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The Production and Properties of Zinc-Nickel and Zinc-Nickel-Manganese Electroplate

By

Harriet Jill Kimpton

A Doctoral thesis submitted in partial fulfilment of the requirements for the award of Doctor of Philosophy of Loughborough University

2002

Supervisor: Dr G. D. Wilcox
IPTME, Loughborough University,
Loughborough, Leics, LE11 3TU

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Abstract

The aim of this research project was to produce compositionally modulated zinc-nickel and zinc-nickel-manganese coatings using a single bath process by variation of the applied electroplating current density. These could then be considered as possible replacements for electroplated cadmium. Zinc-nickel electrodeposits from both a simple bath and one containing the complexant tris(hydroxymethyl)methylamine (TRIS) were produced using either bath or by selective electroplating onto mild steel, 2014-T6 aluminium and 2000 series aluminium alloy connector shells. Zinc-nickel-manganese coatings were electroplated onto mild steel, using both DC and pulse electroplating from sulphate based baths containing either the complexant TRIS or sodium citrate.

The coatings and the various electrodeposition processes were evaluated by thickness measurements, current efficiency calculations, composition determination using energy dispersive X-ray analysis and SEM to examine the morphology. Corrosion characteristics were investigated by neutral salt fog exposure, alternate immersion, atmospheric trials, and electrochemical immersion tests including potential monitoring, galvanic and polarisation measurements. Other properties such as micro-hardness and surface electrical conductivity were also investigated.

Compositionally modulated zinc-nickel and zinc-nickel-manganese were successfully deposited from single baths with nickel contents ranging from 5-20% Ni and manganese contents varying from 0-12% Mn. Current efficiency measurements showed the efficiency to be low especially for the zinc-nickel-manganese coatings, which exhibited a distinct morphology when electroplated from the citrate bath.

Corrosion testing indicated that both coatings had a lower corrosion resistance than cadmium especially in accelerated tests, with a reduction in corrosion resistance being seen as the nickel content was increased, due to a decrease in density of the electroplate. This, and increasing through-thickness porosity promoted ennoblement of zinc-nickel and zinc-nickel-manganese leading to the coatings becoming non-sacrificial to the substrate in accelerated tests. Zinc-nickel-manganese showed less white rust than zinc-nickel and exhibited higher micro-hardness than zinc, cadmium
and zinc-nickel. Electrical measurements indicated that both coatings were sufficiently conductive to meet the surface conductivity requirements for use on electrical connector shells.

Keywords
Zinc alloy electroplating, zinc-nickel, zinc-nickel-manganese, corrosion resistance, corrosion testing, cadmium replacements, complexants.
Acknowledgements

The completion of this work has been greatly facilitated by the support and advice of Dr. G. D. Wilcox and Dr. C. J. E. Smith together with other staff members in the Corrosion protection team at QinetiQ and Loughborough. I would like to thank Dr. M. Ward for help in using the pulse electroplating facilities at Loughborough University, and the Ministry of Defence (MOD) for funding this work.

I would also like to express my gratitude to my family for having tolerated my obsession with this work over the last three and a half years, especially Roy whose support and patience has helped to facilitate its completion.
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Nomenclature

AC = Alternating current

\( a_{\text{oxidised}} \) = Activity of oxidised species

\( a_{\text{reduced}} \) = Activity of reduced species

\( b_a \) = Slope of anodic Tafel region

\( b_c \) = Slope of cathodic Tafel region

CE = Current efficiency

CRL = Composition reference line

DC = Direct current

\( E_{\text{corr}} \) = Corrosion potential

EDAX = Energy dispersive X-ray analysis

\( E_e \) = Equilibrium potential

\( E^{0}_e \) = Standard equilibrium potential

\( E_{\text{plating}} \) = Electroplating potential

F = Faradays constant

\( F_1 \) = Fraction of compound 1 in alloy

\( F_2 \) = Fraction of compound 2 in alloy

\( F_3 \) = Fraction of compound 3 in alloy

\( g_a \) = Actual deposit weight

\( g_t \) = Theoretical deposit weight

I = Current

\( i_{\text{corr}} \) = Corrosion current

\( I_{\text{corr}} \) = Corrosion current density

\( I_p \) = Peak current density for pulse electroplating

LPR = Linear polarisation resistance

L_{7} = Robust design array, 7 factors at 2 levels

\( n_e \) = number of electrons

PTFE = Polytetrafluoroethylene

R = Gas constant

\( R_{\text{ct}} \) = Charge transfer resistance

\( R_p \) = Polarisation resistance

SCE = Saturated calomel electrode

SEM = Scanning electron microscopy
Nomenclature

t = Time of electroplating
T = Absolute temperature
t_c = Charging or on time of pulse in pulse plating
t_d = Discharging or off time of pulse in pulse plating
t_on = On time or charging time of pulse
t_off = Off time or discharging time of pulse
W_a = Chemical equivalent
W_1 = Equivalent weight of compound 1
W_2 = Equivalent weight of compound 2
W_3 = Equivalent weight of compound 3
\Phi = Duty cycle in pulse plating
1 Introduction

Cadmium electroplate is still used as a coating where good corrosion resistance, low amounts of corrosion products, lubricity and galvanic compatibility with aluminium and its alloys are vital. These include electrical connector shells and fasteners for aerospace applications. The search for replacements for cadmium has been continuing for many years, without total success. Nine years ago it was suggested that a replacement for cadmium would be found within the next five years [1]. This was over optimistic and devalued the uniqueness of cadmium and its significant properties. It is hence unlikely that this research programme will find a “drop in” replacement for cadmium. It may, however, increase the knowledge of electroplating alloy systems, their properties and potential as replacements for cadmium.

Zinc based alloy systems have been suggested as cadmium replacements [2,3], but suffer from increased levels of corrosion products and no inherent lubricity. Different methods can be used to make zinc alloy systems more applicable as replacements, these include the use of multi-layer systems, the addition of other alloying elements and the incorporation of lubricity.

1.1 Aims and objectives

This research programme focuses on two methods of increasing the suitability of zinc-nickel coatings as replacements for cadmium. The first method being the use of multi-layer compositionally modulated coatings and the second, the addition of another alloying element, namely manganese to binary zinc-nickel.

In order to electroplate multi-layer coatings from a single electroplating bath a means of controlling the alloy content is required. This investigation concentrates on the variation of the applied electroplating current density to give different compositions of zinc-nickel. The feasibility of producing zinc-nickel coatings with different nickel contents from a single bath is firstly evaluated. Dual layer coatings are then produced to demonstrate the possibility of producing multi-layer coatings.

Accelerated corrosion testing was then undertaken on the coatings produced to assess their suitability as replacements for cadmium. The morphology, composition and
other properties such as micro-hardness and electrical conductivity was also investigated.

The addition of manganese to zinc-nickel requires a solution, which is capable of co-depositing all three metals of the ternary alloy at satisfactory values of applied electroplating current density. This can be achieved by the use of complexants. Two different complexants are investigated. When it was found possible to produce ternary zinc-nickel-manganese coatings, the use of applied electroplating current density as a means of controlling the alloy content was evaluated. This leads to the possibility of combining the two methods used, namely multi-layers and the addition of manganese, to give a coating more suitable as a replacement for cadmium. Like the zinc-nickel coatings the ternary zinc-nickel-manganese coatings were also assessed for their corrosion and other properties.

This report is divided into a number of sections. A literature review is first given, the objective of which is to assess the problems of alloy electroplating, to discuss the various merits of each sacrificial alloy systems and the difficulty of assessing the possible corrosion performance of that system by the use of various accelerated and non-accelerated corrosion tests. Experimental procedures used are then specified. The production of zinc-nickel single and dual layer coatings is then discussed with the composition, morphology and electroplating bath characteristic results being given. Zinc-nickel-manganese coating trials and results of investigating the composition variation and bath parameters follow. Two sections investigating the corrosion performance of firstly, zinc-nickel single and dual layer coatings, and then zinc-nickel-manganese coatings complete the results. A comparison between the two different methods of modifying the properties of zinc-nickel coatings is made throughout the results sections.

The report concludes with a discussion directed at the possibility of using either or both of the two methods investigated as means of changing the properties of zinc-nickel coatings to make them suitable as replacements for cadmium. Here a critical overview of the progress made in this research is given along with suggestions for improvements and further work.
2 Literature Review

2.1 Introduction

In order to look for a replacement for cadmium for aircraft applications, the first thing that is needed is a knowledge of its advantages and disadvantages. Secondly, an understanding of the actual electroplate requirements is needed. It may be possible to replace cadmium using techniques not based on electroplating. Other coating techniques such as sputter deposition [4-7], electroless metallic coating [8-10], and plasma vapour deposition [11,12], can be used to deposit metallic coatings. These methods are not used at present to deposit cadmium. Hence this investigation will be limited to the use of electroplating as a means of producing a possible replacement for cadmium. Electroplating also has several advantages over the other techniques, mainly the variety of metals and alloys that can be produced and the relative low cost of the basic equipment required.

After the problem is defined, the available alternatives need investigating and their advantages and disadvantages assessed. Ways in which other researchers have attempted to improve or modify the coatings need to be understood. Finally, an assessment of the methods of characterising the coatings and undertaking the research is required.

This literature review is hence divided into a number of sections, the first dealing with a definition of the problem, the second with what alternatives are available and their advantages and disadvantages. The next section deals with the mechanics of changing the coating properties to make them more suitable for the applications considered. Finally the characterisation methods that can be employed are reviewed.

2.2 Cadmium electroplate

A replacement for cadmium electroplating is required due to the toxic nature of cadmium and cadmium electroplating processes and the associated cost due to adherence to increasingly stricter health and safety guidelines. The original drive to find a replacement for cadmium came when Japan strictly limited and then outlawed the use of cadmium [13]. In Europe cadmium use is now governed by an EU directive
Current (1995) occupational health levels for air quality are set at 2.5 \( \mu g \, m^{-3} \). The 8 hour Time-Weighted Average Personal Exposure Limit (TWA PEL) is 5 \( \mu g \, m^{-3} \). The annual compliance cost associated with these limits is estimated at $200 million in the USA (1995 figures). Wastewater is also limited to 0.11 mgdm\(^{-3}\) for any single day with 0.07 mg/L as a monthly average [15]. At present the discharge limits for cadmium and other electroplating processes in the USA are under review and are likely to become much more stringent [16-18]. This makes the replacement of cadmium more critical. Wastewater from cadmium electroplating plants can be treated to reduce the amount of cadmium discharged [19], however, this adds to both the cost and complexity of the cadmium electroplating process.

Cadmium electroplating is widely used on aircraft for the corrosion protection of fasteners and electrical components [4,20]. The use of cadmium has advantages and disadvantages. These are summarised in Table 2-1 [21]. At present there is no one substitute with all the advantages of cadmium although several alternatives with some of the beneficial properties of cadmium are available [1], cadmium is still used when coating reliability and overall safety is a major consideration as in the case of electrical connectors and fasteners on aircraft [22].

<table>
<thead>
<tr>
<th>Advantages</th>
<th>Disadvantages</th>
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<tbody>
<tr>
<td>• Good barrier against corrosion</td>
<td>• Toxicity</td>
</tr>
<tr>
<td>• Sacrificial coating</td>
<td>• Electroplating from cyanide baths</td>
</tr>
<tr>
<td>• Galvanically compatible with aluminium alloys</td>
<td>• Hydrogen embrittlement associated with electroplating process</td>
</tr>
<tr>
<td>• Good surface lubricity</td>
<td>• Cost</td>
</tr>
<tr>
<td>• In situ repair by brush plating</td>
<td></td>
</tr>
<tr>
<td>• Low amount of corrosion products formed</td>
<td></td>
</tr>
<tr>
<td>• Low electrical resistance</td>
<td></td>
</tr>
<tr>
<td>• Solderability</td>
<td></td>
</tr>
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</table>

Table 2-1 Advantages and disadvantages of cadmium electroplating

Cadmium electroplate is ideally suited for use on electrical connectors for a number of reasons. Some typical electrical connectors for use on military aircraft are illustrated in Figure 2-1 to help demonstrate the complexity of the problem and why cadmium is used. Electrical connectors for aircraft are normally manufactured from a lightweight strong aluminium alloy (2014-T6 is normally used [3,23]) which is then
nickel electroplated, followed by cadmium and then passivated with olive drab chromate [24,25].

Figure 2-1 Typical electrical connectors [26]

The important properties of cadmium for electrical connectors are the sacrificial nature of the coating, the galvanic compatibility with aerospace alloys, the low amount of corrosion products formed and the electrical resistance of the cadmium. A sacrificial coating is required to prevent corrosion of the substrate even when the coating is damaged. The galvanic compatibility due to connectors being sometimes earthed to the aluminium framework of the aircraft is also important. The low amount of corrosion products and lubricity is due to the requirement for connecting and reconnecting the connectors during service (called mating and un-mating). Low electrical resistance is required due to the need for an adequate electro-magnetic shield around the aircraft [27]. A direct cadmium replacement would need similar properties. The low electrical resistance requirement is only specific to electrical connectors, other areas on an aircraft which use cadmium electroplate such as fasteners do not have this requirement. The need for low electrical surface resistance is one of the main problems with finding a direct replacement for cadmium for electrical connectors. In fact even cadmium has a higher electrical resistance than
would be desirable in a modern aircraft [27], with nickel or palladium being suggested as possible replacements. These are, however, not sacrificial and hence would cause accelerated corrosion of the substrate if damage to the coating was to occur. The electrical specification means that a metallic coating must be used, and that any passivation treatment used must also be conductive. This negates the use of anodising and polymeric finishes.

