σ phase and f) P phase. Zone axes are labelled
<table>
<thead>
<tr>
<th>Phase</th>
<th>Elements (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ni</td>
</tr>
<tr>
<td>(\sigma)</td>
<td>6.7 - 8.9</td>
</tr>
<tr>
<td>(\mu)</td>
<td>9.3 - 10.2</td>
</tr>
<tr>
<td>(\rho)</td>
<td>7.5 - 8.1</td>
</tr>
</tbody>
</table>

Table 7.13 EDX analysis results of the TCP phases present within the interdiffusion zone of RT22 coated CMSX4 sample aged for 1000 hours at 1050°C (obtained using analysis of thin foil samples within the TEM)
7.7.2 Thermal exposure at 1050°C for 2000 hours

The microstructure of the RT22 coated CMSX4 system after thermal aging at 1050°C for 2000 hours is illustrated in Figure 7.78.

![Figure 7.78: SEM micrograph illustrating the overall structure of the substrate and coating of sample aged for 1000 hours at 1050°C, including the coating, the interdiffusion zone and the substrate.](image)

At low magnification, the coating appears to primarily comprise of a single phase, with a few small, lighter grey secondary phases present at the coating surface. On closer inspection, it was observed that both β and γ' remained present in the coating as seen at lower temperatures and shorter exposure lengths. A significant increase in the phase transformation from $\beta \rightarrow \gamma'$ had occurred at the coating surface and towards the interdiffusion zone. This resulted in a layer of the β phase found only within the central section of the coating. The slight contrast variation of the β and γ' phase made them difficult to identify, as illustrated in Figure 7.79.

Complete dissolution of the W/Re-rich precipitates within the bulk of the coating has occurred. This is consistent with the increase in the amount of the γ', and is associated with the phase’s higher solubility for W compared to the β phase. In contrast, γ' phase has a lower solubility for Cr. This explains the precipitation of Cr-rich phases on the β/γ' grain boundaries with sizes ranging from 1.3 to 14.2 μm as observed at 1000 hours. Chemical analysis once again showed these particles to be rich in Cr and Re, together with the presence of carbon,
suggesting that these are M$_{23}$C$_6$ carbides. The measured compositions of these phases between 1000 and 2000 hours are compared in Table 7.14.

![Figure 7.79 SEM micrographs of RT22 coated CMSX4 thermally exposed for 2000 hours at 1050°C, showing a) the γ', β and Cr-rich precipitates throughout the coating structure and b) the same image coloured to define the band of β phase through the central section of the coating](image)

<table>
<thead>
<tr>
<th>Time</th>
<th>Ni</th>
<th>Cr</th>
<th>Co</th>
<th>Mo</th>
<th>Ta</th>
<th>W</th>
<th>Re</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1000 hrs</td>
<td>4.8 - 8.2</td>
<td>47.4 - 52.2</td>
<td>2.8 - 3.1</td>
<td>1.6 - 1.9</td>
<td>1.6 - 2.0</td>
<td>13.6 - 14.8</td>
<td>17.0 - 18.2</td>
<td>4.7 - 5.3</td>
</tr>
<tr>
<td>2000 hrs</td>
<td>4.5 - 7.9</td>
<td>42.2 - 49.6</td>
<td>2.5 - 2.9</td>
<td>1.6 - 1.8</td>
<td>1.1 - 2.3</td>
<td>10.2 - 15.0</td>
<td>15.8 - 24.9</td>
<td>6.4 - 8.1</td>
</tr>
</tbody>
</table>

Table 7.14 EDX analysis results showing the compositions of M$_{23}$C$_6$ carbides in the coating of the samples aged at 1050°C for 1000 and 2000 hours (obtained from the SEM)

The γ' layer has increased from an average thickness of 48.3 μm at 1000°C for 2000 hours to 73.0 μm at 1050°C, illustrating a continued increase in diffusion activity across the coating/substrate interface. As observed at 1000 hours, the continuous γ' layer contains the majority of the carbide and intermetallic phases within the interdiffusion zone, as shown in Figure 7.80. The γ' layer appears to be divided into three layers. The layer closest to the coating contains the larger rounded particles with sizes ranging from 1.7 - 4.1 μm. The central section is made up of smaller spherical precipitates with sizes ranging from 0.4 - 1.2 μm. Finally, the layer adjacent to the substrate contains precipitates of both geometric and acicular morphologies. This change in precipitate morphology across the γ' layer has been observed within samples aged at lower temperatures, however, it has become more defined with the
increase in temperature. A large proportion of the TCP phases across the interdiffusion zone are seen to contain darker centres, similar to those observed at 1000°C. Chemical analysis of the separate areas within the particles showed the outer brighter layer to be rich in W/Re, similar in composition to the TCP phases observed at lower temperatures. The darker core of the particle once more was found to be to be richer in W, with lower amounts of Re than that of the outer layer. In addition oxygen was also detected within the particle cores again similar to the sample aged at 1000°C. Full compositions of the particles are reported in Table 7.15.

Cr-rich phases are present within the γ' layer, similar in composition (SEM analysis) to those observed in the samples for 1000°C for 2000 and 4000 hours, which can be assumed to be M₂₃C₆ carbides. The existence of these carbides after ageing at 1050°C indicates that they can still be thermodynamically stable at this temperature after 2000 hours of ageing.

<table>
<thead>
<tr>
<th>Elements (wt.%)</th>
<th>Ni</th>
<th>Cr</th>
<th>Co</th>
<th>Mo</th>
<th>Ta</th>
<th>W</th>
<th>Re</th>
<th>O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Outer</td>
<td>11.7 - 18.9</td>
<td>8.6 - 9.5</td>
<td>8.7 - 9.5</td>
<td>0.0 - 1.5</td>
<td>2.5 - 4.4</td>
<td>31.1 - 35.7</td>
<td>20.6 - 26.4</td>
<td>-</td>
</tr>
<tr>
<td>Core</td>
<td>8.6 - 15.9</td>
<td>7.9 - 8.8</td>
<td>3.1 - 3.8</td>
<td>0.0 - 1.1</td>
<td>5.6 - 6.8</td>
<td>43.6 - 46.2</td>
<td>1.3 - 7.9</td>
<td>9.6 - 13.4</td>
</tr>
</tbody>
</table>

Table 7.15 EDX analysis results showing the compositions of the different areas of the TCP phases in the interdiffusion zone of the RT22 coated CMSX4 sample aged at 1050°C for 2000 hours (obtained from the SEM)
Figure 7.80 SEM micrographs of RT22 coated CMSX4 thermally exposed for 2000 hours at 1050°C, showing a) the interdiffusion layer structure, b) TCP phases and carbides of geometric morphology within the section of the γ' layer adjacent to the substrate and c) TCP phases containing W-rich oxide cores within the section of the γ' layer adjacent to the coating.
7.7.3 Thermal Exposure at 1050°C for 4000 hours

The microstructure of the RT22 coated CMSX4 system after thermal aging at 1050°C for 4000 hours is illustrated in Figure 7.81.

![SEM micrograph illustrating the overall structure of the RT22 coated CMSX4 sample aged for 1000 hours at 1050°C, including the coating, interdiffusion zone and the substrate](image)

Initial observations of the coating structure indicated that considerable oxidation has occurred at the coating surface. In some areas, the oxidation has occurred to such an extent that half of the coating has been removed. Figure 7.82 shows the oxide scale that follows the contours of the coating surface is highly fractured. It is possible that the spallation of the oxide scale could have occurred during aging or on cooling from the ageing temperature; equally metallographic preparation of the sample may have resulted in this structure. It can be assumed that the oxide has grown into the coating. Essentially the elements from the coating have formed an oxide quite quickly at this temperature and therefore the coating is now being visibly consumed. Recessed lines are present throughout the coating and in some instances leading out to the oxide scale. It has been assumed that these lines are representative of grain boundaries within the coating and chemical analysis showed that there were slight decreases in Al from ~5.5 wt.% detected within the coating, to ~4.0 wt.% within the recessed grain boundaries. This depletion would be expected as diffusion occurs at a faster rate on grain boundaries. Cracks have also been observed within some of the grain boundaries close to the coating surface, as shown in Figure 7.83. This demonstrates possible short circuit diffusion paths for oxygen into
the coating. The inward growth of the oxide scale has even resulted in the isolation of the coating matrix in areas of the sample, supporting the suggestion that this occurs via the grain boundaries.

Figure 7.82 SEM micrographs of RT22 coated CMSX4 thermally exposed for 4000 hours at 1050°C, showing a) the fractured oxide scale on the coating surface, b) and c) higher magnifications of oxide scale growth into the coating resulting in isolated areas of the coating matrix
The increase in exposure length from 2000 to 4000 hours has resulted in the complete dissolution of $\beta$ phase within the coating. Chemical analysis of the $\gamma'$ throughout the coating gave similar results to those observed at 1000°C, as reported in Table 7.16.

<table>
<thead>
<tr>
<th>Temp (°C)</th>
<th>Ni (wt.%)</th>
<th>Al (wt.%)</th>
<th>Ti (wt.%)</th>
<th>Cr (wt.%)</th>
<th>Co (wt.%)</th>
<th>Ta (wt.%)</th>
<th>W (wt.%)</th>
<th>Pt (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1000</td>
<td>54.1 - 59.2</td>
<td>6.7 - 7.8</td>
<td>0.7 - 1.1</td>
<td>1.8 - 2.3</td>
<td>7.2 - 7.8</td>
<td>5.4 - 8.9</td>
<td>3.2 - 5.1</td>
<td>10.9 - 14.6</td>
</tr>
<tr>
<td>1050</td>
<td>51.7 - 56.4</td>
<td>5.8 - 8.8</td>
<td>0.5 - 0.8</td>
<td>3.2 - 3.7</td>
<td>5.5 - 7.0</td>
<td>4.2 - 6.0</td>
<td>3.5 - 6.1</td>
<td>13.2 - 15.8</td>
</tr>
</tbody>
</table>

Table 7.16 EDX analysis results showing the compositions of the $\gamma'$ phase in the coating of the samples aged for 4000 hours at 1000 and 1050°C (obtained from the SEM)

In comparison to the sample aged at 2000 hours, the relative amount and size of the W/Re rich precipitates within the interdiffusion zone have decreased substantially. The large rounded particles that precipitated in a linear array parallel to the coating substrate interface are no longer present, with the W going back into solution. However, holes of a similar size and shape were observed within the same region in which these phases precipitated at lower temperatures, as shown in Figure 7.84. Chemical analysis taken of the central section of the holes proved similar to that of the surrounding $\gamma'$ matrix phase. The formation of voids within similar coating systems have been observed\cite{87,106,158}. The common explanation for void formation in coatings is by the Kirkendall mechanism. Several theories on how Kirkendall porosity occurs within these systems have been proposed. One suggestion is that incoherent phase boundaries in the matrix create areas of localised stress, increasing the concentration of...
vacancies. These vacancies subsequently lead to the formation of voids. It is unclear if these voids are associated with the preceding W/Re rich precipitates.

![Image of SEM micrographs](image)

**Figure 7.84** SEM micrographs of RT22 coated CMSX4 thermally exposed for 4000 hours at 1050°C, showing the holes within the interdiffusion zone showing similarities to the W/Re rich precipitates observed at lower temperatures.

The bright particles with sizes ranging from 2.2 - 4.0 μm present in the interdiffusion zone are Ta, Ti and Hf rich MC carbides, as observed in all of the samples investigated. It was noted that the Hf content of the MC has increased from an average of 3.8 wt.% at 1000 hours to 11.5 wt.% at 4000 hours. The remaining smaller W/Re rich precipitates present were identified as σ and P phase using the combination of SEAD and EDX analysis, as illustrated in Figure 7.86. No μ phase was identified within the TEM samples, however, due to the small number of precipitates extracted it cannot be concluded that μ phase no longer exists within the interdiffusion zone. Chemical analysis of the identified TCP phases shows an increase in Re content, and indeed it becomes the principal element. Particles surrounded by dark bands similar to those observed in the sample aged at 1000°C for 2000 hours are seen close to, or on, the TCP phases, as shown in Figure 7.85. Once more chemical analysis revealed them to be W-rich oxides with smaller amounts of Ta and Cr, ~ 7 and 9 wt.% respectively. These oxides that form on the TCP phases are consistent throughout the interdiffusion zone, continuing on to the segmented needle-like phases that extend out into the substrate.
Figure 7.85 SEM micrographs of RT22 coated CMSX4 thermally exposed for 4000 hours at 1050°C, showing a) the rounded TCP phases surrounded by W-rich oxides within the interdiffusion zone (IDZ) and b) carbides and TCP phases present within the IDZ adjacent to the substrate.

Figure 7.86 TEM micrographs of RT22 coated CMSX4 thermally exposed for 4000 hours at 1050°C, showing SADP of a) P phase and b) α phase. Zone axes are labelled.