In addition, certain bath characteristics are required in order to electroplate connectors. As can be seen from Figure 2-1, electrical connectors are complex in shape with details such as threads, which need to be electroplated evenly. This requires the electroplating bath to have good throwing power (the ability to coat complex shapes evenly). Due to this, cadmium is normally electroplated from cyanide based baths because of their high throwing power, however, the toxicity of cyanide is another problem [22]. Good bath ageing characteristics, low operating temperature and high efficiency are also important for most electroplating processes as is the number of stages within the overall process. This needs to be minimal to reduce costs.

The replacement of cadmium on electrical connectors is hence a complex dilemma. The substitute coating would have to be metallic, highly conductive, galvanically compatible with aerospace materials, with a low corrosion rate and non-voluminous corrosion products, but sacrificial to the main body of the connector shell. It would also have to have inherent lubricity and be hard enough to withstand mating and unmating cycles. It would need to cover complex shapes evenly and be easy and cheap to produce. It would also have to be less toxic than cadmium and be electroplated from an environmentally acceptable electrolyte.

2.3 Sacrificial electroplated coatings

There are a number of metals, which are sacrificial to steel and aluminium alloys under immersion conditions. The galvanic series of some metals and alloys is given in Table 2-2. As can be seen cadmium, pure aluminium, zinc and its alloys, manganese and its alloys, and magnesium and its alloys are all sacrificial to both 2024 aluminium and steel in seawater. However, the order of the galvanic series is different in different media, hence although zinc is sacrificial to steel in sea water in hot tap water it is not [28]. Under most atmospheric conditions zinc is sacrificial to steel and aluminium.
<table>
<thead>
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<th>Potential versus SCE/ V</th>
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<tr>
<td>Graphite</td>
<td>0.19 to 0.25</td>
</tr>
<tr>
<td>Gold</td>
<td>0.2</td>
</tr>
<tr>
<td>Platinum</td>
<td>0.19 to 0.23</td>
</tr>
<tr>
<td>Titanium</td>
<td>-0.06 to 0.06</td>
</tr>
<tr>
<td>Silver</td>
<td>-0.15 to -0.1</td>
</tr>
<tr>
<td>Lead</td>
<td>-0.35 to -0.22</td>
</tr>
<tr>
<td>Tin</td>
<td>-0.33 to -0.3</td>
</tr>
<tr>
<td>Steel</td>
<td>-0.72 to -0.58</td>
</tr>
<tr>
<td>Cadmium</td>
<td>-0.75 to -0.70</td>
</tr>
<tr>
<td>2024 Aluminium alloy</td>
<td>-1.0 to -0.71</td>
</tr>
<tr>
<td>Commercially pure aluminium</td>
<td>-1.0</td>
</tr>
<tr>
<td>Zinc and zinc alloys</td>
<td>-1.10 to -0.98</td>
</tr>
<tr>
<td>Manganese and manganese alloys</td>
<td>-1.15 to -1.05</td>
</tr>
<tr>
<td>Magnesium and magnesium alloys</td>
<td>-1.65 to -1.50</td>
</tr>
</tbody>
</table>

Table 2-2 Galvanic Series of some metals and alloys in seawater [28,29]

Magnesium, magnesium alloys, aluminium and its alloys are too reactive to be electroplated from aqueous solution, although aluminium may be electroplated from non-aqueous media [30]. This is a difficult process and the use of aluminium as a coating is unlikely to meet the conductivity requirements for connector shells as aluminium spontaneously forms an oxide layer on contact with the atmosphere or water.

This leaves manganese, its alloys and zinc and its alloys. Manganese can be electroplated but suffers from low current efficiency and poor throwing power. The current efficiency of the process can be increased by the addition of selenium [31]. Manganese electroplate is very brittle, has a high hardness and is initially very reactive. Its corrosion products are deep coloured. The brittle nature of manganese and its poor throwing power would make it unsuitable as a replacement for cadmium. There is also a question as to its corrosion resistance in atmospheric conditions and under immersion conditions [31].

Hence this review will concentrate on zinc and its alloys. Binary alloys of zinc, which have been investigated include zinc-nickel, zinc-iron, zinc-cobalt and zinc-manganese.
2.4 Zinc electroplate

Zinc coatings, especially galvanised zinc, are used extensively for the protection of steel. They provide sacrificial protection in most environments [2]. Electroplated zinc is also used as a coating for non-aerospace electrical connectors onto 2000 series aluminium alloys, but relies on a thicker chromate passivate to achieve corrosion resistance similar to cadmium [3].

The corrosion rate of zinc is approximately linear with time in most aggressive environments and is higher than cadmium, except in acidic sulphur containing industrial environments [2]. Milder atmospheres usually will enable zinc to form a more protective corrosion product layer hence reducing corrosion rates [32].

The corrosion rate increases with an increase in the amount of sulphur compounds in the atmosphere. Chlorides and nitrogen oxides usually have a lesser effect but can be significant in combination with sulphate. The presence of sulphur compounds in alkaline media also have a large effect on the corrosion rate [33]. This is due to the corrosion products of zinc only being stable over a very limited pH range, leading to dissolution of the protective passivation layer in polluted atmospheres [34]. The morphology of the coating can also affect the corrosion performance [35].

The corrosion rate increases with the time of wetness of the zinc. When zinc electroplate is stored under wet conditions, a wet storage stain is produced. This is sometimes referred to as "white rust" and is voluminous, white and powdery. "White rust" formed in uncontaminated air usually consists mainly of basic zinc carbonate mixed with zinc oxide. When no carbon dioxide is present only hydrated zinc oxide forms. The white, powdery zinc oxide corrosion products of zinc make it seem unsuitable as a replacement for cadmium. However, the level of "white rust" is very dependant on the level of carbon dioxide present, with some accelerated tests used by industry as a means of assessing coatings, producing excessive "white rust" discouraging the use of zinc as a replacement for cadmium. The primary electrochemical reaction leading to the formation of "white rust" in the presence of air and moisture is [28]:
Zn$^{2+}$ + 2OH$^-$ → Zn(OH)$_2$↓ \[\text{Equation 2-1}\]

The zinc hydroxide that is precipitated from this reaction then reacts further;

Zn(OH)$_2$ → ZnO + H$_2$O \[\text{Equation 2-2}\]

or

5Zn(OH)$_2$ + CO$_2$ → 2ZnCO$_3$.3Zn(OH)$_2$ + 2H$_2$O \[\text{Equation 2-3}\]

or

5ZnO + 2CO$_2$ + 3H$_2$O → 2ZnCO$_3$.3Zn(OH)$_2$ \[\text{Equation 2-4}\]

The higher corrosion rate of zinc and the increase in corrosion products when compared with cadmium make the reduction in corrosion rate possible by modification of the structure or properties of the zinc electroplate and passivation layer attractive. The use of alloying elements such as nickel and cobalt to the zinc electroplate is one method of possibly achieving this goal. Another method that has been investigated is the co-deposition of inert particles within the zinc electroplate. This has the effect of reducing the corrosion rate of the zinc electroplate when measured using neutral salt fog testing. The co-deposition of particles of manganese oxide, iron oxide, silicon carbide and titanium nitride have all been investigated [36], as has the co-deposition of silicon carbide with and without aluminium oxide additives [37]. By adding between 5-6% of these inert particles the wearability, hardness and corrosion resistance were improved. The increase in corrosion resistance was thought to be due to the inert particles acting as a physical barrier and shielding the zinc from aggressive species [36]. This shielding of the zinc would be important when assessing its corrosion rate using neutral salt fog, which prevents the formation of the more stable zinc carbonate species leading to excessive “white rust” formation. Whether the addition of inert particles would also increase the atmospheric corrosion resistance of zinc or prevent the formation of a stable continuous passive layer of zinc
carbonate would need to be evaluated before it was suggested as a means of increasing the corrosion resistance of zinc electroplate. The co-deposition of inert particles may also increase the electrical resistance of the zinc electroplate, but it may be useful as a means of imparting some lubricity to the system [38].

Normally zinc electroplate and other zinc alloys are passivated with chromate to increase the corrosion protection offered. However, chromates are also subject to legislation and replacements are being sought. One such replacement is a molybdate/phosphorous system [39]. The corrosion rate of chromated zinc has also been found to be dependent on both the atmospheric conditions and the nature of the passivated film. Zinc, in neutral environments, has a corrosion rate more dependant on the nature of the passivation rather than the thickness of the zinc layer on steel, whilst in acid environments, the overall corrosion rate is more dependant on the thickness of the zinc electroplate [40]. Whether this change in performance of the chromate passivation is limited to chromate or is applicable to other non-chromate treatments has not been investigated. This means it is not known which species (the chromate layer or the underlying zinc electroplate) is the cause of the change in behaviour of the zinc in acid conditions.

Other properties of zinc electroplate which may affect its suitability for use as a cadmium replacement are its wear properties, which are dependant on the level of corrosion present on the surface of the zinc [41] and lack of lubricity. Hence, in order to make zinc a suitable replacement for cadmium electroplate, its corrosion resistance needs to increase, its corrosion products to decrease and its lubricity and wear characteristics to improve.

The advantages of using zinc electroplate rather than cadmium are related to the ease of the electroplating process and of the lower toxicity of the electroplate. The electroplating of zinc coatings is a very mature technology, which has been practiced for nearly one hundred years. Up until about 1915 all zinc electroplating was carried out from acid electrolytes. In the 1920s alkaline cyanide baths took over with formulations containing about 7.5 g dm$^{-3}$ zinc metal, sodium cyanide and approximately 30 g dm$^{-3}$ of sodium hydroxide. Modern alkali cyanide baths are based on these [42]. Bright zinc deposits appeared in the 1930s and have a whiter and more
lustrous appearance. Additives to the basic cyanide solutions include molybdenum, tungsten and manganese as well as aromatic aldehydes and colloids such as gelatine. Cyanide zinc is still used for the electroplating of aluminium connector shells because of its good throwing power [3]. This is helped by the inverse relationship between the current efficiency and the cathodic current density [43]. Attempts have been made to use other complexing agents to replace cyanide, which are more environmentally friendly. One such replacement is aminotris(hydroxymethyl)methane [44]. This, however, is said to require the use of other additives such as EDTA to give bright deposits, making the bath chemistry more complicated, and effluent treatment more costly.

Acid zinc baths are cheaper to operate than the alkaline cyanide baths but a reduction in throwing power is observed. The deposits tend to be coarser grained than those produced from alkaline cyanide baths. Acid zinc baths do not cause the level of hydrogen embrittlement that alkaline zinc electroplating can cause on high strength and alloy steel substrates. They are also easier to effluent treat as they do not contain complexants. However, ammonium chloride is sometimes used in the bath, and this then increases the difficulty of waste treatment [45]. Other salts tend to be added to acid zinc sulphate baths both to improve the conductivity of the solution and to improve the throwing power. Satisfactory zinc deposits are obtained in the pH range 3.5-4.5. At lower pH values, the anode consumption markedly increases owing to chemical attack by the solution. At higher pH values Zn(OH)₂ may precipitate leading to a rough deposit. Both aluminium sulphate and boric acid are used to help stabilise the pH.

The level of hydrogen embrittlement of alkaline zinc baths can be reduced by the addition of additives to the bath [46]. The can reduce the original rate of the hydrogen reaction on steel and hence lessen the amount of hydrogen absorbed into the steel, hence reducing hydrogen embrittlement. Additives that can be used in alkaline zinc baths include vanillin and complexing agents such as EDTA [47].

Because the electroplating of zinc is fairly easy, cheap, has good throwing power and well defined bath characteristics, such as high current efficiency, good ageing properties, zinc electroplate would make a suitable replacement for cadmium from a
production point of view. This does not, however, override the fundamental flaws in
the corrosion resistance and other properties of the coating.

To improve the corrosion resistance properties of zinc electroplate research has
focused on the alloying of zinc with other elements, these include nickel, cobalt and
iron.

2.5 Alloy electroplating

By co-depositing zinc with another metal, the corrosion resistance of the electroplate
is said to increase [48-50]. However, most testing of zinc alloy coatings has focused
on accelerated testing including neutral salt fog. As mentioned previously the use of
neutral salt fog to assess the corrosion of zinc alloys may be flawed, as zinc does not
form the passive carbonate film seen in atmospheric conditions inside the neutral salt
fog cabinet. It therefore produces excessive “white rust” in accelerated testing. The
commercially available alloys of zinc are shown in Table 2-3 along with some
information about their alloy composition and electroplating parameters.

<table>
<thead>
<tr>
<th></th>
<th>Acid Zn/ Co</th>
<th>Alkaline Zn/Co</th>
<th>Zn/Fe</th>
<th>Acid Zn/Ni</th>
<th>Alkaline Zn/Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>Typical alloy content</td>
<td>0.4-1.0%</td>
<td>0.4-1.0%</td>
<td>0.3-1.0%</td>
<td>7-13%</td>
<td>4-7%</td>
</tr>
<tr>
<td>Electrolyte</td>
<td>Potassium chloride, ammonium chloride or boric acid</td>
<td>Hydroxide</td>
<td>Hydroxide</td>
<td>Ammonium chloride</td>
<td>Hydroxide</td>
</tr>
<tr>
<td>Electroplating efficiency</td>
<td>95-100%</td>
<td>50-80%</td>
<td>50-80%</td>
<td>90-95%</td>
<td>30-50%</td>
</tr>
<tr>
<td>Throwing power</td>
<td>Poor</td>
<td>Good</td>
<td>Good</td>
<td>Poor</td>
<td>Good</td>
</tr>
<tr>
<td>Materials required for equipment</td>
<td>Acid resistant</td>
<td>Mild steel</td>
<td>Mild steel</td>
<td>Acid resistant</td>
<td>Mild steel</td>
</tr>
</tbody>
</table>

Table 2-3 Major zinc alloys industrially available [48-50]

As the electroplating of alloy coatings is more complicated than the deposition of
single metal coatings it was thought prudent at this stage to review the basic
mechanisms of alloy deposition [51].
Each metal has a different electrochemical potential. It therefore becomes difficult to deposit two or more metals together and to control the amount of each metal deposited. If the equilibrium potentials ($E_e$) are close together it is a relatively easy task to co-deposit the metals. Slight differences within the potential and current curves for the metals allow for changes in the composition of the alloy produced.

If the slopes of the potential versus current curves are very different from each other, it then becomes possible to deposit alloys of varying composition by changing the overpotential or current applied to the solution.

If the metals to be electroplated have very different potentials, the only way to co-deposit them is to change the activity of one or more within the solution. This can be done either by complexing one of the metals whilst leaving the other as a simple salt or by complexing both metals where one metal complex is stronger than the other, this changes the activities and hence the potentials according to the Nernst equation (Equation 2-5).

$$E_e = E^\circ_e + \frac{RT}{n_eF} \ln \frac{a_{\text{oxidised}}}{a_{\text{reduced}}}$$

*Equation 2-5*

where $E_e = \text{equilibrium potential}$, $E^\circ_e = \text{standard equilibrium potential}$, $R = \text{gas constant}$, $F = \text{Faradays constant}$, $n_e = \text{number of electrons}$, $T = \text{absolute temperature}$ $a_{\text{oxidised}} = \text{the activity of the oxidised species}$, and $a_{\text{reduced}} = \text{the activity of the reduced species}$.

Both these methods have the effect of moving the potential-current curves closer together, hence allowing the metals to be co-deposited.

The way in which each metal co-deposits within a given alloy system has been categorised based on the nobility or activity of each metal present, to assist in the definition of a given alloy system. According to Brenner [31], alloy deposition can be divided into 5 different types;
1. Regular co-deposition
2. Irregular co-deposition
3. Equilibrium co-deposition
4. Anomalous co-deposition
5. Induced co-deposition

In regular co-deposition, the deposition is under diffusion control, the ratio of metals in the alloy are determined from diffusion theory. The percentage of the more noble metal within the alloy increases with an increase in the amount of that metal in the electroplating bath and with a decrease in current density. Regular co-deposition is most likely to occur in electroplating baths containing simple salts and when the metals to be co-deposited have very different static potentials and do not form solid solutions on deposition.

Irregular deposition is characterised by sometimes being diffusion controlled while at other times being more dependant on the potentials of the different metals. Thus irregular deposition gives rise to alloy compositions, which are contrary to diffusion theory. The effects of electroplating variables on the final alloy composition, such as metal ion concentration and current density, are much smaller than for regular co-deposition. Irregular deposition is more likely to occur when both metals are complexed, especially if the equilibrium potential of one of the metals is significantly affected by the complexing ion.

In equilibrium deposition the solution used is in chemical equilibrium with both the metals in solution. The composition of the alloy produced will be the same as the ratios of the metal ions in solution.

In all these first three types of alloy deposition, the more noble metal will deposit preferentially. They can therefore be termed normal co-deposition. In the remaining two types of alloy deposition this is not the case and the more reactive metal can be deposited preferentially.

In anomalous co-deposition the least noble metal deposits preferentially. With a given deposition bath, anomalous co-deposition only occurs under some conditions of
concentration and operating variables, such as current density. Anomalous co-deposition is quite rare but occurs with deposits containing one or more of the iron group metals, iron, nickel and cobalt. Anomalous co-deposition of the zinc-iron group metals is illustrated in Figure 2-2.

Region I is normal co-deposition, Region II is anomalous co-deposition and Region III is where normal deposition again starts to occur [52]. Anomalous co-deposition of zinc-cobalt is thought to be due to the hydroxide suppression mechanism [53]. This mechanism suggests that when a more noble metal is co-deposited with a less noble metal, the pH at the substrate surface rises due to hydrogen evolution, concurrent with the zinc-cobalt electroplating process, forming a hydroxide of the less noble metal, which then inhibits the deposition of the more noble metal. However, the anomalous co-deposition of zinc-nickel has been investigated using chrono-amperometric techniques [54] and has been found to be possibly not due to the hydroxide suppression mechanism but to the ease of the hydrogen-nickel reaction. Here it was found that, initially, the reaction was dominated by the formation of Ni-H on the surface. As the reaction proceeded, more zinc became deposited on the surface. The hydrogen reaction on zinc is difficult [55], hence the rate of the hydrogen reaction...
was slowed. The hydrogen reaction is shown in Equation 2-6. This decreases in turn the rate of formation of Ni-H and hence, reduces the rate of nickel incorporation. Zinc is therefore deposited preferentially.

\[ 2H^+ + 2e^- \rightarrow H_2 \]

*Equation 2-6*

This mechanism rather than the hydroxide suppression mechanism has also been found to occur with nickel-cobalt electroplating [56] where the anomalous co-deposition was attributed to a high exchange current density of the cobalt reaction. This lead to the cobalt reaction in nickel-cobalt proceeding at about the same rate as in pure cobalt electroplating, whereas the nickel reaction was significantly slowed down by the presence of the cobalt giving anomalous co-deposition. It was also found that anomalous co-deposition did not occur in nickel-cobalt when a complexing agent was added. This was attributed to the fact that the complexing agent significantly affected the rates of both the nickel and cobalt reactions, with a more significant effect on the nickel reaction, resulting in normal co-deposition.

The problem with the hydroxide suppression mechanism theory is that it requires a large increase in localised pH at the interface between the substrate and solution. Whether such a large pH change can occur is debatable. However, if mono-hydroxide formation was responsible for the reluctance of the more noble metal to be deposited, a large pH change would not be a pre-requisite. The anomalous co-deposition of nickel-iron has also been investigated. The mechanism of deposition from a simple additive free sulphate solution was found to be due to mono-hydroxide formation *i.e.* NiOH\(^+\) and FeOH\(^+\) rather than Ni(OH)\(_2\) and Fe(OH)\(_2\) showing that a pH rise was not a necessary pre-requisite of anomalous co-deposition [57]:

The addition of additives such as oxygen and boric acid were found to influence the composition of the plated alloy. Boric acid was found to increase the rate of iron deposition as did the removal of dissolved oxygen, suggesting that indeed the hydroxide or mono-hydroxide was responsible for the anomalous co-deposition [58]. When there was less oxygen within the solution the formation of the mono-hydroxide
was inhibited causing an increase in the more noble metal, in this case iron, within the coating. The formation of the normal hydroxide could also have caused this effect but the ease of the hydrogen reaction on the metal surface would not have changed with the removal of oxygen, hence in this solution this is not the dominant mechanism.

The reasons for anomalous co-deposition are not therefore fully understood with several theories being available. It may be that all the possible reasons for anomalous co-deposition occur to a greater or lesser extent within a given system i.e. in some systems the ease of the hydrogen reaction is significant, in others the formation of the mono-hydroxide and in others the formation of the hydroxide. Even although the mechanisms are not understood, a given alloy system can still be characterised as being anomalous or not.

Induced co-deposition occurs with metals, which cannot be deposited alone such as tungsten and molybdenum. Metals, which increase the amount of deposition of these "reluctant" metals, are inducing metals. Iron group metals tend to be inducing metals. This type of deposition is not normal and the more noble metal is not deposited preferentially. Recently investigations have been carried out to investigate the co-deposition of compositionally modulated cobalt-tungsten alloys by using pulse plating [59]. The percentage of the reluctant metal tungsten could be changed by adding an anodic etch cycle to the pulse plating resulting in thin layers of alloy of different composition from the same bath.

2.6 Zinc-nickel

Zinc-nickel is an alloy system, which exhibits anomalous deposition. The least noble metal, in this case zinc is deposited preferentially over certain regions of current density or temperature. The addition of nickel to zinc electroplating helps to improve the deposit characteristics. Nickel is known to help improve the levelling power and brightness of deposits and is commonly used as an intermediate plated layer in many processes [60], hence its addition to zinc should help increase some of the deposits characteristics, namely levelling and brightness.
Zinc-nickel has been shown to offer higher corrosion resistance than either zinc-cobalt or zinc-iron in neutral salt fog corrosion testing, but is more expensive [61]. The perceived improvement in corrosion resistance may not occur in natural environments and may not justify the increased cost. Zinc-nickel does not give as good corrosion resistance when also subjected to abrasion or wear [62]. This would limit its application as a replacement for cadmium on fasteners and electrical connectors as these are both subjected to wear. Acid zinc-nickel has been shown to offer higher corrosion resistance than pure zinc (about 5-6 times better measured by neutral salt fog) [48,63] especially if applied in compositionally modulated layers [64]. Again, these measurements of corrosion resistance were limited to accelerated test methods which may have biased the results in favour of zinc-nickel, which definitely shows a reduction in “white rust” on exposure to neutral salt fog. It also exhibits a longer time to red rust in accelerated testing. The improvement in “white rust” formation could be due to the suppression of the formation of zinc oxide due to the presence of the more noble nickel. This would in turn lead to a reduction in corrosion rate and hence a longer time to red rust. In the atmosphere, however, the suppression of the formation of zinc oxide may inhibit the formation of the protective zinc carbonate on the surface hence increasing the actual corrosion rate. In fact in atmospheric trials the addition of nickel has been shown to reduce the corrosion resistance of zinc [65].

The optimum percentage of nickel is between 10-15% for direct current electroplating and between 12-20% for pulse plated zinc-nickel as measured using salt fog and potentiodynamic corrosion tests [66]. The difference in the percentages of nickel required to produce optimum corrosion performance in accelerated tests for the two different electroplating methods is thought to be related to the surface morphology [35]. Direct current electroplated zinc-nickel exists as a single η-phase structure up to about 15% nickel. In pulse-plated zinc-nickel the single-phase structure exists up to 20% nickel. This single-phase structure is thought to be partly responsible for the increased corrosion resistance, with the dual phase structure existing above 20% nickel forming localised corrosion cells, hence increasing the corrosion rate. Pulse
plating is thought to increase the percentage of $\eta$-phase by selective dissolution of the other $\gamma$-phase during the off-time of the pulse.

When electrodeposition onto pure aluminium the percentage of nickel needs to be less than 16% in order to keep the aluminium more noble than the coating [67]. Zinc-nickel suffers from de-zincification with time, especially if immersed and in alkaline environments [52,68]. This can lead to the zinc-nickel coating becoming non-sacrificial to the substrate, causing pitting and localised corrosion on the substrate in damaged areas.

The morphology of the coating also has a significant effect on the corrosion properties of the coating, with a polished zinc-nickel coating giving higher corrosion resistance as measured using polarisation techniques, than an “as deposited” coating [35]. This dependency of the corrosion performance has already been observed for zinc electroplate [28]. Again, however, the corrosion resistance was measured using an accelerated test, in this case immersion. In fact the polishing of the coating may just be reducing the actual surface area (a smoother surface will have a reduced surface area). This reduction in surface area would cause a reduction in the measured corrosion current density and hence a reduction in the corrosion rate. Additives such as primary and secondary brighteners, and levellers can be added to the baths to improve the deposit characteristics achieved. It has been found that the addition of between 3 and 7 g dm$^{-3}$ of a phenolic derivative as a primary brightener will improve the surface morphology and reduce the corrosion rate even when the percentage of nickel is below 2% [69]. Again, this reduction in corrosion rate may be due to a reduction in surface area.

The suggested mechanism for the reduction in corrosion rate due to the addition of nickel is that the nickel retards the dehydration of Zn(OH)$_2$ to ZnO hence decreasing the corrosion rate, as cathodic reduction on ZnO is possible (ZnO is a semiconductor) but not on Zn(OH)$_2$ as this is insulating [70,71]. This has, however, been found to be
untrue in long term corrosion studies [72], where zinc-nickel was still found to offer better protection than zinc but not due to the presence of nickel salts within the corrosion products. In fact, the increased corrosion protection offered in this case was attributed to the cracked morphology of the zinc-nickel coating, with the cracking corrosion process developing with time. The cracked structure provided an increase in the cathodic protection offered to the steel. This does not occur in alkaline environments when the cracked morphology of zinc-nickel is thought to be responsible for the reduction in corrosion resistance of zinc-nickel down to the same level as zinc [68]. There is also evidence of an enrichment of the surface layer with nickel on exposure (neutral salt fog), this may help to reduce the corrosion rate [66,72], but could make the zinc-nickel appear more noble than the substrate. The more noble effect of de-zincification would be offset in a micro-cracked structure due to the increased availability of fresh zinc-nickel surfaces for de-alloying to occur on, as the micro-cracking progressed with exposure.

The statement that the corrosion rate of zinc-nickel in atmospheric tests was greater than zinc is in contrast to other work [65]. However, it is not clear whether the coatings in [65], were micro-cracked. As this was the main reason cited for the increase in corrosion performance of [72], the apparent discrepancy may be due to morphological differences between the samples i.e. zinc-nickel only offers increased atmospheric corrosion resistance when micro-cracked.