The segmented needle-like phases have increase in thickness and length, extending up to ~180 μm into the substrate alloy, as shown in Figure 7.87. The growth of these TCP phases has increased the actual thickness of the interdiffusion zone from ~16 μm, observed in the as-received condition, to ~240 μm. This illustrates the extent at which the microstructure changes as a result of the interdiffusion of elements across the coating/substrate interface and the implications this has on the mechanical properties of the system. Bright particles of blocky morphology are seen intermingled with the needle-like TCP phase. Chemical analysis showed them to be rich in Ta, Ti and Hf ~ 68, 11 and 4 wt.% respectively. These elements coupled
with the detection of carbon indicated the particles are most likely MC carbides. Although MC carbides have not been observed within the substrate section of the interdiffusion zone, it is not implausible seeing that they occur throughout the substrate alloy as discussed in Chapter 4. In comparison however, slight differences in composition and microstructure were observed and are reported in Table 7.17. Figure 7.88 shows that the MC carbides within the interdiffusion zone are surrounded by a band of $\gamma$ as opposed to $\gamma'$ as seen within the bulk of the alloy. The $\gamma$ band suggests the carbides have grown, and in doing so have depleted the surrounding matrix of Ta and Ti, resulting in the phase transformation from $\gamma' \to \gamma$. Consequently, it is possible the carbides have precipitated within the interdiffusion with the increase in temperature and exposure length, as opposed to being ‘frozen’ within the substrate alloy from the initial high temperature treatments.

Figure 7.87 SEM micrographs of RT22 coated CMSX4 thermally exposed for 4000 hours at 1050°C, showing the extension of the segmented needle-like precipitates from the $\gamma$ layer in the IDZ into the substrate alloy
Figure 7.88 SEM micrographs of RT22 coated CMSX4 thermally exposed for 4000 hours at 1050°C, showing a) the MC carbides within the interdiffusion zone surrounded by bands of γ and b) MC carbides in the substrate alloy surrounded by bands of γ'.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Elements (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ni</td>
</tr>
<tr>
<td>MC_{IDZ}</td>
<td>3.2 - 3.6</td>
</tr>
<tr>
<td>MC_{S}</td>
<td>2.9 - 4.2</td>
</tr>
</tbody>
</table>

MC_{IDZ} - MC carbides within the IDZ
MC_{S} - MC carbides within the substrate

Table 7.17 EDX analysis results of MC carbides present within the oxide interdiffusion zone and the substrate alloy of sample aged for 4000 hours at 1050°C (obtained from the SEM)
7.8 Microstructure of the CN91 Coated CMSX4

The CN91 coated CMSX4 samples were investigated in the as-received condition and following isothermal exposure at 1000ºC for 1000 hours, in order to make a comparison with the RT22 coated CMSX4 thermally exposed under the same conditions. The comparison of these two commercial PtAl coatings demonstrates how the different growth directions (i.e. inward and outward) influence the coating microstructure and its development upon isothermal heat treatment. It should be noted that the platinum aluminide coating CN91 has been applied to the 'standard' CMSX4 with low carbon content. Therefore in comparison, a small number of carbides (or indeed none) should be expected within the coating microstructure.

7.8.1 Microstructure of the CN91 Coated CMSX4 As-Received

The microstructure of the CN91 coated CMSX4 system in its as-received condition is shown in Figure 7.89.

The initial comparison between the two commercial platinum aluminide coatings shows that in the CN91 coating there is a lack of precipitates within the bulk of the coating. This is due to CN91 being an outward grown (low activity) coating, in which the outward diffusion of Ni from the substrate is much greater rate than that of the Al diffusing inwards. Therefore,
smaller concentrations of alloying elements from the substrate move into the coating, resulting in a precipitate free coating. As observed for RT22, the coating structure consisted mainly of a single phase being $\beta$-NiAl, which is enriched in Pt, resulting in the $\beta$ phase being $\beta$-(Ni,Pt)Al. Chemical analysis of the $\beta$ phase throughout the coating shows the Pt content is at its maximum of \(~31\) wt.% at the coating surface. This value decreases slightly with increasing distance from the coating surface to \(~21\) wt.% within the interdiffusion zone, and finally to zero within the substrate. The profile shown in Figure 7.90 shows a more even distribution of Pt throughout the coating, with significantly higher concentrations within the interdiffusion zone compared to those observed in the RT22 coating.

![Figure 7.90 Compositional profile of Pt with increasing distance from the coating surface of RT22 and CN91 as-received samples](image-url)

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Large dark particles rich in Al and O were located on the interface between the coating and the interdiffusion zone. It is most likely that these are alumina particles entrapped from the grit blasting used to prepare the substrate surface prior to coating, as also used in the RT22 coating process. These particles therefore give a good indication of the original surface of the substrate. The differences in location of the alumina grit particle with the two coatings indicate to which direction the majority of the coating has grown and are consistent with RT22 being an inward and CN91 being an outward grown coating respectively.

The interdiffusion of elements across the coating/substrate interface has resulted in an interdiffusion zone with an average thickness of 30 µm. This is a significant increase from that observed on the RT22 sample, as the majority of the refractory elements are concentrated solely within the interdiffusion zone of the CN91 sample. The interdiffusion of elements has encouraged the precipitation of intermetallic phases, the majority of which are observed as a high density band of precipitates with sizes ranging from 0.4 - 2.3 µm within the coating section of the interdiffusion zone, as shown in Figure 7.91. As observed in the RT22 coating, the precipitates appear to show some alignment indicating the initial growth of the particles in line with the direction of diffusion of the elements from the substrate into the coating. Chemical analysis of the precipitates showed them to be rich in W, Re, Cr and Ta, and they were conclusively identified as the η phase with the combined use of SAED and EDX analysis. No o or P phase was identified in CN91, in contrast to the interdiffusion zone of the RT22 sample. However, due to the small scale of the area analysed it is possible that other

<table>
<thead>
<tr>
<th>Phase</th>
<th>Elements (wt.%)</th>
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<tbody>
<tr>
<td></td>
<td>Ni</td>
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<tr>
<td>βcs</td>
<td>39.9 - 40.8</td>
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<tr>
<td>βbc</td>
<td>39.4 - 42.2</td>
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<tr>
<td>βIDZ/C</td>
<td>39.5 - 45.7</td>
</tr>
</tbody>
</table>

βcs - β phase at the coating surface
βbc - β phase within the bulk of the coating
βIDZ/C - β phase adjacent to the IDZ

Table 7.18 EDX analysis results of β phase present with increasing distance from the coating surface in as-received sample (obtained using SEM)
TCP phases may be present within the interdiffusion zone. Typical patterns are shown in Figure 7.92 and compositions given in Table 7.19. Within this band of precipitates, light grey phases with 'vein-like' morphologies were observed, as shown in Figure 7.91 b). Chemical analysis showed these particles contained a lower Al (~8.5 wt.%) and higher Ta (~12.4 wt.%) concentration than that of the β matrix, therefore thought to be γ'-Ni₃Al. This was confirmed by the use of selected area diffraction of the particles, as shown in Figure 7.92. The phase transformation from β → γ' indicates increased diffusion of the Al from the coating in towards the substrate alloy. It is possible the vein-like morphology of the phases follow the β grain boundaries.

![Figure 7.91 SEM micrographs of CN91 coated CMSX4 in as-received condition, showing a) the interdiffusion layer structure containing a high density band of precipitates and the γ' layer and b) small light grey γ' precipitates forming on the β grain boundaries within the coating section of the interdiffusion zone](image)

<table>
<thead>
<tr>
<th>Phase</th>
<th>Ni (wt.%)</th>
<th>Cr (wt.%)</th>
<th>Co (wt.%)</th>
<th>Mo (wt.%)</th>
<th>Ta (wt.%)</th>
<th>W (wt.%)</th>
<th>Re (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>μ</td>
<td>6.6 - 11.2</td>
<td>13.7 - 16.8</td>
<td>9.1 - 15.2</td>
<td>2.3 - 5.2</td>
<td>0.0 - 13.8</td>
<td>29.7 - 45.1</td>
<td>7.9 - 19.4</td>
</tr>
<tr>
<td>SRZ</td>
<td>6.6 - 9.7</td>
<td>13.9 - 18.5</td>
<td>8.5 - 11.7</td>
<td>0.2 - 6.5</td>
<td>0.0 - 4.2</td>
<td>23.8 - 40.9</td>
<td>20.0 - 32.4</td>
</tr>
</tbody>
</table>

Table 7.19 EDX analysis results of the intermetallic and TCP phases present within the interdiffusion zone and secondary reaction zone of sample in as-received condition (obtained using SEM)
Figure 7.92 TEM micrographs of CN91 coated CMSX4 in as-received condition, showing bright field image a) of the precipitation of various phases present within the interdiffusion zone; SADP of b) µ phase and c) γ’; zone axes are labelled.

A continuous γ’ layer with a thickness of 7 µm was observed within the interdiffusion zone. It has been reported that this layer forms due to a net increase of Al in the substrate and nickel into the coating. This results in the transformation of the γ phase adjacent to the interdiffusion zone into γ’. Islands of β are observed within the γ’ layer, therefore suggesting this layer extends/grows onto the coating, or that the increase in Al within the interdiffusion zone has resulted in the phase transformation from γ’ → β, indicating a very complex microstructure. Small needle like phases rich in Cr, W and Re are present within the γ’ layer, as shown in Figure 7.93. These phases form to accommodate the excess Cr and Re produced as a result of the phase transformation from γ to γ’, as γ’ has a reduced solubility for these elements compared to γ. Due to the small size of these particles, a viable SAED pattern proved difficult to obtain.
The random occurrence of isolated ‘cells’ of $\gamma'$ containing bright needle phases were observed within the interdiffusion zone, as shown in Figure 7.94. These have been previously reported to be secondary reaction zones (SRZ) that grow from independently nucleated discontinuous phase precipitation\cite{31, 89, 159}. The constituent $\gamma'$ and TCP phases of the SRZ are separated from the substrate $\gamma'/\gamma'$ by a high angle grain boundary. This is in contrast to the generation of $\gamma'$ layer within the interdiffusion zone as this forms continuously with the substrate. It is also possible these isolated cells are areas of recrystallisation of the substrate which has occurred during the coating process\cite{160}. Grit blasting and possible machining processes can deform the alloy surface, and in doing so, induce stresses into the system. Consequently these areas of induced stress at the alloy surface, once coated become contained within the interdiffusion zone. CN91 aluminisation is carried out at 1080°C as opposed to 875°C for the RT22 coatings. This increase in temperature is close to, if not above, the substrate’s recrystallisation temperature. During heat treatment the stressed regions relax and result in multi-grained areas of $\gamma'$ containing randomly orientated TCP phases. The EBSD technique was used to examine the microstructure of the cells to identify whether these areas precipitated with the substrate $\gamma'$ structure or were separated by high angle grain boundaries. The image quality map of the area containing the cell is illustrated in Figure 7.95 a). This is a fairly light image indicating that the diffraction patterns produced are of a good quality. The darker areas within the image are produced by overlapping effects at grain boundaries where the software finds it harder to index the diffraction patterns, which would account for the darker areas towards the higher
density of TCP phases. The second map shown in Figure 7.95 b) has the rotation angle of the grain boundaries superimposed onto the image quality map. The blue lines indicate the presence of high angle grain boundaries with angles ranging from 15 - 180°, whereas the red lines indicate low angle grain boundaries with angles ranging from 2 - 15°. The map shows a distinct blue line surrounding the cell which confirms both suggestions of a SRZ and of recrystallisation as high angle grain boundaries are characteristic in both new grains formed from recrystallisation and the formation of the SRZ's. Figure 7.95 c) shows an inverse pole figure map of the same area, which illustrates the crystal alignment of the grains and how this relates to the phases present within the structure. This map shows a single alignment within the substrate alloy, which is to be expected, as this is a single crystal superalloy grown in one direction. However, the cell is seen to comprise of 3 main grains that all show different orientations to that of the substrate, which supports the theory that these are areas that have recrystallised during the high temperatures used in the coating process.
Figure 7.94 SEM micrographs of CN91 coated CMSX4 in the as-received condition, showing a) the interdiffusion zone containing randomly dispersed isolated γ', and TCP cells, b) and c) higher magnification of these cells showing the isolated TCP phases within a γ' matrix.

Figure 7.95 Electron backscatter diffraction (EBSD) taken over an area containing a SRZ, showing a) image quality (IQ) map, b) Grain boundary rotation angle superimposed on a IQ map and c) inverse pole figure (IPF) map.
7.8.2 Thermally Exposed at 1000°C for 1000 hours

The microstructure of the CN91 coated CMSX4 system after thermal aging at 1000°C for 1000 hours is shown in Figure 7.96.

![Microstructure of CN91 coated CMSX4 system after thermal aging](image)

**Figure 7.96** SEM micrograph illustrating the overall structure of the substrate and coating of the CN91 sample aged for 1000 hours at 1000°C, including the coating, the interdiffusion zone and the substrate

The bulk of the coating has remained a single phase, unlike that of the RT22 which contained large γ' particles within the central section of the coating and towards the coating surface, as shown in Figure 7.97. Chemical analysis of the β matrix within the bulk of the coating showed a decrease in Al, therefore indicating that there had been diffusion of Al from the coating out towards the coating surface and in towards the substrate. This decrease in Al content, however, is not sufficient enough to initiate a phase transformation from β to γ'. An increase in substrate elements such as Ni, Cr, Co and Ta were also present in the β phase, indicating an increase in diffusion across the coating/substrate interface with thermal aging. Particles of γ' with sizes ranging from ~1.0 - 2.6 μm were present within the band of precipitates observed in the coating section of the interdiffusion zone, suggesting that the Al is primarily diffusing from the coating into the substrate.
<table>
<thead>
<tr>
<th>Elements (wt.%)</th>
<th>As-received</th>
<th>1000</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>39.4 - 42.2</td>
<td>40.8 - 49.4</td>
</tr>
<tr>
<td>Al</td>
<td>15.0 - 17.6</td>
<td>10.9 - 13.1</td>
</tr>
<tr>
<td>Cr</td>
<td>0.8 - 2.4</td>
<td>3.2 - 3.9</td>
</tr>
<tr>
<td>Co</td>
<td>3.0 - 5.4</td>
<td>5.3 - 6.4</td>
</tr>
<tr>
<td>Ta</td>
<td>0.0 - 0.9</td>
<td>2.4 - 4.2</td>
</tr>
<tr>
<td>W</td>
<td>2.9 - 4.8</td>
<td>0.4 - 0.7</td>
</tr>
<tr>
<td>Re</td>
<td>0.5 - 1.5</td>
<td>-</td>
</tr>
<tr>
<td>Pt</td>
<td>23.8 - 31.1</td>
<td>15.5 - 19.1</td>
</tr>
</tbody>
</table>

Table 7.20 EDX analysis results showing the compositions of β phase (wt.%) in the CN91 coated CMSX4 in the as-received condition and the sample aged for 1000 hours at 1000°C (obtained using SEM).

Figure 7.97 SEM micrographs of CN91 coated CMSX4 thermally exposed for 1000 hours at 1000°C, showing a) the overall coatings structure with the absence of second phase particles and b) the blocky γ' particles present within the precipitate band on the interdiffusion zone.

Figure 7.98 shows the microstructure of the interdiffusion zone within the sample. In comparison to the same aging conditions, the RT22 and CN91 coatings have interdiffusion zones with similar thicknesses of ~ 44 μm. Significant coarsening of the precipitates within the band adjacent to the coating/substrate interface was observed, indicating an increase in diffusion of the refractory elements from the substrate into the coating. Chemical analysis of these precipitates once more proved them to be enriched in W, Re, Cr and Mo, with compositions similar to the μ phase identified within the as-received sample. Ta-rich MC
carbides with a globular morphology are present within the precipitate band, this proved similar to the RT22 sample thermally aged for the same time/temperature conditions, even though the substrate contains significantly less carbon. This indicates that even small amounts of carbon present within the substrate or the coating will form carbides within the interdiffusion zone.

The interdiffusion of elements between the coating and substrate has resulted in the formation of a $\gamma'$ layer, as observed in the as-received condition, which has increased in thickness to $\sim 25 \mu$m. In comparison to the as-received sample the $\gamma'$ layer was continuous throughout the thickness with no entrapment of $\beta$ particles. The isolated 'cells' of $\gamma'$ containing TCP phases observed in the as-received sample were no longer present within the interdiffusion zone following isothermal ageing. This suggests that the $\gamma'$ layer has grown out into the substrate encompassing the $\gamma'$ cells, and therefore supports the theory that these areas were areas of residual stress which had recrystallised upon heat treatment. Previous work has found that SRZ's increase in size with aging, which is not the case in this research$^{[31,159]}$. Throughout the interdiffusion zone the W/Re rich precipitates are seen to contain an outer layer and an inner core defined by a slight difference in contrast. This was more clearly identified with the use of secondary electron (SE) imaging as shown in Figures 7.98 b) and c). Chemical analysis of the separate layers proved difficult due to overlapping activation volumes, however oxygen was detected within the central section of the precipitates up to values of 7.3 wt.%. It is interesting to note that W-rich oxides have now been observed in both types of PtAl coated samples, which have different process parameters.
Figure 7.98 SEM micrographs of CN91 coated CMSX4 thermally exposed for 1000 hours at 1000°C, showing a) the interdiffusion zone structure containing band of precipitates and $\gamma'$ layer, b) backscattered image of the TCP phases and carbides within the interdiffusion zone and c) secondary electron image of the same area.
7.9 Discussion

This section discusses the main microstructural changes that occur within the coating and interdiffusion layer with increasing temperature and exposure time. The main sections included are:

- Oxide growth
- Coating microstructure
- Interdiffusion zone

7.9.1 Oxide Growth

This research was mainly focussed on the microstructural changes that occur within the bulk of the coating and the interdiffusion zone. However, in order to validate the diffusion based modelling approaches, oxide thickness measurements were made. This section presents a brief overview of the oxide growth, although the exact nature of the oxide scale has not been determined during this work.

It is known that coatings attain their protective action from the interaction/reaction with oxygen present in the working environment. This interaction with oxygen results in the formation of a dense, adherent oxide scale on the surface of the coating which is seen to increase in thickness with time and temperature. Figure 7.99 shows the growth of the oxide layer as a function of exposure time, for each of the ageing temperatures investigated.

Figure 7.99 Plot showing the thickness of the oxide scale on the coating surface of RT22 coated CMSX4 samples as a function of exposure time for different temperatures
Following the solution heat treatment and ageing processes during coating, a thin oxide scale of ~0.4 μm had formed on the coating surface. The scale growth is determined by the diffusion of Al from the coating to the oxide/coating interface together with an influx of oxygen from the working environment. This oxide scale consisted mainly of an Al and O rich layer, thought to be Al₂O₃, containing small amounts of solid solution elements Cr and Ni. After ageing at 850°C for 1000 hours, the oxide scale had an average thickness of ~0.9 μm. This indicated a very small increase in thickness from that of the as-received sample and suggested that the Al diffusion from the coating was not large enough to significantly affect the growth of the oxide scale under these conditions.

After ageing at 900°C for 1000 hours, a light grey band was observed throughout the central section of the oxide scale, as shown in Figure 7.100 b). Chemical analysis of the band showed it to be rich in Al, Ta and O (approximately 39.3, 35.4 and 19.8 wt.% respectively), confirming the tendency of Ta to diffuse from the substrate towards the outer surface of the coating. This band increased in definition with increased ageing, with the 4000 hour at 900°C sample displaying an oxide scale with a well-defined two layer structure, as shown in Figure 7.100 c). The thin darker inner layer consisted mainly of Al and O, with smaller amounts of Ta, Hf, Ni and W ~ 12.7, 5.4, 5.2 and 3.8 wt.% respectively, whereas the light grey outer layer had a similar composition to that observed at 1000 hours. It has been suggested that this outer layer contains several transient oxides that initially develop due to the influx of oxygen at the coating surface. The oxygen pressure at the oxide/coating interface subsequently decreases, allowing the stable Al₂O₃ to form. The result is a continuous Al₂O₃ scale on which remnants of the transient oxide phases remain[105].

The oxide scale following ageing for 2000 hours at 950°C showed a significant increase in growth, with double the thickness compared to that observed at 900°C for 2000 hours. The oxide scale again comprised of two layers, as observed in the samples aged at 900°C with the inner and outer layers having similar thicknesses. Therefore this suggested that the majority of the thickness was a direct result of the growth of the inner Al₂O₃ layer. After 4000 hours ageing at 950°C, cracks which appeared to break up the two distinct layers of the oxide scale were observed, as shown in Figure 7.100 e). Cracking/spalling of the oxide scale may have occurred on aging, or during cooling from temperature. It is also possible that these cracks
were formed during metallographic preparation of the sample, indicating a possible weakness between the transient oxides and the alumina layer.

The oxide scale following ageing at 1000°C for 1000 hours, appeared to have a similar thickness to that observed at 950°C, indicating no significant growth of the oxide between these temperatures. After 2000 hours, the oxide scale thickness had increased with no apparent spallation, however its size was considerably smaller comparison to the sample aged at 950°C for 2000 hours. It would appear from both the microstructural observations and the graph shown in Figure 7.99, that there may be a change in mechanism associated with the oxide formation at 950°C. This requires further investigation.

At 1050°C the growth of the oxide scale shows similar trends to those observed at the lower temperatures. However, after 4000 hours considerable oxidation had occurred at the coating surface, with the loss of large sections of the coating in some areas. Figure 7.100 f) shows that the oxide scale which followed the contours of the coating surface was highly fractured. The inward growth of the oxide scale has even resulted in the isolation of the coating matrix in areas of the sample, suggesting that there is enhanced oxidative attack along the grain boundaries.
Figure 7.100 SEM micrographs showing the size and morphology of the oxide scale present on the coating surface of RT22 coated CMSX4 samples isothermally aged for a) 1000 hours at 850°C, b) 1000 hours at 900°C, c) 4000 hours at 900°C, d) 2000 hours at 950°C, e) 4000 hours at 950°C and f) 4000 hours at 1050°C showing significant spallation.
7.9.2 Coating Microstructure

Platinum Concentration

Both the RT22 and the CN91 coatings in the as-received condition were found to consist of a single phase $\beta$ matrix, indicating that the Pt has enriched the $\beta$ phase, such that it becomes the $\beta$-(Ni,Pt)Al phase. However, a variation in contrast was observed within the RT22 coating that was not present in the CN91, as shown in Figure 7.101. The brighter outer layer of the RT22 coating is associated with higher Pt concentrations within this area. Chemical analysis of the $\beta$ phase throughout both coatings showed that the maximum Pt concentration was at the coating surface, however this decreased rapidly over a distance of $\sim 30$ $\mu$m in the RT22 coating, finally decreasing to zero within the interdiffusion zone. However, in the CN91 coating, the Pt concentration decreased slightly with increasing distance from the coating surface to approximately half of the maximum value within the interdiffusion zone, and finally to zero in the substrate. The profile shown in Figure 7.102 indicates that there is a more even distribution of Pt throughout the CN91 coating, with significantly higher concentrations within the interdiffusion zone compared to those observed in the RT22 coating.

Figure 7.101 SEM micrographs illustrating the overall structure of the substrate and coating of samples in the as-received condition of coating a) RT22 and b) CN91
After ageing the RT22 coated samples for 1000 hours at 850°C, the two contrasting layers of the coating observed in the as-received sample had become less distinct, as shown in Figure 7.103. This indicated that diffusion of the Pt from the higher concentration at the coating surface towards the substrate had occurred, as shown in Figure 7.104. Chemical analysis of the β matrix in which the Pt partitions, confirmed the increase in diffusion of the Pt, with an initial decrease in Pt content at the coating surface from the as-received sample of ~ 44 to 33 wt.% observed, which again decreases with increasing distance from the coating surface. This proved consistent with increasing exposure time, as after 2000 hours ageing the variation in contrast was no longer present. It should, however, be noted that the area underneath the graphs shown in Figure 7.104 should be representative of the total amount of Pt in the coating. The two areas are similar for both of the samples heat treated at 850°C, however, there is apparently much less Pt in the as-received sample. It is possible that there is an extremely high surface concentration which is not being measured accurately using EDX in the SEM, however, it is also possible that the samples do contain different Pt levels despite being initially manufactured at the same time.
Figure 7.103 SEM micrographs showing the variation in contrast throughout the coating in RT22 coated CMSX4 samples aged at 850°C for, a) 1000 and b) 2000 hours

Figure 7.104 Profile of Pt concentration with increasing distance from the coating surface in the RT22 coated samples in the as-received condition and after aging at 850°C for 1000 and 2000 hours

Formation of $\gamma'$

After ageing at 850°C for 2000 hours, light grey phases of blocky morphology with sizes ranging from ~0.6 - 1.2 μm were observed within the coating adjacent to the coating/substrate interface. Chemical analysis showed that these particles contained a lower Al and higher Ta concentration that that of the surrounding $\beta$ matrix and were therefore thought to be $\gamma'$-Ni$_3$Al. The phase transformation from $\beta \rightarrow \gamma'$ indicated an increased diffusion of Al from the coating
in towards the substrate alloy. The presence of $\gamma'$ would also have been expected at the coating surface due to the Al diffusion out towards the oxide scale, however, no particles were observed. It has been suggested that the transformation from $\beta \rightarrow \gamma'$ is not solely due to the diffusion of Al out of the coating into the substrate but also the diffusion of Ni from the substrate into the coating, which could explain why $\gamma'$ was only present close to the coating/substrate interface. On the other hand, the $\beta$ stability at the coating surface can possibly be attributed to the high concentration of Pt, as Pt is reported to lower the rate by which $\beta$ transforms to $\gamma'$.[55] The number and size of the $\gamma'$ particles within the coating were seen to increase with temperature and exposure time, with the majority of the particles located in the central regions of the coating and towards the coating/substrate interface, as shown in Figure 7.105.

A significant increase in the size of the $\gamma'$ particles within the coating was observed after ageing at 950°C for 1000 hours, as shown in Figure 7.105 d). The composition profiles taken across the coating indicate that the main concentration changes between the temperatures 900 and 950°C are for the elements Pt, Cr, Co and Ta, as illustrated in Figure 7.106. It is possible that these elemental changes have affected the stability of the $\beta$ and $\gamma'$ phases, however, there are relatively small differences in the composition of each element. The largest differences appear to be related to the Ta concentration, which will affect the $\gamma'$ stability. It is also possible that the precipitation kinetics are generally more rapid at 950°C.
Figure 7.105 SEM micrographs showing the size and morphology of the \( \gamma' \) particles observed in the coating of RT22 coated CMSX4 samples isothermally aged for, a) 2000 hours at 850°C, b) 4000 hours at 850°C, c) 4000 hours at 900°C, d) 1000 hours at 950°C, e) 2000 hours at 950°C and f) 4000 hours at 1050°C showing the parallel bands representative of martensitic phase transformation in the \( \beta \) phase significant.
The morphology of the $\gamma'$ particles varied after 2000 and 4000 hours ageing at 950°C, ranging from rounded to blocky, and they were even observed in platelet form, as shown in Figure 7.105 e). Narrow, straight parallel bands were also observed within several areas of the $\beta$ phase in the bulk of the coating after 4000 hours ageing, as shown in Figure 105 f). These bands have previously been reported to be a result of a martensitic transformation of $\beta$ from
the B\textsubscript{2} crystal structure to the martensitic L\textsubscript{10} structure upon cooling, which can occur when a certain chemical composition is reached\cite{147,154-156}. It is likely that the diffusion conditions at this particular time/temperature condition are such that this transformation becomes favourable, which may explain why this phenomena was only observed in a limited number of samples.