Zinc-nickel can be chromated to reduce the corrosion rate, however, the chromate layer can be very uneven over complex shapes (especially if barrel electroplated) due to the range of compositions of zinc-nickel obtained as the current density varies across the surface [73]. This reluctance of zinc-nickel to promote an even chromate passivate due to the presence of nickel, would detrimentally affect the overall corrosion performance of the system (coating plus passivate), and limit its applicability for use as a cadmium replacement. This would only be important if chromate was continued to be used as a passivation treatment.
Zinc-nickel has also been suggested as a hydrogen permeation inhibitor for steel. It is thought that the addition of a third alloying element would increase the inhibitor efficiency of zinc-nickel by reducing the difference in potential between the coating and the steel, while still maintaining the sacrificial benefits of the coating [74]. The addition of a third element to the binary zinc-nickel system may also help to reduce the effects of de-zincification, and perhaps even inhibit further the reduction of zinc to zinc oxide. The third element could not be aluminium or lead as these both increase the corrosion rate in the atmosphere when present as impurities in zinc electroplate and could therefore detrimentally affect the corrosion rate of zinc-nickel [28].

To produce zinc-nickel a number of different electroplating baths can be used. Acid zinc-nickel baths are more common in Europe with formulations based on sulphates, chlorides and sulphate/chloride combinations [70,75]; with or without additions of ammonium sulphate or other ammonium salts [31]. Sometimes sodium sulphate can be added to increase the conductivity of the bath [64]. Ammonium chloride can be added to chloride baths [76] especially when electroplating on high strength steels. A typical bath composition is 0.92 mol dm$^{-3}$ of zinc and 0.58 mol dm$^{-3}$ of nickel, both as their sulphates [52]. A surfactant such as polyoxyethylene sorbitan monolaurate can be added to reduce the number of surface defects within the electroplate. This may, however, have a detrimental effect on the corrosion performance if the increased corrosion resistance of zinc-nickel is indeed caused by micro-cracking and surface defects within the coating. The use of bath additives to increase the corrosion resistance of zinc-nickel has also been studied [63,77], again, however, the increase in corrosion resistance was only measured using accelerated testing. In fact, the addition of additives improved the surface characteristics of the zinc-nickel plated reducing the micro-cracking of the coating. This may actually decrease the atmospheric corrosion resistance.

Acid zinc-nickel baths based on zinc and nickel acetate with additions of acetic acid have also been investigated. The deposition was again found to be anomalous with the deposition of both hydrogen and nickel being inhibited. The addition of an AC component during plating was also found to improve the surface characteristics, reducing the grain size and making the deposit more compact [78].
more compact morphology on the corrosion properties was not determined. Acid zinc-nickel has a high current efficiency but a low throwing power. Its cost tends to be higher than alkaline zinc-nickel due to the presence of weak complexing agents making effluent treatment more difficult [62,79].

Alkaline zinc-nickel baths are based on non-cyanide zinc baths with the addition of nickel salts [70]. They tend to have a lower current efficiency (typically about 40-65%) than acid zinc-nickel (about 85-95% efficient) and cause more hydrogen embrittlement when electroplated onto high strength steel [80]. However, they increase the range of current densities over which a single alloy composition can be electroplated [48]; this may allow a better, more even chromate passivate to be formed, hence improving the corrosion properties of the overall system. The levelling power is also better than acid Zn-Ni [79]. Brush plating for repair can be carried out using both acid and alkali zinc-nickel electroplating solutions [81,82].

When compared to zinc electroplate zinc-nickel seems to offer better corrosion performance. Certainly, it shows a reduction in corrosion products which would be beneficial for use on fasteners and connector shells. It is, however, harder and more expensive to electroplate than zinc. There is reduction in throwing power if acid zinc-nickel is used and a reduction in current efficiency if alkaline zinc-nickel is used. Zinc-nickel has no inherent lubricity and its wear properties under corrosion conditions significantly reduce the corrosion resistance. These factors may affect the suitability of zinc-nickel as a replacement for cadmium on both fasteners and electrical connectors.

2.7 Zinc-cobalt

Like zinc-nickel, zinc-cobalt also exhibits anomalous co-deposition with the less noble zinc being deposited preferentially. Anomalous co-deposition of zinc-cobalt has been found to occur for both direct current electroplating and for pulse plating [53]. Less cobalt is required to reduce the corrosion rate compared to zinc-nickel; percentages as low as 0.6% have been reported to significantly reduce the corrosion rate when measured using neutral salt fog exposure, provided that the zinc-cobalt is chromate passivated [70]. Zinc-cobalt has been in industrial use in Europe since its
introduction in 1982 [26,61,62]. Zinc-cobalt can also be brush plated for repair although no commercial baths are at present available [82].

Zinc-cobalt has a lower corrosion rate than pure zinc with only the addition of a small percentage of cobalt. It is thought that the cobalt reduces the corrosion rate of zinc-cobalt when used in conjunction with a chromate passivation layer by acting as a catalyst to help thicken the chromate film. The presence of the chromate layer is vital in improving the corrosion resistance. Without chromate the corrosion resistance of zinc-cobalt is similar to zinc [68]. A modified chromate treatment can be used on zinc-cobalt alloys to produce a wide range of finishes, from blue through yellow to black. The modified chromate bath for zinc-cobalt contains a higher concentration of chromate ions [49]. This higher level of chromate ions within the passivation treatment and passivation bath for zinc-cobalt means that the replacement for chromate passivated cadmium electroplate is also toxic, with an increased presence of chromate in the passivation treatment in the case of zinc-cobalt. This is not ideal.

However, zinc-cobalt is sometimes used as a replacement for cadmium in aerospace and non-aerospace applications [26]. When chromated it can produce the same colour range as cadmium electroplate unlike zinc-nickel, which only gives yellow and black chromate finishes. Olive drab chromate can be produced on zinc-cobalt provided the cobalt content does not exceed 0.25% [61]. Zinc-cobalt, unlike cadmium, does not have any inherent lubricity. But the most serious drawback for the use of zinc-cobalt is the reliance on the chromate passivation treatment to impart the increase in corrosion performance, when compared to zinc.

Either mildly acid baths (with chloride anions) or baths based on alkaline cyanide free formulations can be used to deposit zinc-cobalt. Acid baths tend to produce alloys with less than 1% cobalt and have less throwing power than alkaline zinc-cobalt [79]. Alkaline zinc-cobalt baths contain a very low level of cobalt (1-3 g dm$^{-3}$) and can produce deposits of uniform composition over a wide current density range. They are ammonia and cyanide free [49], which makes effluent treatment easier and cheaper. Additives such as brighteners and levellers can also be added to the bath, one such
additive, a brightener (benzylacetone), has been found to deposit preferentially on any surface projections, hence increasing the throwing power [53].

The structure and morphology of the resultant zinc-cobalt coating depends largely on the bath parameters. Zinc-cobalt tends to be porous and changes its structure with an increase in cobalt concentration in the bath and with the temperature of electroplating. The hardness of the deposit also increases with increase in cobalt content [83].

Hence from an electroplating process point of view, zinc-cobalt is fairly easy to deposit and passivate. The process has good throwing ability if an alkaline bath is used, and good composition control. However, the fundamental reliance on the chromate passivate to give increased corrosion protection means that if chromate passivation treatments are in the future replaced, the perceived improvement in corrosion performance of zinc-cobalt when compared to zinc may not occur, making zinc-cobalt an unsuitable long term replacement for cadmium. Like zinc-nickel the lack of inherent lubricity may also be a problem.

2.8 Zinc-iron
Zinc-iron has been reported to give twice the corrosion protection of pure zinc [70,81] in accelerated corrosion tests, but does not give as large an improvement as zinc-nickel; however, it is significantly cheaper. It provides a sacrificial coating to steel but may suffer from de-zincification with time. Moreover, its corrosion products are unsightly and voluminous due to the formation of red iron hydroxide and this may limit its applications. 15-20% iron is reported to give the best corrosion resistance whereas 60-80% iron gives the best adhesion by paint, if a phosphate treatment is used as an interim step. Compositionally modulated zinc-iron has been investigated as a means of providing both the reduction in corrosion rate and the improvement in paintability [84,85], as have dual layer zinc-iron coatings [81]. Dual layer coatings showed better corrosion resistance than zinc when painted, but although the production of compositionally modulated layers from a single bath was shown to be feasible, no details of any improvements in properties, such as paintability or corrosion resistance, were given. Alloys containing much smaller percentages of iron
(between 0.4 and 1.5%) have also shown a reduction in corrosion rate, but only when chromated [86] and are in industrial use in Europe in the automotive industry [61,62]. Atmospheric corrosion tests have shown chromated zinc-iron to give better corrosion performance than zinc. However, non-chromated zinc-iron was not evaluated. Without chromate (as with zinc-cobalt) the corrosion resistance of these low iron content alloys is similar to zinc [79].

The surface morphology is again thought to affect the corrosion rate with low percentage iron alloys (1%) having a hexagonal structure and increased corrosion performance [35]. The corrosion was assessed using polarisation techniques. Whether this improvement in corrosion resistance would still occur if other corrosion tests, such as atmospheric testing, were undertaken, is not discussed.

The baths for zinc-iron are based on sulphates or chlorides with the latter having a number of advantages over the sulphate bath, namely a higher conductivity and better current efficiency. Alkaline zinc-iron baths have excellent throwing power and produce a more uniform black chromate. They do, however, suffer from slow electroplating rates, need tight temperature control and only give yellow and black chromate passivate [79].

Zinc-iron therefore is cheap to deposit, it can produce even coatings on complex shapes, it shows an improvement in corrosion performance when compared to zinc, but suffers from voluminous corrosion products and must be chromated or painted to give any significant improvement in corrosion performance. It does not produce an olive drab chromate coating, which is required by the electrical connector industry for military aerospace applications [24]. At present, therefore, zinc-iron is not a suitable replacement for cadmium. The production of compositionally modulated zinc-iron may improve the corrosion performance, but would still require passivation treatment or painting. Due to the electrical conductivity requirement for electrical connectors, painting is not an alternative finishing treatment. Like zinc-nickel and zinc-cobalt, zinc-iron does not possess any inherent lubricity. Again this may limit its applicability for use on electrical connectors and fasteners.
2.9 Zinc-manganese

Zinc-manganese is another zinc based alloy, which is nominally sacrificial to steel and aluminium. There are no commercial zinc-manganese coatings, and most of the work on zinc-manganese is still at the laboratory stage of development. Zinc-manganese is said to offer very good corrosion protection [52]; 50-65% manganese is required to offer high corrosion resistance although 14% manganese has been shown to offer better corrosion resistance than zinc alone [87] as measured using polarisation and immersion weight loss measurements. The increase in corrosion resistance is thought to be due to the formulation of $\gamma$-Mn$_2$O$_3$ on the surface of the alloy. This is a dense corrosion product and suppresses the cathodic oxygen reduction reaction and hence the corrosion rate [70]. The oxygen reduction reaction is given in Equation 2-7.

$$\text{O}_2 + 2\text{H}_2\text{O} + 4e^- \rightarrow 4\text{OH}^-$$

_Equation 2-7_

Even as low a percentage as 0.5% Mn has been shown to offer better corrosion resistance than pure zinc [88]. Here it was proposed that the presence of manganese helped suppress the formation of ZnO and Zn(OH)$_2$ on the surface, and hence reduce the corrosion rate. This mechanism for the reduction in corrosion rate is probably more likely under immersion conditions than the formation of dense Mn$_2$O$_3$, which may not be completely formed under continuous immersion in high chloride solutions. The increase in corrosion resistance was only small and obtained from polarisation measurements. Other corrosion testing, including atmospheric testing of thermally produced zinc-manganese coatings showed poor corrosion resistance for zinc-manganese coatings containing 50% manganese [31], with electroplated zinc-manganese suffering from micro-pores, which caused the substrate to corrode in alternate immersion tests, giving poorer corrosion resistance than both zinc and cadmium. No atmospheric testing of electroplated zinc-manganese coatings was undertaken during this study. The fact that the presence of micro-pores causes substrate corrosion suggests that zinc-manganese does not remain sacrificial to steel under alternate immersion conditions. This may be due to the formation of Mn$_2$O$_3$ changing the corrosion potential of the coating, making it non-sacrificial to the substrate.
The possible increase in corrosion resistance of zinc-manganese when compared to zinc would perhaps make zinc-manganese a suitable replacement for cadmium. Certainly, the probable reduction in the amount and volume of corrosion products would be beneficial to connector and fastener applications.

Most zinc-manganese baths are based on sulphates with the addition of citrate, to complex the manganese and zinc. It complexes the former more strongly and hence, makes the electroplating potentials close enough for co-deposition to occur. But they suffer from low cathodic efficiency. Additions of sodium thiosulphate have been found to increase the cathodic current efficiency perhaps by inhibiting the hydrogen reaction. The bath is also unstable, with the formation of a white precipitate of manganese (III) citrate possible, the level of which can be reduced by the addition of a mineral acid or zinc metal, which also improves the ageing characteristics of the bath. Small quantities of gelatine can also be added to the bath [87]. The pH of the bath is critical as is the order in which the chemicals are added to the bath during preparation [89]. Due to the instability of the citrate bath to pH and to variations in the current density causing large changes in the Mn content of the alloy, citrate baths may not be of practical application for normal zinc-manganese coatings. However, they may have application for the formation of compositionally modulated alloy coatings, which may be useful in providing a higher manganese content at the surface, leading to more dense corrosion products, while still giving a relative high overall current efficiency due to a lower manganese content near the substrate. This would have an advantage for connectors and fasteners, where the volume of corrosion products is one of the main reasons for not using zinc as a replacement for cadmium. A recent development has been the fluoroborate bath, which is said to increase the cathodic current efficiency to up to 80% [70]. However, this uses a fluoride based complexant, which necessitates the use of plastic, inert and more expensive electroplating equipment. The bath also becomes harder to effluent treat.

In summary zinc-manganese could potentially reduce the level of corrosion products and increase the corrosion resistance compared to zinc, making it a possible alternative to cadmium. However, it suffers from low current efficiency, bath instability and poor throwing power [31]. It is also not a well-characterised coating
and is not commercially available. Significant research would therefore be required to assess its suitability as a replacement for cadmium, especially as there are questions about its corrosion performance.