After ageing at 1000\textdegree C for 1000 hours the RT22 coating was found to contain large $\gamma'$ particles at the coating/oxide interface and throughout the bulk of the coating. However, in the CN91 coating under the same aging conditions, $\gamma'$ particles were only observed within the coating adjacent to the interdiffusion zone, even though the Al content is lower than that of the RT22 coating, as shown in Figure 7.107. It was therefore possible that the RT22 coating had a higher oxidation rate than the CN91 coating, allowing more Al to diffuse out of the coating, and initiating the phase transformations. However, the $\gamma'$ particles were present throughout the coating not only at the coating/oxide interface. Another possibility was that the concentration of elements within the coating affected the stability of the $\beta$-NiAl phase. Investigations have been carried out in order to indicate the effect of alloying elements on the stability of $\beta$\cite{153}. In low Al concentrations, it has been found that the elements which stabilise $\beta$ are Cr and Co, and that Ti, Ta, Mo and W have a destabilising effect. However, the concentration of these elements was very similar in both of the coatings, as presented in Table 7.21. The main compositional difference between the two coatings is the Pt concentration. Several authors have differing views on the stabilising effect Pt has on $\beta$\cite{52,61,161}, however due to the different Al and Pt concentrations within the two coatings it is difficult to precisely state the influence of Pt on the stability of the $\beta$ phase.
Figure 7.107 SEM micrographs showing the amount of $\gamma'$ particles after ageing for 1000 hours at 1000°C in the
a) RT22 coated CMSX4 and b) CN91 coated CMSX4

<table>
<thead>
<tr>
<th>Elements (wt.%)</th>
<th>RT22</th>
<th>CN91</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>48.5 - 49.5</td>
<td>46.9 - 49.4</td>
</tr>
<tr>
<td>Al</td>
<td>13.9 - 14.7</td>
<td>12.7 - 13.1</td>
</tr>
<tr>
<td>Ti</td>
<td>0.4 - 0.5</td>
<td>0.5 - 0.6</td>
</tr>
<tr>
<td>Cr</td>
<td>4.1 - 4.2</td>
<td>3.6 - 3.8</td>
</tr>
<tr>
<td>Co</td>
<td>6.7 - 6.8</td>
<td>5.8 - 6.4</td>
</tr>
<tr>
<td>Ta</td>
<td>2.3 - 3.5</td>
<td>3.4 - 4.1</td>
</tr>
<tr>
<td>W</td>
<td>0.1 - 0.5</td>
<td>0.4 - 0.6</td>
</tr>
<tr>
<td>Re</td>
<td>0.0 - 0.6</td>
<td>-</td>
</tr>
<tr>
<td>Pt</td>
<td>19.7 - 21.0</td>
<td>17.0 - 19.1</td>
</tr>
</tbody>
</table>

Table 7.21 EDX analysis results showing the compositions of the $\beta$ phase in the RT22 and CN91 coated CMSX4
samples aged for 1000 hours at 1000°C (obtained using SEM)

The amount and size of the $\gamma'$ particles continued to increase with temperature and exposure
time, until a complete dissolution of the $\beta$ phase had occurred at 1050°C after 4000 hours. The
absence of the $\beta$ phase within the coating confirms that $\beta$ acts as the initial Al reservoir in the
coating for the production and sustainability of the protective oxide scale.
Precipitates

Clusters of spherical precipitates of the order of 100 nm in diameter were observed throughout the RT22 coating in the as-received condition, as shown in Figure 7.108 a). Chemical analysis of these precipitates showed them to be rich in W, Re, and Cr, with smaller amounts of Ta and Mo. The particles were further identified as $\alpha$-W ($a_0 = 3.16 \text{ Å}$), the Re-rich tetragonal $\sigma$ phase ($a_0 = 9.12 - 9.3 \text{ Å}$ and $c_0 = 4.72 - 4.86 \text{ Å}$) and the W-rich orthorhombic $P$ phase ($a_0 = 17.2, b_0 = 4.86$ and $c_0 = 9.2 \text{ Å}$), using a combination of selected area diffraction patterns and EDX analysis. It has been reported that these precipitates form primarily as a consequence of the inward diffusion of Al, which results in the entrapment of W, Re, Mo and Ta due to the low solubility of these refractory elements in $\beta$-NiAl grains\[53,54,144\]. In comparison, the CN91 coating contains no precipitates within the bulk of the coating. This is due to CN91 being an outward grown (low activity) coating, in which the outward diffusion of Ni from the substrate is at a much greater rate than that of the Al diffusing inwards. Therefore, smaller concentrations of alloying elements from the substrate move into the coating, resulting in a precipitate free coating.

The small W-rich precipitates were seen to increase in size, with temperature and exposure time, which in turn reduced the cluster formation observed in the as-received condition. However, at 900°C only the tetragonal $\sigma$ phase and orthorhombic $P$ phase were identified within the coating, therefore indicating the dissolution of the $\alpha$-W phase above 850°C. It has been reported that Pt in high concentrations may have a stabilising effect on the $\alpha$-W phase. Consequently the redistribution of the Pt that occurred with the increase in temperature resulted in lower Pt concentrations, allowing the dissolution of the W-rich phase. The Ta content within the precipitates was also seen to decrease with temperature and exposure time; this can be associated with development of $\gamma'$ particles within the coating, as Ta is a stabilising element of $\gamma'$. After 4000 hours ageing at 900°C the W-rich particles appeared to be surrounded by an area of brighter contrast, as illustrated in Figure 7.108 d). Chemical analysis of the particles indicated that they had similar compositions to those observed at lower time and temperatures, however, values of oxygen up to 4 wt.% were also detected. One possibility is that this was due to surface contamination, however, levels of only ~ 0.3 wt.% were detected in the adjacent matrix and therefore it was thought that this was a genuine result, and that the W-rich particles do contain oxygen.
At the higher temperatures of 950–1050°C, the W/Re-rich precipitates experienced significant growth and also appeared to have decreased in area fraction with the temperature and exposure time, until complete dissolution occurred after 2000 hours at 1050°C. The decrease in area fraction of the precipitates may have been a result of the increase in γ′ within the coating because γ′ is known to have a higher solubility for W than that of the β phase. Therefore, the implication is that the W was diffusing from the substrate into the coating and partitioning to the γ′ phase, preventing the precipitation and growth of these precipitates.

Particles rich in Cr and Re were also observed within the bulk of the coating at the higher temperatures of 950–1050°C and exposure times 2000–4000 hours. The Cr-rich particles were generally located on the β′/γ′ grain boundaries, Therefore it was possible that the increase in diffusion of Cr and Re across the coating/substrate interface and their low solubility within γ′ and β has resulted in the precipitation of Cr-rich phases within the coating. Due to the presence of carbon within these particles, they were initially identified as M_{23}C_{6} carbides.
Figure 7.108 SEM micrographs showing the amount, size and morphology of the W-rich particles observed within the bulk of the coating of RT22 coated CMSX4 samples

a) in the as-received condition and isothermally aged for b) 1000 hours at 850°C, c) 1000 hours at 900°C, d) 4000 hours at 900°C, e) 1000 hours at 1000°C and f) 1000 hours at 1050°C.
7.9.3 Interdiffusion Zone

Interdiffusion of elements between the coating and the substrate occurred during the coating process heat treatment and formed an interdiffusion zone (IDZ) containing several intermetallic phases. The interdiffusion zone consisted of two main layers in the as-received condition. The first layer was observed as a band of precipitates adjacent to the coating/substrate interface. Chemical analysis of these precipitates indicated that they were mainly composed of W, Re, Ta and Cr with additions of Mo, and were identified as a mixture of W/Re-rich $\sigma$ phase ($a_o = 9.12 - 9.3\text{Å}$ and $c_o = 4.72 - 4.86\text{Å}$), $\mu$ phase ($a_o = 4.73 - 4.75$ and $c_o = 25.54 - 25.8 \text{Å}$) and P phase ($a_o = 17.2$, $b_o = 4.86$ and $c_o = 9.2\text{Å}$). The relative amount of each of these phases could not be determined due to the relatively small number of particles conclusively identified using electron diffraction. The second layer comprised of a continuous $\gamma'$ layer that separated the coating from the substrate. This has been suggested to form due to the net increase of Al in the substrate and Ni in the coating\[52,61,89,162], therefore resulting in the transformation of the $\gamma$ phase from the substrate adjacent to the coating, into the $\gamma'$ layer. Small, needle-like precipitates rich in Cr, Re and W, identified as $\sigma$ phase, were also observed within this $\gamma'$ layer. These phases are known to form in order to accommodate the excess chromium and rhenium produced as a result of the phase transformation from $\gamma$ to $\gamma'$, due to their reduced solubility in $\gamma'$ compared to $\gamma$\[1,52,61,89,144,147].

The interdiffusion zone was seen to increase in thickness with increase in temperature and exposure time. At the lower temperatures, below $950^\circ$C the increase in thickness was mainly attributed to the increase in thickness of the $\gamma'$ layer, as a direct result of Al diffusing from the coating into the substrate and Ni from the substrate into the coating. At the higher temperatures the growth of the needle-like TCP phases from the $\gamma'$ into the substrate was the main contributing factor to the thickness, as shown in Figure 7.109. This statement excludes $950^\circ$C, which will be discussed in more detail later in this section.
After ageing at 850°C for 1000 hours the morphology of the W-rich precipitates, \( \sigma \), \( \mu \) and P phase, appeared to be more rounded, therefore indicating the onset of coarsening. The precipitates continued to increase in size with increase in temperature and exposure time, ranging from hundreds of nanometres to several microns, as a result of the diffusion of elements such as W, Re and Cr across the coating/substrate interface, as shown in Figure 7.110. However, in the sample aged for 4000 hours at 900°C the precipitates began to display a variation in contrast similar to those observed within the bulk of the coating. Once again chemical analysis of the particles detected oxygen up to values of 4 wt.%.

**Figure 7.109** Plot of interdiffusion zone thickness for RT22 coated CMSX4 samples aged for 1000 hours at increasing temperatures, and the contribution the thickness of the \( \gamma' \) layer has on the overall thickness

**Figure 7.110** SEM micrographs showing the size of the W-rich precipitates in the interdiffusion zone of RT22 coated CMSX4 samples aged at a) 850°C for 1000 hours and b) 900°C for 2000 hours

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W-rich oxides were observed in the centre of the TCP phases located within the interdiffusion zone of samples aged at the higher temperatures and times, as shown in Table 7.22. However, these oxides demonstrate a variation in their morphology within the samples. At 950 and 1050°C the oxides consisted of separate areas defined by a variation in contrast, as shown in Figure 7.111. The outer brighter layer had a similar composition to the W-rich precipitates observed in the interdiffusion zone at the lower times and temperatures and oxygen values ranging from 5 to 10 wt. % were detected within the area of darker contrast. EDX analysis within the TEM enabled a more quantitative chemical composition of the oxides, showing them to be rich in W and O with smaller amounts of Cr, P and Ca. It is interesting to note that W-rich oxides were also observed in the CN91 coated samples, which have different process parameters to the RT22 coated samples. As the W-rich oxides were observed within the core of the TCP particles, this suggested that they have formed initially within the sample and subsequently the W/Re-rich particles precipitated around them. However, the W/Re-rich TCP phases were present within the interdiffusion zone at the lower temperatures and exposure times, in which no oxygen was detected. It is unclear at this point how the limited amount of oxygen had diffused into the coating and why it reacted with the W to form W-rich oxides, as opposed to elements such as Al and Cr also present within the coating. One suggestion is that the oxygen originated from the Al₂O₃ grit particles used in the coating process. The grit particles used can vary significantly in size with very fine particles being embedded, as well as the large particles observed within the SEM micrographs. Although Al₂O₃ is a stable phase it is possible that it can be reduced within a nickel matrix under certain conditions, with oxygen combining with reactive elements within the interdiffusion zone. The oxygen would ideally travel to the free surface, however it becomes trapped resulting in a reaction with W, Re and Cr present in high concentrations within precipitates. Further investigation is required to determine why the oxygen would partition to the W rather than with more reactive elements such as Cr.
Table 7.22 Illustrating the times and temperatures of the RT22 coated CMSX4 samples in which the W-rich oxides were observed within the interdiffusion zone

<table>
<thead>
<tr>
<th>Time (hours)</th>
<th>900</th>
<th>950</th>
<th>1000</th>
<th>1050</th>
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<td>1000</td>
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<tr>
<td>4000</td>
<td>✓</td>
<td>✓</td>
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</tbody>
</table>

At temperatures below 950°C, islands of $\gamma'$ were observed within the $\gamma'$ layer of the interdiffusion zone. It had been suggested that these occur as a result of the growth of the layer, in which $\gamma'$ was nucleated within the coating and continued to grow upwards to meet the $\gamma'$ layer, and in doing so encases some $\beta$ particles\(^{149}\). In contrast it has been reported that the initial high interdiffusional flux of Al and Ni within the interdiffusion zone caused local phases transformations from $\gamma'$ to $\beta$\(^{145}\). Due to the low solubility of W in $\beta$ this resulted in the precipitation of W-rich TCP phases. However, it had also has been reported that the formation of the W-rich precipitates within the $\gamma'$ layer create a local depletion of elements such as W, Re, Cr and Co. The decrease of W in particular reduces the destabilising effect on $\beta$\(^{61}\), and therefore allows the matrix surrounding the precipitate to transform from $\gamma'$ to $\beta$. At 950°C the $\beta$ particles are no longer present within the $\gamma'$ layer, indicating the increase in diffusion of Al has resulted in the $\beta$ particles transforming back in $\gamma'$.

The small precipitates within the $\gamma'$ layer were seen to have changed in morphology becoming increasingly needle-like with increased time and temperature. These needle-like precipitates initiated within the interdiffusion zone and extended up to ~160 $\mu$m into the substrate at an angle of ~45° at the highest temperatures and times. At 900°C however, the alignment of the needle-like precipitates within the $\gamma'$ layer appeared to differ with position within the sample. It is possible that these changes in alignment could be due to varying diffusion kinetics and slight microstructural differences within the interdiffusion zone around the sample’s surface; resulting in different values of stress, due to differing thermal expansion coefficients of the coating and substrate during aging. It is also possible that there are different amounts of residual stress around the circumference of the sample as a result of initial sample processing.
It is apparent that the needle-like TCP phases increase in quantity and size as the aging temperature and exposure time is increased, resulting in significantly coarsened, segmented needle and blocky type structures, as shown in Figure 7.112. Within the samples exposed at the lower temperatures below 950°C, the needle-like TCP phases were predominantly identified as the Cr-rich $\sigma$ phase, while at higher temperatures, the predominant phases observed were the W/Re-rich $\mu$ and P phase indicating the high temperature stability of these phases.
Figure 7.111 SEM micrographs of RT22 coated CMSX4 showing the different forms of W-rich oxides observed within RT22 coated CMSX4 samples aged at, a) 950°C for 4000 hours, b) 1000°C for 2000 hours and c) 1050°C for 4000 hours.

Figure 7.112 SEM micrographs of RT22 coated CMSX4 showing the morphology and growth of the needle-like TCP phases extending out of the γ' layer into the substrate of samples isothermally aged for a) 1000 hours at 850°C, b) 1000 hours at 900°C and c) 4000 hours at 1000°C.
MC and $M_{23}C_6$ carbides were also observed within the interdiffusion zone of the samples investigated. The temperatures and times of the samples in which these two phases have been identified are presented in Table 7.23.

<table>
<thead>
<tr>
<th>Time (hours)</th>
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<th>900</th>
<th>950</th>
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</thead>
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<td>✓</td>
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<tr>
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<tr>
<td>4000</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
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<td>✓</td>
</tr>
</tbody>
</table>

✓ - MC carbide
✓ - $M_{23}C_6$ carbide

Table 7.23 Illustrating the times and temperatures of the samples in which the MC and $M_{23}C_6$ carbides were observed within the interdiffusion zone

The MC carbides rich in Ta and Hf were observed scattered throughout the band of TCP phases adjacent to the coating/substrate interface in all samples investigated. The only distinguishing feature of the MC carbides compared to the surrounding TCP phases was their slight increase in size, which continued to increase with time and temperature. Ta-rich MC carbides were also present within the precipitate band of the CN91 coated sample aged for 1000 hours at 1000°C, even though the substrate contained significantly less carbon. This therefore indicated that even small amounts of carbon present within the substrate or the coating will form carbides within the interdiffusion zone. Excluding 950°C, the $M_{23}C_6$ carbides rich in Cr and Re were present within the $\gamma'$ layer at all exposure temperatures, but at the higher times of 2000 and 4000 hours, aside from 4000 hours at 1050°C where the dissolution of most secondary phases had occurred. At temperatures below 950°C the $M_{23}C_6$ carbides displayed a lath like morphology and were located near the $\beta$ particles also within the $\gamma'$ layer, as shown in Figure 7.113 a). The morphology of the carbides changed with temperature, with them becoming more rounded and globular. However, following ageing at 950°C for 2000 and 4000 hours the carbides were usually found to border the large W-rich precipitates, as shown in Figure 7.113 b), which could be a result of the rejection of Cr from these phases.
The microstructure of the RT22 coated CMSX4 system after thermal aging at 950°C for 2000 and 4000 hours showed distinct differences to the other samples investigated, therefore resulting in changes in size, morphology and stability of the phases present as discussed previously. The interdiffusion zone again consisted of two distinct layers on either side of the interface; however the continuous γ’ layer was present within the coating adjacent to the interface, as opposed to the substrate as seen in the other samples. The second layer was a layer of γ'/γ’ which resembled a highly rafted substrate structure. The coalescence of adjacent γ’ particles had occurred within some areas of this layer, forming regions of continuous γ’, also containing very small acicular precipitates. It would appear that 950°C is a ‘special’ temperature in respect to the kinetics of the various diffusional and oxidative processes for the coating system. The implication of this microstructural change for components in service requires further investigation.

7.10 Summary

Platinum modified aluminide diffusion coatings are produced by both inward and outward growth methods, and each mechanism forms a distinctive coating microstructure. This chapter has presented and discussed the results of the detailed study of the microstructural evolution of two commercial Pt modified aluminide diffusion coatings, RT22 and CN91, applied to the Ni-based superalloy CMSX4. The RT22 coatings, which were the subject of the bulk of the experimental work, were inward grown, whereas the CN91 coatings were outward grown. A number of phase transformations and microstructural changes as a result of interdiffusion between the coating and the substrate have been examined in detail using a variety of electron microscopy techniques.
microscopy techniques. These experimental observations are compared with detailed microstructural investigations carried out on RT22 coated CMSX4 ex-service blades presented in the following chapter.
Chapter 8

Microstructural Characterisation of Ex-Service Blades

8.1 Introduction

Platinum aluminide coatings have been used extensively for the protection of Ni-based turbine blades from the aggressive conditions in which both industrial and aero gas turbines operate. The commercial Pt modified aluminide diffusion coating RT22 applied to the single crystal Ni-based superalloy CMSX-4 was investigated and discussed in detail in Chapter 7. The RT22 coated CMSX4 samples in the form of cylindrical bars were isothermally aged in a controlled combustion gas at temperatures and exposure lengths representative of service conditions experienced by gas turbine blades. However, during service the response to load across a gas turbine blades is not uniform, therefore, differences in temperature and stress are experienced over the surface of the aerofoil. The temperatures are reported to vary from a maximum of the order of 1100°C at the leading and trailing edges to approximately 650°C at the centre of the blade and near the blade's root[10], however, these temperatures prove quite difficult to measure in reality and are dependent on the size and geometry of an individual blade and its exact location within an engine. The amount of microstructural evolution within the coating and substrate therefore varies substantially across a blade due to this range in temperatures experienced. Consequently, there is a need to transfer the knowledge gained of the degradation processes of coated Ni-based superalloys under controlled laboratory conditions to components in service.

This chapter presents and discusses the results of the detailed microstructural investigations carried out on RT22 coated CMSX4 ex-service blades, in order to make a comparisons with the microstructures observed in the isothermally aged RT22 coated CMSX4 samples. The gas turbine blades investigated are 1st stage high pressure turbine blades from an aero gas turbine. Although this research has been focused on industrial gas turbines used for power generation, a set of ex-service aerospace blades were made available for this research because they had a well documented service history. The blades investigated were run with a similar amount of cycles, ~ 4000, however were in service for 6,752 hours and 22,021 hours; full details are reported in Table 8.1. Cross sections were taken at ~ ½ and ¾ of the aerofoil height of the
turbine blades and characterisation was carried out at various points around the aerofoil surface, as illustrated in Figure 8.1, to encompass any microstructural differences both around the surface profile of the blade and from the root to the shroud. A variety of experimental techniques have been used in the study of the coating system. These include field emission gun scanning electron microscopy (FEGSEM) and energy dispersive X-ray analysis (EDX). A dual beam focussed ion beam FEGSEM has also been utilised to make site specific samples for high resolution transmission electron microscopy (TEM) analysis as described in Chapter 3.

<table>
<thead>
<tr>
<th>Description</th>
<th>Material</th>
<th>Coating</th>
<th>Hours</th>
<th>Cycles</th>
</tr>
</thead>
<tbody>
<tr>
<td>HPTRB</td>
<td>CMSX4</td>
<td>RT22</td>
<td>6,752</td>
<td>3763</td>
</tr>
<tr>
<td>HPTRB</td>
<td>CMSX4</td>
<td>RT22</td>
<td>22,021</td>
<td>4017</td>
</tr>
</tbody>
</table>

Table 8.1 Description of the ex-service blades examined within this chapter

Figure 8.1 Schematic diagram of a service run turbine blade, showing the 1/3 and 2/3 positions which a cross-section was extracted and the areas examined across the aerofoil surface, which are defined as area 1, 2, leading edge and trailing edge respectively.

- 100mm
- 5mm

(a) Suction side

(b) Pressure side
8.2 Microstructure Characterisation of PtAl coated Blade in Service for 6,752 hours

8.2.1 Microstructure of Aerofoil taken at 1/3 Blade Height

**Suction Side (Area 1)**

Figure 8.2 shows a representative microstructure taken from the RT22 coated CMSX4 ex-service blade located within the central section of the suction side of the aerofoil. This is from area 1 of the aerofoil shown in Figure 8.1.

![Figure 8.2](image)

*Figure 8.2* SEM micrograph of area 1, 1/3 height of the RT22 coated CMSX4 blade in service for 6,752 hours, illustrating the overall structure of the coating, substrate and interdiffusion zone

The coating observed within this area of the aerofoil was approximately 60 μm thick and comprised of single phase β (NiAl) enriched with Pt, forming the Ni(Al,Pt) phase. This single phase coating was similar to that observed within the isothermally aged RT22 coated CMSX4 samples. A variation in contrast was observed across the coating, the brighter outer layer corresponding to higher platinum concentrations levels towards the coating surface. Chemical analysis of the β matrix showed a Pt content of ~ 36.5 wt.% at the coating surface, which decreased with increasing distance to ~ 12 wt.% in the interdiffusion zone. The amount of variation in contrast and corresponding chemical profile of Pt across the coating was similar to that observed within the sample isothermally aged at 850°C for 1000 hours, as shown in Figure 8.3. The Pt curve for the isothermally aged sample has shifted slightly to the right indicating an increased diffusion into the substrate than at area 1 of the ex-service blade.
Therefore, as these turbine blades have been in service for approximately 6,700 hours, it was suggested that this area of the aerofoil has experienced an effective thermal exposure less than the equivalent of 1,000 hours at 850°C, which could be expected due to internal cooling of these blades.

Figure 8.3 Compositional profile of Pt across the coating, interdiffusion layer and substrate of RT22 coated CMSX4, area 1 ½ height in service for 6,752 hours (blue) and isothermally aged for 850°C for 1000 hours (red)

Figure 8.4 SEM micrographs of RT22 coated CMSX4 comparing the clusters of TCP phases within the bulk of the coating within a) area 1, ½ height of the ex-service blade aged for 6,752 hours and b) isothermally aged sample exposed for 1000 hours at 850°C
Clusters of small bright particles are present throughout the coating with sizes in the region of 100 - 200 nm, as shown in Figure 8.4. These particles form as result of the inward diffusion of Al during the coating process. Consequently elements such as W, Re and Ta are entrapped within the coating allowing these phases to form due to the low solubility of these elements in β. High resolution analysis of a site specific FIB sample taken across the coating, indicated that the majority of the W-rich precipitates are located along the β grain boundaries, as shown in Figure 8.5. Chemical analysis reported in Table 8.2 showed the precipitates to be rich in W and Re (~ 35 and 24 wt.%) with smaller amounts of Ta and Mo. Similar precipitates observed in the isothermally aged samples were identified as α-W (a₀ = 3.16 Å), Re-rich tetragonal σ phase (a₀ = 9.12 - 9.3 Å and c₀ = 4.72 - 4.86 Å) and the W-rich orthorhombic P phase (a₀ = 17.2, b₀ = 4.86 and c₀ = 9.2 Å). The small W-rich precipitates show similarities in chemical composition to those observed in the as-received sample; however no viable diffraction patterns were acquired using SAED method. Therefore it can only be assumed that the same phases are present within the blade. The cluster formation of the W-rich precipitates again proves very similar to those observed within the sample aged at 850°C for 1000 hours, as illustrated in Figure 8.4 b).