2.10 Methods of improving coating performance

There are several ways of improving the properties of the available sacrificial cadmium alternatives to make them more suitable as replacements. The adhesion of the electroplate to the substrate can be improved. This helps reduce coating removal and damage in use. A ternary element can be added to the alloying system in an attempt to modify the coating to make it more suitable. Examples of ternary zinc alloy electroplate include zinc-nickel-phosphorous, where the phosphorous is added to the alloy system to increase the hardness of the electroplate, and reduce the level of dezincification observed under immersion conditions. As already mentioned [84,85], compositionally modulated or layered coatings can be used in an attempt to modify the final coating properties, such as in the case of zinc-iron with paint adhesion.

Another potential way of modifying the coating properties is to try and change the morphology and/or alloy content, by the use of pulse rather than DC electroplating, bath additives or by variation of other facets of bath chemistry. It may thus be possible to improve the morphology of, for example, zinc-manganese and remove the micro-pores, which were reported as detrimentally affecting the accelerated corrosion behaviour [31].

2.10.1 Pre-treatment

The pre-treatment of the substrate can be modified to improve the subsequent adhesion of the electroplate. This is especially important when electroplating onto aluminium and its alloys as they are very reactive and form an oxide film on contact with air or aqueous solutions. The oxide film is amphoteric in nature; this complicates the possible reactions which can occur either during or after the surface has been prepared for electroplating. Aluminium has a low $E_{corr}$ value within the electrochemical series and can subsequently act as a substrate for immersion deposits with a large number of metals; this can also affect the adhesion of electroplating on this type of metal surface [90]. Aluminium alloys also suffer from the problem of having a difference in potential between the aluminium rich parts of the
microstructure and the aluminium deficient parts. For example with the 2000 series alloys, some areas are more rich in copper than others.

A large number of cleaning and etching processes exist [91-95] in order to remove grease and contaminates from aluminium alloy surfaces. However, their use is widespread and not limited to electroplating. The optimisation of the cleaning and etching processes will therefore not be evaluated, suffice it to say that the aluminium surface should be thoroughly clean and possibly etched to provide a good key for the subsequent electroplating pre-treatment.

There are many methods available for the pre-treatment of aluminium specifically for electroplating [96-100]. The most widely used and investigated process is that based on a zincate immersion technique. The zincate process is relatively cheap, reliable and a fairly simple, normally single step process. A suitable solution consists of zinc oxide and high concentrations of sodium hydroxide [90]. The adhesion of a zincate immersion deposit to the substrate depends on a number of things, the level of zinc oxide and sodium hydroxide in the solution [101], the immersion time, the temperature, the nature of the aluminium alloy, the synergistic use of ultrasonic agitation and the use of additives to the basic zincate solution [92,102-104]. The nature of the zinc immersion deposit has been shown to directly affect the corrosion resistance of the resultant electroplate [98], with a thinner more compact zincate layer providing better adhesion and hence better corrosion resistance.

A double zincate process can also be used when the first zinc immersion layer is stripped off in nitric acid prior to a second layer of zinc being applied. This is said to improve the adhesion of the second zinc layer [93,95,105]. The zincate treatment produced a copper rich layer adjacent to the 2000 series alloy surface, which was not removed in the double dip process hence improving adhesion. The normal strength zincate bath is subject to high drag out losses. More dilute modified zincate baths have been developed which reduce these drag out losses [106].

The modification of this pre-treatment process could therefore affect the corrosion resistance of the electroplate, making it possibly more suitable as a replacement for cadmium. On its own with a non-suitable replacement alloy coating it cannot produce
an alternative to cadmium. Modification of the pre-treatment will only serve to optimise an already promising alloy system to further improve the coating properties. Even the use of a double dip process, although able to improve adhesion, will not make an unsuitable coating a viable alternative to cadmium. As the double dip process increases the complexity and number of pre-treatment stages, significant improvement in the coating properties would have to result before its use became time and cost effective.

There are a number of methods of preparing steel for electroplating, namely abrasive cleaning, acid pickling, salt bath descaling, alkaline cleaning and acid cleaning [107,108]. Unlike aluminium and its alloys no additional pre-treatment is required.

A number of different mineral acids can be used for acid pickling. The most common is sulphuric acid. This is normally used because of its cost. The rate of attack is influenced by the acid concentration and the temperature. An inhibitor can be added to the acid to reduce the rate of metal attack whilst keeping the rate of attack of the scale high [109]. Normally 10% sulphuric acid at between 20-45 °C is used [91]. Some developments have been made in recent years with the addition of additives to improve the properties of the mineral acid treatments [110].

Hydrochloric acid is more expensive but can be used at room temperature, again a concentration of 10% is normally used. Phosphoric acid is intermediate in cost and can also be used but must again be used at elevated temperature or at a higher concentration. Normally a concentration of 50% is used at room temperature or 30% at 60-70°C.

All the acid pickling cleaning methods are normally preceded with emulsion cleaning to remove organic residues. All acid pickling can lead to hydrogen embrittlement of susceptible steels. A different cleaning method is therefore required for high strength steels [111].

Alkaline descaling uses strongly caustic solutions with chelating agents such as sodium heptonate or gluconate. It can be carried out either with or without the application of a current giving either anodic or cathodic electrolytic cleaning.
Cathodic cleaning can be used to prevent hydrogen embrittlement but is not as efficient as anodic electrolytic cleaning.

Prior to electroplating it may be necessary to remove any inhibitor used in acid pickling either by the use of an acid dip in 5-10% sulphuric or hydrochloric acid, or in an alkaline solution. The adhesion of electroplate onto steel is not as much of a problem as it is on aluminium. Steel is a very common substrate on which to electroplate and its pre-treatment is well characterised and optimised. It is therefore unlikely that any changes in the normal pre-treatment cycle will significantly increase the adhesion and so the corrosion resistance of electroplated steel. A different pre-treatment cycle, however, may have some affect on the composition of the resultant electroplate, and may hence need to be considered.

2.10.2 Addition of another alloying element

In order to improve or modify the properties of a binary zinc alloy a third alloying element can be added. Work on ternary zinc alloys is not very common and in most cases is still in the experimental stage. The only exception is zinc-cobalt-iron, which is in commercial use. This alloy has recently been introduced into Europe, with initial work being undertaken on this alloy in Japan. It contains only small amounts of cobalt and iron (0.25-0.5%), and is used in the automotive industry. The corrosion resistance is said to be greater than zinc-cobalt when passivated. The addition of iron is thought to increase the thickness and adhesion of the chromate passivation [61]. Like zinc-cobalt and zinc-iron the improvement in corrosion performance is only achieved when the zinc-cobalt-iron is chromate passivated, however, olive drab chromate cannot be produced. When passivated it gives about half the corrosion resistance in neutral salt fog testing as zinc-nickel and about twice the corrosion resistance of zinc-cobalt and zinc-iron, however, no data is available for atmospheric corrosion testing. The addition of the third alloying element has therefore improved the thickness of the chromate passivate and hence the corrosion resistance of the alloy, without being as expensive as zinc-nickel.

Some work has been carried out on a ternary alloy system of zinc-nickel-iron from an acidic chloride bath [112]. The electroplating system was studied and found anomalous with iron acting to inhibit the deposition. Alloys of between 2 and 5% iron
and between 13 and 20% nickel were produced by changing the nickel and iron molar concentrations within the bath. Fine-grained structures were produced which were said to have better corrosion performance, when compared to zinc-nickel. The nature of the corrosion testing undertaken was not specified, with reference being made to a yet unpublished paper. The main advantage of alloying zinc-nickel with iron was the removal of the need for organic brighteners within the electroplating bath, while still producing bright electrodeposits. This would reduce the cost of waste treatment on the electroplating bath.

Work has also been carried out on incorporating a small percentage of phosphorous into zinc-nickel alloys to try to reduce the de-zincification observed [102]. Between 0.01 and 0.1 wt% phosphorous was incorporated into zinc-nickel containing approximately 14% nickel. The effect of aeration and stirring on the bath was also investigated. Aeration was found to reduce the amount of porosity whereas stirring gave more even deposits on steel. Both the nickel and phosphorous contents in the alloy increased as the electroplating voltage was increased. This suggested that they were both being deposited by an induced co-deposition method [113]. It was shown that the addition of phosphorous retarded the de-zincification of zinc-nickel in immersion tests. This suggests that the addition of phosphorous may be beneficial in reducing the corrosion rate of the zinc component of the alloy leading to increased corrosion resistance. Further corrosion characterisation was not undertaken [102]. Other corrosion tests on zinc-nickel-phosphorous and zinc-iron-phosphorous showed good corrosion resistance under neutral salt fog conditions, but although zinc-nickel coatings were also tested, no mention as to the possible corrosion improvement when using phosphorous was given [32]. However, the adhesion of the electroplate when compared to zinc-nickel was reduced.

The use of phosphorous with zinc-nickel may also have a detrimental effect on the wear properties especially when joint wear and corrosion are evaluated. This has certainly been shown for nickel-phosphorous coatings where the reduction in wear resistance under corrosive conditions was attributed to incomplete formation of a protective oxide layer [114].

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Hence, although both zinc-nickel-phosphorous and zinc-iron-phosphorous have been electroplated, further work on the advantages of adding phosphorous needs to be undertaken, as the corrosion resistance and benefits of adding phosphorous to the binary alloys are, as yet, largely undetermined.

Some work has been undertaken on the addition of manganese salts to zinc-nickel sulphate baths to produce an alloy of zinc-nickel-manganese [115]. The percentage of manganese in the alloy was small being less than 1%. The nickel content varied from between 6 to 10% nickel. The percentages of both nickel and manganese increased as the current density increased from 1.0 to 3.0 A dm$^{-2}$ and as the temperature was raised. Two additives were used, thiourea and ascorbic acid, but only in very low concentrations. No complexants were added to the bath. An investigation into throwing power was undertaken, with a lower temperature and pH giving slightly better values. No corrosion evaluation of the resultant thin films was carried out, as the coatings were destroyed in order to determine their composition.

Further investigation of this alloy would be required to ascertain the effect of manganese on the properties of zinc-nickel, hence making this alloy a possible viable alternative for cadmium rather than just a curiosity.

2.10.3 Use of multilayer or graded coatings

Rather than the addition of another alloying element to try to change the properties of the resultant coating, another way is by the use of multilayer or graded coatings. Multilayer or graded coatings have been shown to increase the corrosion resistance of zinc-iron especially if nano-layers are used [113,116]. These results were in both cases determined using accelerated neutral salt fog corrosion tests and electrochemical data. Longer term atmospheric monitoring would be required to substantiate the corrosion resistance improvement. However, multilayer structures can suffer with problems of adhesion between the layers, which may in fact reduce the corrosion performance [117]. Graded coatings help overcome this adhesion problem, resulting in substantially better adhesion and better corrosion performance in accelerated corrosion tests [113]. Multilayers of nickel are common, with a coating consisting of bright and semi-bright nickel layers, which are used as an underplate in decorative chromium plating. These significantly increase the corrosion resistance of the coating.
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[118], in both accelerated and longer term testing. However, in this case the nickel coating is acting as a barrier rather than sacrificial coating. The use of multilayer or graded coatings could therefore offer potential as a means of improving the resultant coating properties. Whether the added complexity of producing multilayer or graded coatings will be offset by the improvement in corrosion resistance, or other coating properties, is yet to be fully evaluated for zinc alloy systems.

2.10.4 Changing bath variables

There are numerous changes, which can be made to an electroplating system to attempt to alter the morphology or composition of the alloy produced and hence possibly improve its properties. Electroplating system variables include the use of pulse electroplating rather than direct current, the variation of bath parameters such as pH and temperature and changes to the bath chemistry by the use of complexants and other additives. Firstly, the effect of pulse electroplating on morphology, composition and other coating properties such as corrosion resistance, wear and roughness will be evaluated. This will be followed by an examination of the effect of different bath parameters such as temperature, agitation and pH. Finally, the effect of different bath chemistries will be considered.

2.10.4.1 Pulse electroplating

A number of different shaped pulses can be used for pulse plating. The main types are illustrated in Figure 2-3. Complicated program controlled pulses can also be used to produce coatings which have less internal stress and higher hardness by producing graded alloy coatings [119]. Anodic pulses can also be used, these are said to allow selective dissolution of the more active sites and help stop dendrite formation, improving the characteristics of the coatings [119]. However, the nature of the pulses needs to be tailored to the application, with reverse anodic pulses being mainly suited to certain applications [120]. The duration and spacing of the pulses are important. If the pulses are of too short a duration, the double layer cannot respond quickly enough and the maximum current is not reached. Similarly, if the duration of the off time is too short the double layer cannot again respond and the actual current never returns to zero. This is illustrated in Figure 2-4. If this flattening of the pulse occurs the improvements in the morphology of the resultant coating will be lost [121].
In plain pulsed electroplating (see Figure 2-3 a)), three different parameters can be varied, $I_p$ the peak pulsed current density, $t_c$ the charging time or length of the pulse (also called $t_{on}$) and $t_d$ the discharging or off time of the pulse (also called $t_{off}$). Other parameters, which are sometimes varied for pulse plating, include the frequency of the pulse, which is related to $t_c$ and $t_d$, and the duty cycle $\Phi$. The equation for the relationship between the duty cycle and $t_c$ and $t_d$ is given in Equation 2-8.

$$\Phi = \frac{t_c}{t_c + t_d} \times 100\%$$

*Equation 2-8*
However, by using either pulse frequency or duty cycle, both $t_e$ and $t_d$ are varied at the same time, making the attribution of results difficult. By using $t_e$, $t_d$ and $I_p$ as the factors, which are varied, this complication is avoided [122]. Both zinc and cadmium electroplating tend to prefer a lower value of duty cycle, while the opposite is true for copper and gold electroplating [123], showing the need to tailor the pulse conditions to the electroplating process.

Pulse plating offers a number of advantages over conventional DC electroplating. These are summarised in Table 2-4 [14,124,125]. Pulse electroplating does not increase the speed of electroplating but enables electroplating to be carried out at higher current densities often with less hydrogen evolution. The high operating voltages lead to a decrease in grain size [126].

A less porous coating with a decrease in grain size normally increases the corrosion resistance of that coating, hence improvements in deposit properties such as ductility, porosity and grain size will all increase the corrosion protection offered by that alloy. Grain size also affects the internal stress and the hardness of coatings [127,128]. This possible reduction in grain size may, however, adversely affect the electrical conductivity of the coating leading to a more resistive coating, which would not be suitable for electroplated connector shells [129]. Other morphological considerations such as grain orientation can also be varied using pulse electroplating [130], however,
in some cases the composition of the alloy coating has a much larger influence on the
morphology than the use of the pulse electroplating [131,132].

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Improvement with pulse electroplating</th>
</tr>
</thead>
<tbody>
<tr>
<td>Deposit properties</td>
<td>Porosity [133], ductility, hardness, electrical conductivity, wear resistance and roughness, reduction in internal stress</td>
</tr>
<tr>
<td>Alloy deposition</td>
<td>Can deposit alloys with composition and structure unobtainable using DC electroplating</td>
</tr>
<tr>
<td>Electroplating parameters</td>
<td>Alloy composition tends towards that of electrolyte, electroplating thickness distribution improved [134-136], cathodic current efficiency improved, small improvement in deposition rate, reduces non-metallic deposition (impurities), increases possible plating current density [98]</td>
</tr>
<tr>
<td>Other considerations</td>
<td>Composition changes in alloy electroplating possible by changing shape of pulse wave and by the use of pulse electroplating [128,131,132,137,138]</td>
</tr>
</tbody>
</table>

*Table 2-4 Advantages of pulse electroplating*

Pulse plating also increases the throwing and levelling power of a solution compared to DC electroplating [136,139]. For bi-polar pulse plating a low duration on the anodic cycle \( t_a \) (anodic) improves the levelling power, as does an increase in the height of the cathodic pulse, \( I_p \) [140]. However, the best improvements in levelling can still be achieved by adjustment of the geometry of the bath and samples or by using multiple alternating anodes, \( i.e. \) a separate anode for any reverse pulse [141]. Other ways of increasing the throwing power of a given solution are the reduction of the metal ion concentration, increasing the anion concentration and by the addition of complexing agents [142]. Other electroplating parameters such as the maximum current density that can be used to undertake electroplating can also be increased by the use of pulse electroplating, especially with the use of reverse (anodic) cycles [143].

The composition of the resultant alloy can also be changed by variation in the pulse parameters. The use of pulse electroplating could therefore be a means of, either producing alloy contents not possible using DC electroplating, or of varying the composition of the coating through the thickness, leading to graded coatings [128,131,132,137,138]. Pulse electroplating is therefore a viable means of producing, morphological and compositional changes to the coating, possibly making the use of that coating more suitable as a replacement for cadmium. On its own, however, it will
never be able to change significantly the coating properties enough to make an unsuitable coating good enough to replace cadmium. For example, improving the corrosion resistance of zinc coatings, may make them have corrosion properties nearer to cadmium, but would not significantly effect other properties such as lubricity, still making zinc an unsuitable replacement for cadmium on fasteners and electrical connectors.

2.10.4.2 Bath parameters

Certain bath parameters can be changed in order to vary the composition of the alloy or to change its surface morphology. These are applied electroplating current density, temperature, bath geometry, the nature of the anode and the level of agitation within the electroplating bath.

For most systems, changing the current density changes the alloy composition. A notable exception is for tin-zinc, which has a stable composition over a wide current density range [99]. For anomalous co-deposition, the change in composition tends to follow that illustrated in Figure 2-2. The position on the curve is dependant both on the alloy system, and the nature of the electrolyte. This can be clearly seen in Figure 2-5 where comparisons between different electrolytes for zinc-nickel and zinc-iron are shown [31]. For zinc-iron there is a large change in alloy content with current density, facilitating the production of multilayer coatings from a single solution [85]. Changing the applied electroplating current density to give a change in composition of alloy is only viable if the intention is to produce multilayer or graded coatings from the same solution. It is easier to change the alloy content by modification of the chemistry of the bath in other circumstances. Any increase in applied electroplating current density may lead to porous, spongy and burnt deposits, which would give a reduction rather than an improvement in corrosion performance. A substantial decrease in current density to obtain the alloy of choice could lead to such a small value of applied current density as to give very long, impractical, electroplating times.
The effect of temperature on the composition of an alloy deposit is complex. It depends on the nature of the alloy deposition [31] and thus on the diffusion of ions and also on the polarisation. Which of these two will dominate depends on the nature of the solution and of the alloy. They have opposite effects on the change of composition with temperature, with the diffusion of ions tending to decrease the percentage of the less noble metal and the polarisation phenomenon favouring an increase. For zinc-nickel alloy deposition from a simple sulphate bath, the percentage of the more noble nickel tends to increase with temperature [52], showing the diffusion ability of the ions to be the dominating process in this case. For non-anomalous co-deposition again the effect of temperature on the alloy composition depends on the diffusion ability, this is illustrated in brass electroplating where the percentage of copper increases as the temperature is raised [144]. However, changing the temperature of the electroplating bath to vary the composition of the alloy is not a suitable method of producing multilayer coatings as it is a very slow response parameter and cannot be varied quickly, especially on an industrial scale. A knowledge of the change in composition with temperature is only important in determining the suitable bath operating temperature range, or to aid the deposition of a coating with a different overall composition from a bath designed to operate over a
different temperature range. In doing this, however, it must be remembered that the morphology of the coating may also change with variation in temperature, giving the possibility of obtaining a more suitable coating composition, but with for example a larger grain size which reduces the corrosion protection offered by that alloy, rather than increasing it.

Bath geometry can also change the nature of the metal deposited, both in terms of the uniformity of the coating thickness and the composition if an alloy coating is being electroplated. The position of the anodes and the shape of the component to be electroplated affect the throwing power within a given bath, as well as the current density distribution. The throwing power within a bath changes the uniformity of the coating while the current density distribution affects the composition and the uniformity of composition of an alloy over the component to be electroplated [135]. The effect of the cell set up on the thickness distribution can be modelled, using electrochemical techniques. The use of cheaper, simpler thermal analysis boundary element software can also be used. This has been found to compare well with standard electrochemical software calculations except at sharp corners [145]. However, it is much harder to assess the likely change in composition across the surface of the component, especially in a relatively unknown system. Some modelling of the current distribution within a bath can be undertaken, but in order to relate that to compositional changes a good knowledge of the way in which the composition of the alloy varies with current density is required.

The choice of anode for electroplating is important and affects the properties of the resultant electroplate. Either soluble anodes or inert anodes such as platinum, lead and graphite can be used. Soluble anodes prevent the solution becoming depleted in metal ions but must be pure to prevent rough deposits [146], and are hence preferred for industrial electroplating. For alloy electroplating normally one soluble anode of the same composition as the main metallic constituent is used. Alloy anodes can also be used but are problematic because the rate of dissolution of one of the alloy components may be different to its rate of electroplating, leading to solution composition changes with time [147]. The use of two anodes for binary alloy deposition is sometimes used as this will prevent the need to replace salts in the bath when electroplating on an industrial scale. To prevent the anodes dissolving at the
wrong rates, a separate circuit is sometimes used to control the anodes, which prevents the solution becoming depleted in certain metal salts. A separate circuit can also be used to apply an alternating current to anodes preventing passivation [148]. Changing the nature and control mechanisms used for the anodes can have a larger effect on the coating characteristics such as morphology and internal stress than variation in pulse parameters [141]. Hence, choice of anodes and controlling mechanisms for the anodes is vital to ensure good morphology and therefore promote suitable coating properties. Again, like pulse electroplating, changing the anode and control mechanism cannot make an unsuitable coating fit for purpose, but can significantly improve the coating properties to increase, for example, its corrosion resistance. The choice of suitable anodes also facilitates industrialisation of an electroplating bath, leading to stable operation with time, and improved bath aging characteristics, hence reducing operating costs.

The level and nature of agitation can have a significant effect on the composition and morphology of an electrodeposi. This can be studied by the use of a rotating disc electrode, which provides a qualitative means of assessing the level of agitation [85]. But the use of a rotating disc electrode cannot be directly related to agitation rates within an industrial electroplating bath, where increase in agitation is normally obtained by mechanical means, or by the use of air agitation. Hence, although it has the means of providing qualitative information on the effect of agitation, it is not practical on an industrial scale. The level of agitation causes changes in the current efficiency, morphology and composition of an alloy deposit, by reducing the thickness of the diffusion layer as the agitation rate is increased. This also leads to an increase in the range of current densities which can be used for electroplating, in a similar way to the use of pulse electroplating, which also affects the thickness of the diffusion layer [144]. For zinc-nickel and zinc-iron alloy deposition the zinc content has been found to increase with an increase in agitation levels. This also occurred for zinc-nickel-phosphorous [113]. Because changing agitation levels leads to a change in the rate of diffusion of ions to the surface, the effect of agitation can be large and can even mask the effect of other changes like variation in applied electroplating current density [85]. The use of air to increase the agitation within an electroplating bath can also lead to accelerated oxidation of the metal salts and anode within the bath, reducing its lifetime. However, as agitation can significantly increase the applied
electroplating current density which can be used, significant savings in time can be obtained, leading to the possibility of undertaking high speed electroplating. This leads to process efficiency savings making the electroplating process cheaper and hence more amenable to industry. Again, like pulse electroplating, temperature and geometry, variation in agitation although causing significant changes in the efficiency, operating current density and composition, cannot on its own make an unsuitable alloy systems improve their properties so much that they become a replacement for cadmium. It can, however, be used as a control mechanism to produce graded or multilayer coatings from a single bath in much the same way as applied electroplating current density can be used as a control mechanism with possible significant improvements in coating properties [113]. However, it is not as easy to quantify on an industrial scale.

2.10.4.3 Bath chemistry

A large number of chemical parameters can be varied to change the composition and morphology and hence other properties such as corrosion resistance, of the resultant coating, especially when alloy coatings are being deposited.

With a basic, non-complexed, additive-free electroplating bath, the ratio of metal ions, the nature of the anions and the pH of the bath can be varied. Changing the ratio of metal ions will affect the composition of the alloy produced; the level of change will depend on the type of electroplating with anomalous co-deposition resulting in a smaller increase in noble metal content in the alloy for a given change in metal ion concentration [31]. Changing the nature of the anion can also have a marked effect on both the composition and morphology of the coating, with sulphate baths tending to have lower conductivity than mixed sulphate-chloride baths. The low conductivity affects the throwing power of the bath and the current distribution within the bath [149-151], and hence both composition and morphology of the electroplate. The effect of changing the anion can be seen in Figure 2-5 for zinc-nickel acid electroplating from both chloride and sulphate baths. Here it can be seen that changing the anion can have a significant effect on the composition of the electroplate with the acid zinc-nickel chloride bath producing significantly less zinc in the deposit. The pH of the bath can also change the composition, morphology and electroplating parameters required to produce a given electroplate, with very low pH zinc baths
tending to lead to higher hydrogen evolution rates, lower current efficiency and more porous deposits [51].

As well as the metal ions, other components can be added to an electroplating bath. These include complexants, which allow for different alloy coating compositions to be obtained, brighteners, levellers, surfactants, pH stabilisers, wetting agents and conductivity enhancers [2,31,43-47,52,53,63,69,70,77,79,115,122,123,137,152-154]. Of these, the addition of complexants has the largest effect on the alloy composition, morphology and throwing power, with cyanide baths being traditionally used to give good throwing power and small grained deposits [149-151].

Because there are so many different additives that can be used in an electroplating bath, all of which can give some improvement in properties, the formulation of an electroplating bath can become very complex indeed. All additives change the composition-current density curve for a given bath to a lesser or greater degree. Their use is therefore vital in producing the required alloy composition from a given bath. The use of electroplating additives to the bath have been shown to have a larger effect on the composition of the resultant alloy rather than the variation of pulse parameters. Additives can also affect the morphology of the coating to a greater extent than the use of pulse electroplating [146,152]. Additives to the electroplating bath make the cost of solution waste disposal higher and need more solution control than electroplating baths which do not contain additives. Hence, although the use of additives can produce the changes in morphology and composition, their use may not be so desirable.

Variation in bath chemistry either by changing the basic electroplating bath or by the use of complexants and additives is therefore a possible means of changing the composition, morphology and characteristics of a given electroplate, with the possibility of hence improving the properties to such an extent as to make it a suitable replacement for cadmium. But sometimes variation in bath chemistry can have a detrimental effect on the properties of the resultant coating. For example by increasing the ratio of nickel ions in a zinc-nickel bath it may be possible to increase the nickel content of the alloy. The increase may be so large as to make the zinc-nickel coating non-sacrificial, hence decreasing the corrosion protection offered.
Great care must therefore be taken when formulating an electroplating bath to attempt to improve the performance of the resultant coating. The position is further complicated by the non-linear synergistic effect of interactions between different additives within an electroplating bath. Certainly for a relatively unknown system, simplest is probably the best and excess use of different additives would significantly complicate the investigation, leading to the possibility that optimum formulations could be missed. Perhaps the best way to investigate bath chemistry is to start with as simple a solution as possible. If this does not give the required composition, morphology and properties further additives can then be used, but with caution and thorough investigation.