![Figure 8.5](image-url)  
*Figure 8.5 TEM micrographs showing a) low and b) high magnification of the W-rich precipitates forming on the β grain boundaries of the coating in area 1, ¼ height of blade in service for 6,752 hours*
Table 8.2 EDX analysis results of the W-rich phase present within the bulk of the coating at area 1, \( \frac{1}{3} \) height of RT22 coated blade in service for 6,752 hours (obtained using SEM)

<table>
<thead>
<tr>
<th>Elements (wt.%)</th>
<th>Ni</th>
<th>Cr</th>
<th>Co</th>
<th>Mo</th>
<th>Ta</th>
<th>W</th>
<th>Re</th>
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<tbody>
<tr>
<td></td>
<td>1.8 - 9.1</td>
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<td>0.2 - 4.3</td>
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</tbody>
</table>

Interdiffusion of elements between the coating and the substrate during service has formed an interdiffusion zone with an average thickness of 20 \( \mu \)m as shown in Figure 8.6. The diffusion of refractory elements from the substrate into the coating has resulted in the formation of several intermetallic phases. The coating section of the interdiffusion zone consists of a high density band of precipitates with sizes ranging from 0.6 - 1.2 \( \mu \)m, some of which are seen to have coalesced, forming larger particles. These particles tend to be orientated perpendicular to the coating substrate interface possibly indicating their initial growth direction parallel to the diffusion path. Chemical analysis of these precipitates showed them to be mainly composed of W, Re and Ta with additions of Cr, Co and Mo. As observed within the isothermally aged samples, SAED and EDX analysis indicated that these precipitates are a mixture of W/Re-rich \( \sigma \) phase \((a_0 = 9.12 - 9.3 \text{Å} \text{ and } c_0 = 4.72 - 4.86 \text{Å})\), \( \mu \) phase \((a_0 = 4.73 - 4.75 \text{Å} \text{ and } c_0 = 25.54 - 25.8 \text{Å})\) and \( P \) phase \((a_0 = 17.2, b_0 = 4.86 \text{Å} \text{ and } c_0 = 9.2 \text{Å})\). Typical SAED patterns are shown in Figure 8.7. A \( \gamma' \) enriched layer separating the coating from the substrate was present within the interdiffusion zone. This has proved consistent throughout all the RT22 coated CMSX4 samples investigated. Islands of \( \beta \) phase were observed within the \( \gamma' \) enriched layer, as illustrated in Figure 8.6 b). It has been stated that \( \gamma' \) is nucleated within the coating and subsequently grows upwards into the \( \gamma' \) layer, therefore entrapping the \( \beta \) phase in the \( \gamma' \) layer\(^{[149]}\). In contrast it has been reported that the initial high interdiffusional flux of Al and Ni within the interdiffusion zone causes local phase transformations from \( \gamma' \) to \( \beta \)\(^{[145]}\). The increase in Al within this layer however, would help justify the formation of W-rich precipitates on the \( \beta'\gamma' \) grain boundaries. \( \beta \) phase is known to have a lower solubility for W than that of the \( \gamma' \), therefore the phase transformation has resulted in the rejection of W allowing the formation of these precipitate on the grain boundaries. The \( \gamma' \) layer contains small acicular phases \( \sim 0.2 - 0.5 \mu \text{m} \) in size rich in W and Re \( \sim 30 \text{ and } 19 \text{ wt.}% \). Due to the small size of the precipitates no viable selected area diffraction patterns were acquired.
However, the compositions are in close comparison with the $\sigma$, $\mu$ and $P$ phases observed in the isothermally aged samples.

Figure 8.6 SEM micrographs within area 1, 1/3 height of RT22 coated CMSX4 blade in service for 6,752 hours, showing a) the interdiffusion zone structure, b) TCP phases within the $\gamma'$ layer extending into the substrate and c) band of precipitates within the coating section of the interdiffusion zone
Figure 8.7 TEM micrograph and selected area diffraction patterns (SADP) of the TCP phases within the coating adjacent to the IDZ within area 1, ⅔ height of RT22 coated CMSX4 blade in service for 6,752 hours. a) bright field image (BF); SADP for b) μ phase, c) P phase, d) σ phase in which the relevant zone axes are labelled.

Pressure Side (Area 2)

Figure 8.8 shows a representative microstructure taken of the RT22 coated CMSX4 blade in service for 6,752 hours located within area 2 on the pressure side of the aerofoil as shown in Figure 8.1.
Initial observations show a significant increase in oxidation and corrosion products on the coating surface, in comparison to the suction side of the aerofoil, as shown in Figure 8.10. This is to be expected as the corrosion products within the hot combustion gas directly impinge on the pressure side of the blade\textsuperscript{160}.

The bulk of the coating remains single phase, however the contrast variation observed across the coating on the suction side of the aerofoil (area 1), is no longer visible. The platinum concentration across the coating has evened out indicating the increase in diffusion in towards the substrate as a result of exposure to higher temperatures, as shown in Figure 8.9. Chemical analysis confirmed an increase in Pt content of the $\beta$ phase within the IDZ of $\sim$ 24 wt.% as opposed to the 12 wt.% observed in area 1.
Figure 8.9 Compositional profile of Pt across the coating, interdiffusion layer and substrate of ½ height RT22 coated CMSX4 blade in service for 6,752 hours at area 1 and area 2.

The precipitates within the bulk of the coating have increased in size to an average of 0.6 μm compared to ~0.2 μm observed in area 1, as shown in Figure 8.10. It is possible this is due to an Ostwald ripening process in which larger precipitates grow at the expense of smaller ones, therefore reducing the cluster formations observed in the suction side.

Figure 8.10 SEM micrographs of area 2, ½ height of RT22 coated blade in service for 6,752 hours, showing a) the combustion products on the coating surface and b) W-rich precipitates within the bulk of the coating.
In addition, the precipitates that form a band within the interdiffusion zone have increased in size, indicating an increase in diffusion activity of refractory elements such as W and Re from the substrate into the coating. Within this layer, light grey phases of a blocky morphology were observed. The lower Al and higher Ta content of these particles are compared to the surrounding β matrix in Table 8.3, and are thought to be γ' - Ni₃Al. The W-rich precipitates also appear to have altered from their apparently random distribution within the area adjacent to the continuous γ' layer, to a coarsened distribution along the grain boundaries of the γ' phase, as shown in Figure 8.11. The increase in diffusion of Al from the coating and Ni from the substrate alloy has also led to the growth of the γ' layer, which has increased in thickness to ~22 μm. Needle-like phases present within the γ' layer have increased in size and extended out into the substrate at various angles to the interface.

<table>
<thead>
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</tr>
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<tbody>
<tr>
<td></td>
<td>Ni</td>
</tr>
<tr>
<td>β</td>
<td>45.2 - 47.0</td>
</tr>
<tr>
<td>γ'</td>
<td>45.7 - 49.2</td>
</tr>
</tbody>
</table>

Table 8.3 EDX analysis results of β and γ' phase present within the band of precipitates of the IDZ at area 2, ½ height of RT22 coated blade in service for 6,752 hours (obtained using SEM)

The γ'/γ structure within the substrate adjacent to the coating/substrate interface appeared to be rafted parallel to the coating, as shown in Figure 8.11 b). It has been suggested that this rafting is caused by biaxial compressive stresses induced as a result of the formation of the monolithic γ' phase at the coating/substrate due to the differing thermal expansion coefficients of the coating and substrate materials during aging\textsuperscript{163}. Lattice mismatches, thermal expansion mismatches, and diffusion gradients can also be contributing factors\textsuperscript{104}.

These changes in microstructure indicate that the pressure side on the aerofoil experiences higher temperatures than the suction side. This increase in temperature was expected as the hot combustion gases leaving the combustor directly impinges on this surface. However, in comparison to the isothermal RT22 coated CMSX4 samples aged for 2000 hours, the effective temperature experienced on the pressure side is still thought to have been under 850°C.
Figure 8.11 SEM micrographs within area 2, ½ height of RT22 coated CMSX4 blade in service for 6,752 hours, showing a) the interdiffusion zone structure, b) TCP phases within the γ' layer extending into the substrate and c) band of precipitates within the coating section of the interdiffusion zone containing γ' particles

Leading and Trailing Edges of Aerofoil

The microstructure of the coating and substrate observed at the leading and trailing edges of the aerofoil indicated exposure to a lower temperature than expected in comparison to the temperature on the suction side of the blade. Representative microstructures of the coating and substrate at the leading and trailing edge of the aerofoil are illustrated in Figures 8.12 a) and b) respectively. Both the leading and trailing edge show similarities to the microstructure observed in area 1, the suction side of the blade. The coating within the leading and trailing edges was approximately 71 and 84 μm thick respectively with the entrapped Al₂O₃ particles still present in the top 22 μm of the coating. The variation in contrast observed was less distinct, indicating an increase in diffusion of the Pt from the higher concentration at the
coating surface in towards the substrate. This therefore suggests that both the leading and trailing edge of the aerofoil were exposed to slightly higher temperatures than that of the centre of the suction side of the blade.

![SEM micrographs illustrating the overall structure of the substrate and coating of (a) leading edge and b) trailing edge at 1/3 blade height of RT22 coated blade in service for 6,752 hours](image)

Figure 8.12 SEM micrographs illustrating the overall structure of the substrate and coating of a) leading edge and b) trailing edge at 1/3 blade height of RT22 coated blade in service for 6,752 hours

Figure 8.13 illustrates that the small W-rich precipitates present within the bulk of the coating have an average size ranging from 0.4 to 0.8 µm, therefore suggesting a coarsening effect has occurred with the increase in temperature. The chemical composition of these phases show they contain high amounts of W, Re and Ta at ~ 27, 19 and 14 wt.% respectively. ‘Holes’ were also observed within the coating at the trailing edge on the aerofoil, as observed in Figure 8.13 b). However, their size and shape proved similar to the surrounding W-rich precipitates, indicating the possibility of particle pull-out during metallographic sample preparation.
Figure 8.13 SEM micrographs showing the W-rich precipitates and 'holes' within the coating of the (a) leading edge and (b) trailing edge at ⅓ blade height of RT22 coated blade in service for 6,752 hours

The thickness of the interdiffusion zone has increased at the leading edge to ~ 30 µm in comparison to the 20 µm observed at area 1, as shown in Figure 8.14 a). The increase in thickness has occurred mainly through the growth of the γ' layer, which is in turn affected by the net increase of Al in the substrate and Ni in the coating. The trailing edge has undergone similar microstructural evolution with an increase in thickness of the interdiffusion zone, although the zone itself has become less clearly defined and appears to contain a substantial number of 'holes' as observed in the bulk of the coating, as shown in Figure 8.14 b). It is possible that this is a result of particle pull-out, however it is unknown why this occurs in such a localised area. Light grey phases of blocky morphology with sizes ranging from ~ 1.3 - 2.8 µm were observed within the high density band of precipitates adjacent to the coating/substrate interface at both the leading and trailing edges, as shown in Figure 8.14. Chemical analysis showed that these particles contained a lower Al and higher Ta concentration that that of the surrounding β matrix, and were once again thought to be γ'-Ni₃Al. These phases were not observed within area 1 of the aerofoil, therefore confirming the increase in temperature at the leading and trailing edges. In contrast, the W-rich precipitates within the interdiffusion zone at the trailing edge are smaller in size than those observed within the interdiffusion zone of area 1, as shown in Figure 8.15. It is possible that the curvature of the trailing edge results in a smaller volume of substrate alloy in contact within the PtAl coating. This therefore results in a smaller concentration of refractory elements from
the substrate being available for diffusion across the coating/substrate interface in one area, which slows down the growth of the phases rich in refractory elements.

Figure 8.14 SEM micrographs showing the structure of the interdiffusion zone, including the band of precipitates and γ’ layer at the a) leading edge and b) trailing edge at 1/3 blade height of RT22 coated blade in service for 6,752 hours

Figure 8.15 SEM micrographs showing the size of the precipitates within the interdiffusion zone in the a) trailing edge and b) area 1 at 1/3 blade height of RT22 coated blade in service for 6,752 hours
8.2.2 Microstructure of Aerofoil taken at 2/3 Blade Height

The cross section of the turbine blade aerofoil at 2/3 height of the blade illustrated similar microstructural variations around the aerofoil surface.

Suction Side (Area 1)

The central section of the suction side of the blade (area 1) once more displayed a microstructure that was representative of the lowest temperature experienced, as shown in Figure 8.16. The variation in contrast of the β phase across the coating remains present, the brighter area representative of the higher Pt concentration towards the coating surface as observed in the ½ height cross-section.

![Figure 8.16 SEM micrograph of area 1, ½ height of the RT22 coated CMSX4 blade in service for 6,752 hours, illustrating the overall structure of the coating, substrate and interdiffusion zone](image)

The small W, Re and Ta rich precipitates observed throughout the bulk of the coating have coarsened very slightly to an average size of 0.4 µm, owing to the reduction of the sub-micron clusters observed in the ½ section, as illustrated in Figure 8.17. The interdiffusion zone shows similar characteristics to the ½ section with the presence of a band of bright precipitates, mainly composed of W, Re, Ta and Cr with additions of Mo. Particles rich in Ta, Hf and Ti, ~42, 4.9 and 3.5 wt.% respectively were observed scattered throughout the band of TCP phases adjacent to the coating/substrate interface. Due to the high proportions of Ta and Hf and the presence of C, these particles were likely to be MC carbides. This proved similar to the RT22 sample isothermally aged samples, even though the substrate contains significantly less carbon. The band of precipitates was followed by a γ’ enriched layer at the coating/substrate
interface, with an average thickness that has doubled from 6.5 μm to 13 μm moving up the blade towards the shroud. The growth of the γ' layer, both into the coating and substrate, illustrates an increase in diffusion of Ni into the coating and Al into the substrate resulting in the phase transformations $\beta \rightarrow \gamma'$ and $\gamma \rightarrow \gamma'$. The increase in Al from the coating into the substrate is confirmed by the presence of small light grey γ' particles with an average size of 0.6 μm within the band of precipitates of the interdiffusion zone, as shown in Figure 8.18.

Figure 8.17 SEM micrographs showing the size and distribution of the W-rich precipitates within the coating at area 1 of the RT22 coated blade in service for 6,752 hours at a) ⅞ height and b) ⅝ height

Figure 8.18 SEM micrographs within area 1, ⅞ height of RT22 coated CMSX4 blade in service for 6,752 hours, showing a) the interdiffusion zone structure, b) higher magnification showing γ' particles in the band of precipitates within the interdiffusion zone
**Pressure Side (Area 2)**

The combustion products deposited on the coating surface of the pressure side have begun to corrode the coating, creating an irregular surface, as shown in Figure 8.19. In some instances the corrosion and oxidation has removed up to ~10 μm of material and even incorporating the line of embedded alumina particles which marked the original interface.