Variation in bath chemistry offers the potential of improving a coating's characteristics, or of producing novel coating compositions, but is very cumbersome to investigate. Again it may be debatable as to whether changing the alloy content produced or the morphology would give enough of a change in resultant properties, such as corrosion resistance and wear as to make an unsuitable alloy system significantly better to be offered as a replacement for cadmium. The problem of quantifying the level of change also exists, with the difficulty of different tests, especially corrosion tests, giving dissimilar results.

2.10.5 Summary
A summary of the main methods of attempting to improve the properties of the available sacrificial coatings to attempt to make them more suitable as replacements for cadmium is given in Table 2-5.
<table>
<thead>
<tr>
<th>Method</th>
<th>Use</th>
<th>Possible level of change</th>
</tr>
</thead>
<tbody>
<tr>
<td>Optimising pre-treatment</td>
<td>Can improve adhesion and coating morphology</td>
<td>Small but dependant on initial adhesion level</td>
</tr>
<tr>
<td>Addition of another alloying element</td>
<td>Could change all coating properties even lubricity</td>
<td>High but requires significant investigation</td>
</tr>
<tr>
<td>Use of multilayer or graded coating</td>
<td>Could have significant effect on corrosion resistance but electroplating process becomes more complicated</td>
<td>Medium but must have a suitable method of controlling alloy deposited</td>
</tr>
<tr>
<td>Changing bath variables</td>
<td>Variable effect, which may be detrimental, numerous ways of changing bath variables including pulse electroplating, electroplating current density, temperature, bath geometry, nature of anode, agitation levels and bath chemistry. Very complex</td>
<td>Low to medium effect depending on which variable is changed. Very complex to investigate</td>
</tr>
</tbody>
</table>

Table 2-5 Summary of methods of changing electroplated coating properties

2.11 Testing of Coatings

To determine whether a coating may be a suitable replacement for cadmium for use on electrical connectors or fasteners, testing must take place. Firstly, a knowledge of the effects of the various bath parameters such as applied electroplating current density on the composition, in the case of an alloy coating, and morphology will be required. Further characterisation of the corrosion performance and other coating properties will then need assessment.

Before a coating can be tested it needs to be produced. An indication of the way in which the characteristics of the coating change with variation in electroplating bath variables will also be needed. In order to make effective use of resources some knowledge of experimental design methods may be required.

2.11.1 Experimental design

There are several methods of designing experiments to give as much knowledge about a system as possible. The simplest is the classical experiment [155]. This is where one variable at a time is changed and the results monitored. This method is useful when investigating an unknown system to give an indication of how it might respond to a given change, such as variation in applied electroplating current density. It does not
give any information about any interactions between variables within a system. Other design methods are more complicated. The factorial experiment was first proposed by Fischer in 1920 [156] and consists of changing more than one variable at a time in a balanced manner to give an indication of the effect of interdependent parameters within a system. It is very time consuming and requires much experimentation but is good at determining interactions between variables. The factorial method is hence a good way of further investigating a known system. However, each variable analysed must be capable of being controlled. Any factors within a system such as ageing characteristics of the bath cannot be easily investigated using this method as they are hard to control. They can also significantly affect the result, especially if the level of variance within a system is more governed by the uncontrollable variables than the ones being controlled. This leads to a large spread of results, which can mask the effect of the variables being investigated, making the undertaking of the experimental set inconclusive. Robust design is another experimental method which is supposed to overcome some of the drawbacks of the factorial experiment [157-159]. It is based on a part factorial experiment so requires less experimentation than a full factorial set. It requires less experimentation than the classic experiment, and can account for uncontrollable variables, although like factorial experiments uncontrolled variables cannot be directly assessed [160]. It enables some of the interlinking variables within a system to be assessed, but if there are serious interactions between variables the results may not be reproducible as the mathematics behind the method assume no major interactions. Compared to the factorial experiments, robust design can give an indication of a non-linear affect for significantly less experimentation, but is not as good at investigating non-linear responses as the classic experiment. It must also be used with considerable care to prevent any interactions nullifying the results obtained. Other design methods, which attempt to overcome the drawbacks of the robust design method include D-optimal design [161-165], but again this method has its own shortcomings. These are the total reliance on computers to produce the most effective design matrix and the need to know initially what levels each variable is required to take. Unlike both factorial and robust design it can cope with missing data, as can the classical experiment but not as easily. It is therefore more applicable to optimisation of known systems rather than the investigation of unknown systems.
2.11.2 Corrosion tests

For coatings to be suitable replacements for cadmium they need to have comparable corrosion performance, similar wear characteristics and be capable of forming on complex shapes. Therefore methods of undertaking corrosion tests will be briefly reviewed followed by a review of other important tests.

Numerous different tests exist for the evaluation of corrosion performance. The rate of corrosion is dependent on both the type of metal and the conditions it is subjected to. The most reliable method is long-term corrosion monitoring, where test coupons are subjected to the actual atmospheric conditions which they would see in service. However, this method is very time consuming, and for materials with a low corrosion rate, it may take years for a measurable change in mass or appearance to occur.

For zinc based coatings, long term corrosion monitoring is the only truly reliable method of corrosion testing [32]. Corrosion in natural environments is a step-wise progress with the time of wetness and contact with polluting agents from the air having a direct effect on the instantaneous corrosion rate, and hence contributing to the overall corrosion rate [166]. This process is very hard to model or reproduce. Zinc-nickel, zinc-iron and zinc-cobalt all perform better than pure zinc in accelerated tests but not always in real time atmospheric testing [62,65].

2.11.2.1 Accelerated tests

A large number of accelerated corrosion tests exist, the simplest and most widely used is neutral salt fog exposure. This is normally carried out to ASTM B117-90 [167]. Neutral salt fog exposure involves subjecting the panels to a fog of 5% NaCl at 35°C until the sample fails. For coated steel panels, this failure point is normally taken as the time to 5% red rust. Zinc based coatings are very susceptible to the formation of voluminous white corrosion products (white rust) under wet conditions, so tend to have a very poor performance in neutral salt fog. Under the conditions present in neutral salt fog exposure the zinc coating does not have sufficient time to form any protective corrosion products and hence corrodes at a higher rate. However, neutral salt fog exposure testing is so widely used within industry that, although the true benefit of the test is dubious, it is still normally carried out. Neutral salt fog exposure provides a useful method for ranking coatings. However, it may fail to rank coatings
in the same order as for real time marine exposure. For example [65] 14% zinc-nickel has a much better performance in neutral salt spray than pure zinc, but in marine atmospheric exposure trials, zinc has been shown to perform better than all compositions of zinc-nickel.

There is also significant variation in neutral salt fog results obtained using different laboratories [62]. This may be due both to the wide range of fallout rates of salt solution specified in the standard and also due to the subjective nature of the test, with time to 5% red rust being determined visually. Results obtained using neutral salt fog corrosion testing should therefore be treated with care, with the results being used to give an indication of a possible trend rather than an absolute idea of the corrosion rate. Ideally the results should not be used in isolation and other corrosion tests should also be used to give a more complete schematic of the corrosion process.

Other accelerated corrosion tests include alternate immersion [168], where samples are subjected to alternate immersion in sodium chloride solution followed by a drying cycle in a humid atmosphere. This test would be more suitable for zinc-based coatings as the zinc coating may have time to form protective corrosion products during the drying cycle. It has been shown that a modified low chloride alternate immersion test [65] gives the same ranking order as marine exposure. Other cyclic tests can also be carried out. These range in complexity from the simple alternate immersion tests, to cycles with multiple steps at various different humidities and temperatures [62]. The effect of pollutants, such as sulphur dioxide, can also be evaluated in a number of different accelerated tests. The Kesternich test is one such test widely used in the automotive industry. Again, like neutral salt fog testing the results obtained may not correlate with in-service performance [62].

2.11.2.2 Electrochemical tests
A large number of electrochemical tests can be carried out. The simplest is where the test sample's potential is monitored over time. This gives information on the sacrificial properties of the coating with time under immersed conditions. However, it cannot give any information on how a coating may perform in the atmosphere, as there is no chance for passivation of the coating to occur due to the presence of carbon.
dioxide, although limited passivation due to the presence of oxygen within the solution can occur.

In direct current polarisation, a potentiodynamic polarisation sweep is carried out in either an anodic or a cathodic direction or both. The voltage is swept while the current is measured. The length of the sweep is dependent on the characteristics of the metal under test. Long anodic scans can give information about the passivity of a metal in a particular electrolyte. The scan rate chosen reflects the different information required from the test with a slow scan rate being employed for tests looking at passivation. A three electrode system is normally used, with a reference, auxiliary platinum electrode and working electrode. Corrosion rate calculations can be carried out from the tafel portion of the curves (the straight line portion of the curve near to $E_{corr}$). By combining direct current polarisation with other tests, such as wear resistance measurements, substantially more information on the coatings can be obtained [114]. Again as this test is undertaken under immersed conditions it may not be truly indicative of a coating’s performance in the atmosphere. This is especially the case for zinc and zinc-based coatings. The presence of carbon dioxide from the air is required to allow zinc and its alloys to fully passivate. This is not present under immersed conditions.

In linear polarisation resistance tests (LPR), a potentiodynamic polarisation sweep is carried out within the range ±20 mV of the $E_{corr}$ value, the corrosion potential. The voltage is stepped while the current is measured. The resulting plot of current versus potential can then be used to calculate the corrosion parameters, $E_{corr}$ the corrosion potential and $i_{corr}$ the corrosion current. Again a three-electrode system is used and the system is allowed to stabilise for 30 minutes prior to testing, although the stabilisation period can be omitted especially when assessing very active coating systems. A standard solution of 3.5% NaCl is normally used to carry out the tests. LPR calculations are carried out as in [169] to find the corrosion rate. LPR tends to be less destructive than direct current polarisation as the potential is not varied over such a large range. The calculation employed does not depend on accurate extrapolation of the tafel portion of the curve so has an advantage over direct polarisation tests. However, as the scan is carried out over a very limited range it cannot give additional information about the possible passivity of the coating. As the scan range is restricted
it does not affect the surface of the coating as much as direct polarisation allowing information on the way in which the corrosion process changes with time if linear polarisation resistance is repeated after a set time. Again like potential monitoring and direct polarisation tests linear polarisation resistance measurements are undertaken under immersion conditions. This may affect the validity if the results, especially for zinc-based coating systems.

In AC impedance tests the working electrode is subjected to a sinusoidal variation in voltage of varying frequency, usually about the corrosion potential ($E_{corr}$), and the current produced is measured. The applied voltage is divided by this measured current. Since both the voltage and current have a sinusoidal component with respect to time and are usually out of phase, the division results in the impedance. The impedance is divided by the nominal unit area giving the impedance units of $\Omega \, \text{cm}^2$. Details of this technique are given in ASTM G106-89 [170]. AC impedance measurements have been used in the study of the action of additives to zinc chloride electroplating baths [171]. AC impedance studies show direct correlation between the surface morphology of coatings produced, with or without additives and the shape of the impedance plots. AC impedance has also been carried out at different points on a cyclic voltammetry plot for zinc electroplating, giving useful mechanistic information [172]. Figure 2-6 illustrates a typical complex plane plot for the electroplating of zinc from chloride solutions, showing the reduction in the efficiency of an additive with increased electroplating current density.

Either a two or three-electrode system can be used. The three-electrode method the system under test to have a relatively stable value of $E_{corr}$. A two-electrode system is more suitable for systems where the $E_{corr}$ varies with time as in the case of aluminium alloys. In this case, the voltage is perturbed around the given value of potential, at the time the measurement is made, and does not rely on the potential remaining constant throughout the duration of the test.
The data collected during an AC impedance measurement can be represented in a number of different ways, as a complex plane or Nyquist plot, or as a Bode plot [173]. Corrosion rate, or more specifically $I_{\text{corr}}$, can be related directly to either the polarisation resistance $R_p$ of the coating or the charge transfer resistance $R_{\text{ct}}$ which are both obtained from the complex plane plot. The nature of the relationship is governed by the kinetics of the reaction, for example for a one step reaction controlled by electron transfer, the relationship between $I_{\text{corr}}$ and $R_p$ is shown in Equation 2-9. $R_p$ can be measured directly from the complex plane plot, and is related to the size and position of the semi-circle.

$$R_p = \frac{b_e b_a}{2.303 (b_e + b_c)} \frac{1}{I_{\text{corr}}}$$

Equation 2-9

where $R_p =$ polarisation resistance, $b_c =$ slope of the cathodic Tafel region, $b_a =$ slope of the anodic Tafel region and $I_{\text{corr}} =$ corrosion current density.
A comparison between neutral salt fog and AC impedance measurements made after 24 hours immersion in 3.5% sodium chloride has been made for organic paint systems [156]. A simplified equivalent circuit was used with $R_e$ representing a measure of the pitting resistance and the total resistance of the surface coating. $R_e$ was found to be comparable with the neutral salt fog results, with coatings giving a high value of $R_e$ passing the neutral salt fog test with less than 3 pits after 168 hours exposure. AC impedance was found to be slightly more sensitive at the extremities of the testing conditions, i.e. with the poorest and the very best performing coatings. However, by using a simplified circuit and only measuring the AC response after 24 hours mechanistic information about the nature of the corrosion process and the action of any inhibitors present was lost.

Measuring the change in the impedance response in a stripping cell can also be used to assess the thickness of the coating produced [174]. This is a suitable method of calculating thickness where an appropriate stripping solution for the coating can be found, which does not attack the substrate. It is, however, a destructive technique so no further testing can be carried out.