![SEM micrograph of area 2, ½ height of the RT22 coated CMSX4 blade in service for 6,752 hours, illustrating the overall structure of the coating, substrate and interdiffusion zone](image)

**Figure 8.19** SEM micrograph of area 2, ½ height of the RT22 coated CMSX4 blade in service for 6,752 hours, illustrating the overall structure of the coating, substrate and interdiffusion zone

Light grey phases of blocky and vein-like morphologies, thought to be γ’ were observed throughout the coating, as illustrated in Figure 8.20. The γ’ phase was predominantly located along the β grain boundaries and in the interdiffusion zone. The W-rich precipitates observed within the bulk of the coating have increased in size to an average of 0.8 μm and decreased in area fraction. This decrease in area fraction may be a result of the increase in γ’ within the coating, as γ’ is known to have a higher solubility for W than that of the β phase. Once again these microstructural changes indicate a difference in temperature between the suction and pressure sides of the aerofoil. As observed on the suction side of the blade, slight changes in microstructure have occurred between the ⅓ and ⅔ sections as a result of the increase in diffusion of elements within the system, which in turn suggests that the ⅔ section has experienced an increase in temperature with respect to the ⅓ section.
Figure 8.20 SEM micrograph of area 2, 7/8 height of the RT22 coated CMSX4 blade in service for 6,752 hours, showing a) the W-rich precipitates and γ′ particles with the bulk of the coating and b) higher magnification of the same area.

**Leading and Trailing Edges of Aerofoil**

The leading and trailing edges of the aerofoil demonstrated the most significant changes in microstructure between the 1/8 and 7/8 sections of the blade. The surface of the coating has been attacked by corrosion and oxidation resulting in the removal of substantial amounts of coating material, leaving a highly irregular surface, as shown in Figure 8.21. This increase in corrosion indicates the leading edge has experience higher temperatures than that of the 7/8 section.

In contrast to the leading edge at 7/8 section, γ′ particles with both blocky and vein-like morphologies were present throughout the bulk of the coating at the 1/8 height. The vein-like particles appear to follow the β phase grain boundaries, confirming the diffusion of Al occurs at a faster rate within these areas. The W-rich precipitates have increased in size from 0.6 μm observed in the 7/8 section to 1.2 μm, however these remain in cluster formations throughout the coating, as observed in areas exposed to lower temperatures. The chemical analysis of theses precipitates also showed a reduction in Ta content; which can be readily associated with the development of γ′ particles within the coating since Ta is a stabilising element of γ′.
Figure 8.21 SEM micrographs showing the overall structure at the leading edge of RT22 coated CMSX4 blade in service for 6,752 hours at a) ½, b) ½ height and high magnification of the coating at c) ½ and d) ½ height

The increase in temperature has also resulted in an increase in diffusion activity across the interface, with an increase in thickness of the \( \gamma' \) layer from 19 \( \mu \)m at the ½ section to 44 \( \mu \)m. The entrapped \( \beta \) particles within the \( \gamma' \) layer are no longer present at the leading edge, as shown in Figure 8.22.
The coating at the trailing edge of the 7/₄ section was highly fractured, and it is likely that substantial amounts of material had been removed from the surface, as illustrated in Figure 8.23. Cracks are also observed extending through the coating thickness and into the interdiffusion zone. It is possible this cracking occurred during service, through oxidation, corrosion or even erosion. However, comparisons of the trailing edge were not possible due to the damage within this area.

Figure 8.23 SEM micrograph showing the damage to the leading edge at 7/₄ height of RT22 coated CMSX4 blade in service for 6,752 hours

Figure 8.22 SEM micrographs showing the γ' layer in the interdiffusion zone of RT22 coated CMSX4 blade in service for 6,752 hours at (a) 7/₄, (b) 7/₄ height
8.3 Microstructure Characterisation of PtAl coated Blade in Service for 22,021 hours

8.3.1 Microstructure of Aerofoil taken at 1/3 Blade Height

The cross sections of the turbine blade in service for 22,021 hours, showed similar temperature variations around the surface of the aerofoil, which are illustrated in Figure 8.24. The main microstructural changes are discussed within this section.

The areas within the gas turbine blade that have been exposed to lower temperatures and stress proved to be towards the root section and within the central area of the suction surface. The coating within this area again comprises of β- Ni(Al,Pt) which demonstrates a variation in contrast across the coating. The coating surface showed a brighter contrast, which was associated with higher platinum concentration levels. As the temperature at which the surface is exposed to increases, the contrast between the two layers present in the coating becomes less distinguishable as observed on the pressure side, due to the increased diffusion of Pt from the high concentration at the coating surface in towards the substrate.

With increasing temperatures experienced over the aerofoil surface, the sub-micron W-rich precipitates have increased in size throughout the coating with the area fraction decreasing relative to the increase in γ' particles. The phase transformation of β into γ' has occurred on the pressure side of the aerofoil, due to the increased diffusion of Al out towards the coating surface and substrate alloy. As the exposure temperature increases, the γ' grains that are predominantly located along the β grain boundaries within the coating as observed in the 6,752 hour blade are seen to increase in size and frequency.

It is evident that the γ' layer increases in thickness within areas exposed to higher temperatures such as the pressure side, leading edge and trailing edge suggesting increased diffusion activity across the coating/substrate interface causing the growth of the γ'. Small needle-like precipitates rich Re and W are again observed within this γ' layer, the size and quantity of which increased as the temperature experience by the blade increased.
Figure 8.24 SEM micrograph showing the coating structure around the aerofoil at the 1/5 cross section of RT22 coated CMSX4 blade in service for 22,021 hours
8.3.2 Microstructure of Aerofoil taken at 2/3 Blade Height

The microstructure of the leading and trailing edge at the ½ and 2/3 sections of the blade in service for 22,021 hours demonstrated the greatest differences compared to the 6,752 hour blade. The temperatures at which the blade is exposed are reported to reach a maximum at the leading and trailing edges; this was illustrated by the microstructural evolution that has taken place within these areas at the 2/3 height, as shown in Figure 8.25.

![Figure 8.25 SEM micrographs illustrating the overall structure of the substrate and coating of a) leading edge (insert of same area showing the corrosion products on the coating surface) and b) trailing edge at 2/3 blade height of RT22 coated blade in service for 22,021 hours](image)

Considerable oxidation/corrosion has occurred at the coating surface of the leading and trailing edge of the blade at 2/3 blade height. In some instances this has removed the thickness of the coating, creating a peaked surface. The β phase was present within the remaining coating at the leading edge, indicating there is a significant amount of Al still present in order to sustain the protective oxide scale. Therefore it can be assumed that majority of the damage to the coating has been caused by corrosion, however the specific type has not been established in this research.

The γ' precipitates (darker grey phase) present at the leading edge have continued to form and coarsen on the β grains boundaries within the coating, creating a vein-like morphology, as shown in Figure 8.26. The W-rich precipitates present within the remaining coating have coarsened significantly within this area and seem to be surrounded by porosity. Large tantalum and hafnium rich particles were observed along the continuous γ' layer at the
coating/substrate interface. Due to the presence of carbon, these particles were assumed to be MC carbides.

![SEM micrographs showing the phases within a coating and b) interdiffusion zone at the leading edge of the RT22 coated blade in service for 22,021 hours at 3/4 height](image)

The trailing edge has undergone similar microstructural evolution to that of the leading edge, indicating exposure to similar temperatures. The \( \gamma' \) phase is again present within the coating, forming on the grain boundaries of the \( \beta \) phase. The slight contrast variation of the \( \beta \) and \( \gamma' \) phases made them difficult to distinguish, as shown in Figure 8.27. The major differences between the leading and trailing edges were the significant reduction in the number of W-rich precipitates present within the remaining coating. It was suggested that this reduction is associated with the increase in the phase transformation of \( \beta \) to \( \gamma' \), as Re, Cr and W are soluble in \( \gamma' \) whilst only Cr is readily soluble in \( \beta \). Similarly it is possible that the curvature of the trailing edge can affect the amount of refractory elements available for diffusion across the coating/substrate interface in one area, which slows down or even prevents the growth of the phases rich in refractory elements.

A significant number of 'holes' were observed throughout the thickness of the coating, but on closer evaluation, these cavities were seen to have fairly geometric structures. This therefore indicated the removal of precipitates during metallographic preparation techniques as observed in the 6750 hour blade, and evidenced by the fact that they are also visible in the interdiffusion zone.
The $\gamma'/\gamma$ structure of the substrate, adjacent to the interdiffusion zone exhibited extensive rafting in both the leading and trailing edges of the aerofoil, as shown in Figure 8.28. This increased rafting of the substrate alloy could be induced by an increase in both stress and temperature. On closer examination, an abundance of very fine precipitates in the order of 100 nm were observed within the rafted $\gamma$ channels, as shown in Figure 8.29. These precipitates proved too small for single chemical analysis, therefore EDX was taken over several of the precipitates to achieve an average composition. Chemical analysis confirmed the fine precipitates to be $\gamma'$, with a similar composition to that of the surrounding $\gamma'$ rafts. These precipitates have been suggested to be $\gamma'$ re-precipitating during the thermal cycling of the blade when in service. The $\gamma'$ precipitates form on the cooling from each thermal cycle. Due to the low volume fraction of $\gamma'$ at these high temperatures, on cooling more precipitate out within the available space of the $\gamma$ channels. The very fine structure is due to the fast cooling rates within the thermal cycling; therefore the precipitates have time to nucleate out within the channels but insufficient time to grow.
Figure 8.28 SEM micrographs showing the highly rafted γ'γ' structure adjacent to the interdiffusion zone at the 
a) leading edge and b) trailing edge at ⅓ height of RT22 coated blade in service for 22,021 hours

![Image](image1)

Figure 8.29 SEM micrographs at the trailing edge ⅓ height of RT22 coated blade in service for 22,021 hours 
showing a) the fine γ' precipitates within the γ channel, including the EDX results of the different areas indicated 
and b) high magnification of the fine γ' precipitates

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<th>Ti</th>
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</tr>
</tbody>
</table>
8.4 Discussion

This section discusses the results of the detailed microstructural investigations carried out on the RT22 coated CMSX4 ex-service blades, and compares the microstructural differences observed both around the surface profile of the blade, and from the root to the shroud. Figures 8.30 and 8.31 show representative microstructures of the areas around the aerofoil surface discussed in this chapter (i.e. area 1, 2, leading edge and trailing edge) at $\frac{1}{2}$ and $\frac{3}{2}$ height of the RT22 coated blades in service for 6,752 and 22,021 hours respectively.

A comparison of the microstructures of the sections taken at $\frac{1}{2}$ and $\frac{3}{2}$ height in both the 6,752 and 22,021 hours ex-service blades indicated that the $\frac{1}{2}$ height section nearer the root of the blade had been exposed to a lower effective temperature and stress than the $\frac{3}{2}$ height section. However, within all four samples the microstructure in the central area of the suction side of the aerofoil appeared to have been exposed to lowest temperatures. In comparison to the isothermally aged samples, the suction side of the aerofoil (area 1) from each section demonstrated an effective thermal exposure close to an equivalent of 1000 hours at 850°C. The coating within each area 1 comprised of the $\beta$-Ni(A1,Pt) phase, with a variation in contrast across the coating; the brighter outer layer corresponded to higher platinum concentration levels towards the coating surface. Significant amounts of oxidation and corrosion products were observed on the pressure side of the aerofoil (area 2), which was to be expected as the corrosion products within the hot combustion gas directly impinge on the pressure side of the blade\textsuperscript{160}. In both the 6,752 and 22,021 hour blades, these combustion products only appear to significantly affect the coating in the $\frac{3}{2}$ height section, again indicating that in general the $\frac{3}{2}$ height section has been exposed to a higher effective temperature and stress than the $\frac{1}{2}$ height section. The increase in particle size and formation of $\gamma'$ within area 2 on the aerofoil in comparison to area 1 suggests an increase in diffusion of elements within the coating, therefore indicating that the pressure side of the aerofoil experiences higher temperatures than the suction side. It is possible that this increase in temperature is a result of the hot combustion gases leaving the combustor and directly impinging on this surface.

The leading and trailing edges demonstrate that they have experienced the greatest differences in temperature and stress between the $\frac{1}{2}$ and $\frac{3}{2}$ height sections of both the 6,752 and 22,021 hour blades. However, these differences are more pronounced in the 22,021 blade due to the
longer service life. Oxidation/corrosion had occurred at the coating surface of the leading and trailing edge at 2/3 blade height and in the 22,021 hour blade was significant enough in some areas to remove parts of the coating, creating a peaked surface. However, since the β phase remained present within the coating, it could be assumed that the majority of the visible damage to the coating has been caused by corrosion. In comparing the four areas of the aerofoil investigated, it can be suggested from the microstructural evolution that has occurred within the coating at the leading and trailing edges of the 2/3 height sections (including the growth of γ' and the dissolution of TCP phases), that these areas have experienced the highest effective temperature and stresses.
Figure 8.* SEM micrographs showing the coating microstructure around the aerofoil at the ⅓ and ⅔ height sections of the RT22 coated CMSX4 blade in service for 6,752 hours.
Figure 8. SEM micrographs showing the coating microstructure around the aerofoil at the 1/3 and 2/3 height sections of the RT22 coated CMSX4 blade in service for 22,021 hours
8.5 Summary

This chapter has presented and discussed the results of the detailed microstructural investigations carried out on RT22 coated CMSX4 ex-service blades, in order to make a comparisons with the microstructures observed in the isothermally aged RT22 coated CMSX4 samples. Cross sections were taken at ~ ½ and ¾ of the aerofoil height of the turbine blades and characterisation was carried out at various points around the aerofoil surface to encompass any microstructural differences both around the surface profile of the blade and from the root to the shroud.

During service the response to load across gas turbine blades is not uniform and therefore, differences in temperature and stress are experienced over the surface of the aerofoil. The degree of microstructural evolution within the coating and substrate therefore varies substantially across a blade due to this range in temperatures experienced. Consequently, there is a need to transfer the knowledge gained of the degradation processes of coated Ni-based superalloys under controlled laboratory conditions and samples with uniform geometries to components in service.

This chapter has shown that microstructural maps can be used as an indicator of effective thermal exposure, although for a complete life prediction methodology models are required which link the diffusion mechanisms and phase transformations to the effects of both temperature and stress, and ideally corrosion and oxidation phenomena.
Chapter 9
Conclusions and Further Work

9.1 Overview
The aim of this research was to gain a fundamental understanding of the microstructural evolution as a function of time and temperature in two different coated Ni-based superalloy systems. The focus of the research therefore was the microstructural interactions which occur as a result of interdiffusion between the coating and substrate. Detailed microstructural characterisation allowed the identification of features in the coated Ni-based superalloys which change systematically with time and temperature, and which therefore could be used as an indicator of effective thermal exposure.

9.2 Substrate Alloys
The thermodynamic equilibrium calculations carried out on the two CMSX4 alloys showed that the increase in C content of the CMSX4 HC alloy resulted in no significant change in the amount and composition of the γ and γ' phases present within the alloy. In contrast, increasing the C content by a factor of ~10 from the 'standard' CMSX4 to the CMSX4 HC, resulted in a predicted increase in the fraction of MC and M₂₃C₆ carbides by the same factor.

Both the 'standard' and HC CMSX4 microstructures consisted primarily of primary γ precipitates of cuboidal morphology uniformly distributed throughout the alloy. In addition large regions of γ', identified as γ/γ' eutectics and MC carbides, rich in Ta and Hf with various morphologies, were observed within the HC CMSX4 microstructure. After thermal ageing, clusters of blocky and needle-type precipitates, most probably the μ phase, were observed within the bulk of the 'standard' CMSX4 alloy.

9.3 NiCoCrAlY Coated System
The main microstructural features that have been investigated as a function of exposure temperature and time in this research are within the coating and at the coating/substrate interface, with emphasis on the rate on growth of the interdiffusion zone, depleted layers and
the protective oxide scale. The thermodynamic equilibrium calculations performed on the NiCoCrAlY coating were shown to be representative of the amount and composition of the phases present in the microstructure. It should be noted that the thermodynamic calculations predict a change in stability in the majority of the phases between 850 and 1050°C which corresponds to the temperature range experienced by industrial gas turbine blades.

The detailed microstructural investigations carried out on NiCoCrAlY coated CMSX4 samples isothermally exposed at different temperatures and times indicated significant microstructural changes as a result of isothermal exposure. The depletion of Al (and also Cr) from the coating by the formation and growth of the oxide scale at the coating surface and the interdiffusion with the substrate, resulted in the depletion of β NiAl phase. Both the oxide thickness and β depleted zones increased with increasing ageing time and temperatures as expected. At the lower temperatures and times the oxide scale mainly consisted of Al₂O₃, however, with increased thermal exposure particles rich in Ta, Ti, Hf and Y were present within the oxide. It has been stated in previous work that the protective nature of the oxide is related to the fraction of the β phase within the coating, however the protective oxide scale was still intact following the complete dissolution of β and therefore it is suggested that the coating life of MCrAlY systems is more appropriately related to a critical Al content of the coating rather than the volume fraction of the β phase present.

Interdiffusion of elements occurred at the coating/substrate interface during high temperature service due to the differences in chemical composition between the two, thus promoting chemically driven diffusion of certain elements. At the lower temperatures of 850 and 950°C Cr-rich M₂₃C₆ carbides with a globular morphology were observed adjacent to the interdiffusion zone. In addition, at 950°C, Cr-rich M₂₃C₆ carbides with a geometric morphology were observed within the γ' layer. However, these geometric M₂₃C₆ particles contained a larger amount Re, and therefore it was suggested that these had evolved from the pre-existing σ phases observed at lower temperatures. In addition, MC carbides rich in Ta and Ti were observed with increasing temperature, precipitating in a linear array parallel to the coating/substrate interface.

The diffusion of refractory elements across the coating/substrate interface led to the formation of complex plate-like TCP phases. These TCP phases initiated within the
interdiffusion zone and extended significantly into the substrate at angles of ~45 degrees. It was apparent from the investigation that there was an increase in quantity and size of the TCP phases as the aging temperature and exposure time increased, which resulted in significantly coarsened segmented needle and blocky type structures. TEM studies have allowed the identification of the complex TCP phases formed within the interdiffusion zone. Within the samples exposed at the lower temperatures and lower exposure times up to ~1000 hours the predominant precipitates that formed were the Cr-rich $\sigma$ phase, while after prolonged exposure up to 10,000 hours both $\sigma$ and $\mu$ were present within the IDZ. With increase in temperature the phases identified were a mixture of $\sigma$, $\mu$ and P phase, the predominant phases at higher exposure times being the W and Re-rich $\mu$ and P phase, indicating the high temperature stability of these phases.

A one-dimensional diffusion-based model was developed in a parallel project, to predict the concentration profiles associated with the oxidation and interdiffusion that occurs in MCrAlY coated superalloys. The model was capable of simultaneously managing multiple components, multi-phases, and oxidation using a flexible grid-design, flexible component numbers and moving phase boundaries. The predictions of the model were compared extensively with the experimental observations. It was illustrated that in general there was a broad agreement with the predictions of the major phases precipitating as a function of time at temperature. However, at the higher temperatures of 1050°C the model predicts a greater amount of homogenisation across the coating/substrate interface that was observed experimentally. In respect to the formation of carbides, a broad agreement with the experimental observations and the predictions of the model were shown. However, the treatment of carbon diffusion requires closer examination because it appears that once the carbides form in a particular location through the combination of a particular element with the available C, they are very stable, and therefore possibly further C diffusion through the system should then be prevented.

9.4 Pt Aluminide Coated System

A detailed microstructural investigation was carried out on Pt aluminide coated CMSX4 samples, isothermally exposed at different temperatures and times, which showed that there were significant microstructural changes as a result of isothermal exposure.
Both the RT22 and the CN91 coatings in the as-received condition were found to consist of a single phase $\beta$ matrix, indicating that the Pt has enriched the $\beta$ phase, such that it becomes the $\beta$-(Ni,Pt)Al phase. The as-coated $\beta$-(Ni,Pt)Al phase transformed to $\beta + \gamma'$ after ageing at 850°C due to an increased diffusion of Al from the coating in towards the substrate alloy. The initial $\gamma'$ precipitates were observed adjacent to the coating/substrate interface, therefore, supporting the theory that the $\beta \rightarrow \gamma'$ is not solely due to the outward diffusion of Al from the coating but also the diffusion of Ni from the substrate into the coating. The amount and size of the $\gamma'$ particles within the coating increased with temperature and exposure time. At 950°C, narrow straight parallel bands representative of a martensitic transformation of $\beta$ from the B2 crystal structure to the martensitic L1₀ structure were also observed within the coating.

In the as-received condition, the RT22 coating contained clusters of very small W, Re, and Cr-rich spherical precipitates identified as $\alpha$-W, $\sigma$ and P phase. Exposure at the lower temperatures of 850 and 900°C resulted in an increase in size of the precipitates, which in turn reduced the original cluster formations. The precipitates continued to increase in size and decrease in area fraction with temperature and exposure time, until complete dissolution occurred after 2000 hours at 1050°C. The reduction in area fraction of the precipitates appeared to occur as a result of the increasing $\gamma'$ content with the coating, as $\gamma'$ has a higher solubility for W than that of the $\beta$ phase. In addition, M$_{23}$C$_6$ carbides were observed within the bulk of the coating at the higher temperatures of 950 – 1050°C and exposure times of 2000 and 4000 hours. These carbides were generally located on the $\beta$/ $\gamma'$ grain boundaries due to the low solubility of Cr within the $\gamma'$ and $\beta$ phase.

The interdiffusion of elements between the coating and the substrate occurred during the coating process heat treatment and formed an interdiffusion zone (IDZ) containing several intermetallic phases. The interdiffusion zone consisted of two main layers, the first being a band of precipitates rich in W, Re, Ta and Cr adjacent to the coating/substrate interface, identified as a mixture of W/Re-rich $\sigma$, $\mu$ and P phase. The second layer comprised of a continuous $\gamma'$ layer that separated the coating from the substrate. Initially, small needle-like TCP precipitates were also observed within this $\gamma'$ layer, which ultimately increased in quantity and size with thermal ageing. At the highest temperatures and times these needle-like precipitates were seen to initiate within the interdiffusion zone and extend up to $\sim$ 180 $\mu$m into the substrate at angles of $\sim$ 45°. Within the samples exposed at the lower
temperatures below 950°C, the needle-like TCP phases were predominantly identified as the Cr-rich \( \sigma \) phase, whereas at higher temperatures, the predominant phases observed were the W/Re-rich \( \mu \) and P phase, again indicating the high temperature stability of these phases. The interdiffusion zone was seen to increase in thickness with increase in temperature and exposure time. At the lower temperatures below 950°C the increase in thickness was mainly attributed to the increase in thickness of the \( \gamma' \) layer. Whereas at the higher temperatures the growth of the needle-like TCP phases from the \( \gamma' \) into the substrate was the main contributing factor to the thickness.

W-rich oxides with varying morphologies were observed in the centre of the TCP phases located within the interdiffusion zone of samples aged at the higher temperatures and times. Chemical analysis of the oxides showed them to be rich in W and O with smaller amounts of Cr, P and Ca. It has been suggested that the oxygen originated from the \( \text{Al}_2\text{O}_3 \) grit particles used in the coating process. Although \( \text{Al}_2\text{O}_3 \) is a relatively stable phase, it is possible that it can be reduced within a nickel matrix under certain conditions, with oxygen combining with reactive elements within the interdiffusion zone.

During service the response to load across gas turbine blades is not uniform and therefore, differences in temperature and stress are experienced over the surface of the aerofoil. The degree of microstructural evolution within the coating and substrate therefore varies substantially across a blade due to this range in temperatures experienced. Consequently, the knowledge gained of the degradation processes of coated Ni-based superalloys under controlled laboratory conditions and samples with uniform geometries was successfully transferred to ex-service coated turbine blades.

A complete understanding of the diffusion assisted degradation processes and the microstructural changes that take place within the coating, interdiffusion zone and substrate material is crucial in order to develop more accurate life prediction procedures for coatings and coated Ni-based superalloys. Modelling of these diffusion processes which occur during service can be an important tool to predict coating and substrate degradation as a function of time and operating temperature. Such a tool is of great advantage in the estimation of long term component performance, and for the selection and/or development of optimum coating/substrate combinations.
This research has shown that microstructural maps can be used as an indicator of effective thermal exposure, although for a complete life prediction methodology models are required which link the diffusion mechanisms and phase transformations to the effects of both temperature and stress, and ideally corrosion and oxidation phenomena.

9.5 Further Work

A number of areas of further work have been identified as a result of this research. The investigations on the coated superalloy systems in this research have only involved oxide scale thickness measurements as a function of exposure time and temperature rather than their detailed characterisation. A greater understanding of the growth, phase stability and mechanical properties of the oxide scales is required in order to fully understand its effect on the microstructural evolution of coated superalloy systems. A large portion of the research has been concerned with coating/substrate interactions and the various microstructures that form with thermal exposure, focussing on diffusion in an essentially linear manner between the coating and the substrate. It would also be interesting and useful to investigate the morphology of the TCP phases within the interdiffusion zone with the use of serial sectioning in the FIB FEGSEM, with the aim of 3D reconstruction in order to study the relationships between different phases. Further detailed investigations comparing the inward and outward grown PtAl coatings are also required in order to fully understand the differences between and benefits from each system.

In respect of modelling the various interactions, it has been shown that the model developed to date in a parallel project is in broad agreement with the experimental observations for MCrAlY coated superalloys. However, a model that can incorporate the nucleation and growth of particles together with their morphology, such as the phase field technique, with the thermodynamic/kinetic model could allow for a more complete prediction of the evolving phases with time at temperature. Thermodynamic data for platinum aluminide coated systems is required for the development of life prediction models similar to those for MCrAlY coated systems. Work is already underway to link the microstructural evolution models with the mechanical behaviour of a coated system, however, this will also require additional verification in order to provide enhanced life prediction methodologies for these complex coated systems.
References


Figure 6.11  *Simulated predictions of the β phase profiles across the coating at a) 850°C, b) 950°C and c) 1050°C for increasing ageing times.*

Figure 6.12  *Comparison of the predictions and measured experimental data for the β depletion thickness at the coating surface as a function of ageing time at a) 850°C and b) 950°C.*