Like other electrochemical tests, AC impedance is carried out under immersion conditions. This again can be difficult to relate to actual atmospheric corrosion processes as passivation of the coating may not result especially for zinc based coatings as under immersion there is no carbon dioxide present to allow complete passivation. In addition, AC impedance can be difficult to interpret, with a danger of losing mechanistic information by over simplifying the corrosion process, or a danger of not seeing a corrosion process as it occurs over the same frequency range as another process. Hence, although AC impedance has been discussed within this literature review it will probably not be employed as a method of evaluation within this research programme.

All electrochemical techniques suffer from the drawback that they require a solution to undertake a measurement. This means that they are only useful in determining the performance of a coating under immersed conditions. However, they give fast, numeric answers, which can be useful in ranking given coatings, and can give an indication as to how the coating may perform in real time exposure tests. When used
in conjunction with other non-immersion accelerated corrosion tests their use can help to give a fuller understanding of the corrosion mechanisms at work and so help to give an indication of real atmospheric corrosion rates.

2.11.3 Other tests

Numerous other tests will be important in determining whether a given coating would make a suitable replacement for cadmium. These include, for example, porosity, adhesion, wear, hardness, frictional characteristics, thickness and electrical conductivity tests on the coating as well as tests on the electroplating baths, including throwing or levelling power and ageing characteristics.

The porosity of the coating can be estimated by using a potentiodynamic test, carried out at a potential at which the substrate actively dissolves while the coating is passivated [175]. The porosity of a coating can have a direct effect on its corrosion performance and the level of sacrificial protection obtained, but is normally more important for barrier or non-sacrificial coatings. Chrono-amperometric and other related techniques can also be used to study the nature of deposition, normally for single metal coatings, but they can be used, with care, for binary alloys such as zinc-nickel [54,108].

Porosity can also be estimated using chemical tests, such as those based on potassium ferrocyanide, which turns blue when iron is present, so can be used if a steel substrate is employed and the coating contains no iron [176]. There are a number of specifications for different porosity tests, but mainly for noble coatings on less noble substrates where the presence of porosity is more of a problem [177].

Adhesion of the electroplate can also be evaluated by determining the force required to pull off the deposit at right angles. Determination can be made using a spring balance or a tensile testing machine [104]. Other adhesion tests such as cross hatch adhesion can also be used but are more subjective, as with the neutral salt fog corrosion test they rely on ranking by visual means [178].
Various other electrochemical tests are useful in determining the effects of different additives to the electroplating solution. Cyclic voltammetric stripping is one such test, which can be used to determine the way in which an additive works within a solution, and whether it has any levelling capability [179]. Normal cyclic voltammetry can also be used to study the process of electroplating, including the formation of passive films [180]. The nature of the electroplating process can also be studied using cyclic voltammetry for example a plot of cathodic current peak against the square root of the scan rate used will be linear if the electroplating process is under diffusion control [181].

Thickness of the electroplate can be measured using an eddy current method (ASTM Test Method D1186A) if the coating is conductive and on a ferrous substrate. This method does not work for a conductive coating on aluminium [182]. Thickness of the coating is important, especially if corrosion testing is undertaken, as without knowledge of the thickness of the coating it is impossible to correlate any corrosion data obtained.

Other tests, that are important for evaluating the performance of a coating for use on electrical connectors are, wear testing [183-186] and electrical conductivity measurements. Wear testing has been carried out on multilayers of chromium and nickel. The thickness of the multilayers had a direct effect on the wear characteristics and the hardness of the resultant deposits with thin multilayered structures producing harder, more wear resistant coatings [187]. This shows that for the use of multilayers as well as influencing the corrosion performance of the coating, they can give improvements in other properties such as wear. The friction properties of the coating are also important. Additions such as diamond to nickel-phosphorous have been shown to reduce the friction of the coating but makes the coating rougher. The hardness of the coating is also increased [188]. A reduction in friction would be useful for both electrical connectors and fasteners, as it would allow for easier mating, un-mating and unfastening. However, any increase in roughness may lead to detrimental wear properties, especially when the coating is also subjected to corrosion testing.

Electrical conductivity can be measured using the four-point probe method [129], however, this method is not very accurate. A more useful method for low resistivity
coatings is given in [189]. Here the conductivity of a coating is measured by measuring the voltage drop across a set distance when a current of 1 Amp is applied. This method allows for the contact resistance between the voltmeter and the sample, and for any resistances due to the connecting leads [190].

Hardness tests are also important, as they tend to relate to the wear characteristics of a given coating. The relationship is, however, not clear cut with zinc-nickel being known to exhibit a higher hardness than pure zinc [77,86], but showing a decrease in dry abrasive wear resistance [67].

A number of simple empirical tests exist for evaluating the ability of a plating solution to produce even deposits, as apposed to level deposits. The simplest being an experiment, which assesses the different weights of deposit obtained from two samples placed back to back within the plating solution. This gives an indication of the ability of the solution to throw around an object [150,191]. Other tests look at the different amounts of deposit obtained on two samples placed at different distances away from a central flat mesh anode [151]. A rotating cylinder hull cell can also be used to assess both levelling power and the effect of additives on the bath parameters. A rotating cylinder hull cell has a non-uniform primary current distribution, which makes it useful for the assessment of levelling or throwing power [192]. A number of factors govern the throwing power of a solution. In general increasing conductivity increases throwing power, as does reducing the metal ion content of the bath while keeping the conductivity high by adding compounds such as ammonium sulphate to a sulphate bath [151]. For a bath with good throwing power, such as cyanide zinc, the current efficiency changes with current density giving a more even thickness distribution and hence good coverage of complex shapes [193].

The level of brightness and uniformity of a deposit over a given current range can also be important. This can be measured using a rotating cylinder electrode, which provides reproducible results over different current density ranges [194].

2.11.4 Summary

A summary of the results from this section of the literature, testing of coatings is given in Table 2-6.
Experimental design

Different methods of undertaking research. These are the classical experiment, factorial experimentation, robust design and D-optimum design.

Corrosion tests

Long-term corrosion monitoring the most accurate but time consuming. Accelerated tests include neutral salt fog testing, alternate immersion and the Kesternich test. Electrochemical tests include, potential monitoring, cyclic voltammetry, direct current polarisation, linear polarisation resistance and AC impedance. All electrochemical tests need to be undertaken in immersion conditions, reducing their validity.

Other tests

Porosity, more important for noble rather than sacrificial coatings
Adhesion, very important especially when electroplating onto aluminium
Thickness, need to assess in order to quantify corrosion tests
Wear testing, important for mating and un-mating of connectors and for undoing fasteners
Electrical conductivity, very important to be low for electrical connectors, not important for use on fasteners, hard to measure
Hardness, may be related to friction and wear properties of a coating, easy to measure
Throwing power, solution must have good throwing power to electroplate complex shapes

Table 2-6 Summary of testing and experimental design literature section

From the literature it can be seen that no binary zinc alloy would at present give all the properties of cadmium electroplate for use as a replacement for electrical connectors and fasteners on aircraft. It was therefore decided to investigate two methods of modifying the properties of the existing coatings to make them more suitable as cadmium replacements. The first method was the use of multilayer systems. The second was the alloying of zinc-nickel with another metal.

For the multilayer coating work, zinc-nickel was chosen as the binary alloy. Initially investigated was the production of single layer coatings with known variable nickel contents onto aluminium alloy and steel. Dual layer coatings were then produced to assess the feasibility of using multilayer systems. Accelerated corrosion testing and
other tests such as electrical resistance measurements were undertaken on the resultant coatings.

By alloying zinc-nickel with manganese it was hoped to reduce the formation of white rust and hence make the ternary alloy more suitable for the replacement of cadmium on electrical connectors. It was also thought that the addition of manganese might help combat the de-zincification of zinc-nickel which has been observed with time [52]. Zinc-nickel-manganese has been produced before from sulphate based solutions [115], but only with very low percentages of manganese. No corrosion data is available on this alloy. Therefore the aim of undertaking electroplating of zinc-nickel-manganese was to produce, firstly higher percentages of manganese and secondly to undertake corrosion testing to assess the suitability of the alloy as a replacement for cadmium.
3 Experimental techniques

3.1 Introduction

The experimental conditions used are detailed in this Section. Further detail of the zinc-nickel experiments undertaken and initial results on current efficiency calculations, composition change with applied current density, thickness and morphology are then given in Section 4. Section 6 then deals with the corrosion investigation of the zinc-nickel single and dual layer systems.

Further details of the zinc-nickel-manganese experimental conditions are given in Section 5 along with the results of investigating the electroplating solution response, the current efficiency, the thickness, composition and morphology of the deposits. Corrosion results are presented in Section 7.

A discussion of the relative merits and disadvantages of the two systems and their use as potential cadmium replacements is then presented in section 8.

3.2 Experimental techniques

The aim of this Section is to detail all the experimental techniques used, for reference later. The section is divided into parts, dealing with pre-treatment, electroplating, coating analysis, corrosion tests and other tests undertaken. A short summary is given at the end to facilitate the use of this section as a reference for further sections.

3.3 Pre-treatments

3.3.1 Steel

In all cases the steel used was mild steel. The steel was degreased in surfactant (polyoxyethylene sorbiton monohydrate, Tween™) with ultrasonic treatment to remove any grease and oil prior to further pre-treatment. It was then degreased in acetone and hot air dried and stored in a desiccator. Three different pre-treatments were investigated. These are detailed in Table 3-1.
Experimental techniques

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Solution</th>
<th>Treatment time /minutes</th>
<th>Temperature °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Abrasion to 1200 grit</td>
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<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>HCl dip</td>
<td>10% HCl in deionised water</td>
<td>1/2</td>
<td>25</td>
</tr>
<tr>
<td>HCl pickle</td>
<td>10% HCl in deionised water</td>
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<td>50</td>
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</tbody>
</table>

Table 3-1 Pre-treatments for steel

3.3.2 Aluminium alloy

When flat coupons were used 2014-T6 unclad sheet of thickness 1.2 mm was the material chosen. The accepted composition of 2014-T6 is given in [90]. Some electroplating was also undertaken on actual connector shells supplied by Deutsch Ltd. [3]. In all cases the pre-treatment was the same. Firstly the coupons or connector shells were degreased with acetone and allowed to air dry. The samples were then etched, followed by a desmut [91] and then subjected to a zincate immersion pre-treatment to prevent the formation of oxide on the aluminium alloy surface prior to electroplating. Details of the etch, desmut and zincate solutions, the treatment times and temperatures are given in Table 3-2.

<table>
<thead>
<tr>
<th>Pre-treatment</th>
<th>Solution</th>
<th>Immersion time /minutes</th>
<th>Temperature °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Etch</td>
<td>10% sodium hydroxide in de-</td>
<td>1</td>
<td>50</td>
</tr>
<tr>
<td></td>
<td>ionised water</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Desmut</td>
<td>50% nitric acid in de-ionised</td>
<td>0.25</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>water</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zincate</td>
<td>50 g dm⁻³ zinc oxide 400 g dm⁻³</td>
<td>3</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>sodium hydroxide</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 3-2 Pre-treatments for 2014-T6 aluminium alloy flat coupons and connector shells

3.3.3 Detached coatings

Detached coatings were obtained by electroplating onto untreated aluminium foil. The total applied electroplating charge was increased to produce thicker coatings, which could then be easily detached from the substrate. The total charge applied was increased as the current density was increased to allow both for the decrease in current
efficiency observed and also to allow for any dendritic, preferential growth, which would be more likely to occur as the current density increased.

The “as produced” detached coatings were carefully removed from the aluminium foil. Electrical contact was then made to the back of all samples. The coatings were then fastened with adhesive onto a non-conducting backing material to facilitate handling.

3.4 Electroplating

3.4.1 Solutions

Five different solutions were investigated for zinc-nickel electroplating. These are detailed in Table 3-3. Polyoxyethylene sorbiton monolaurate (Tween™) was added to solutions 2, 3, 4, and 5 to reduce the porosity and number of defects in the coating [52]. As this is a surfactant an antifoaming agent was also added to solutions 2, 3, 4, and 5 to enable the use of an air bubbler when tank electroplating was undertaken. Boric acid was added to solutions 1 and 2 to help stabilise the pH. All electroplating was undertaken at room temperature (20°C) with no additional heating or cooling.

| Solution 1 | 0.75 mol dm⁻³ nickel sulphate  
0.75 mol dm⁻³ zinc sulphate  
40 g dm⁻³ boric acid  
pH = 3.0  
Temperature = 20°C |
| Solution 2 | 0.75 mol dm⁻³ nickel sulphate  
0.75 mol dm⁻³ zinc sulphate  
40 g dm⁻³ boric acid  
10 cm³ dm⁻³ Tween™  
10 cm³ dm⁻³ antifoaming agent  
pH = 3.0  
Temperature = 20°C |
| Solution 3 | 0.75 mol dm⁻³ nickel sulphate  
0.75 mol dm⁻³ zinc sulphate  
0.75 mol dm⁻³ tris (hydroxymethyl)methylamine (TRIS)  
10 cm³ dm⁻³ Tween™  
10 cm³ dm⁻³ antifoaming agent  
2 g dm⁻³ gelatine  
pH = 6.5  
Temperature = 20°C |
| Solution 4 | As solution 3 but with 1.0 mol dm⁻³ sodium chloride |
| Solution 5 | As solution 3 but with 2.0 mol dm⁻³ sodium chloride |

*Table 3-3 Zinc-nickel electroplating solutions used*
Two main solutions were investigated for zinc-nickel-manganese electroplating. These are detailed in Table 3-4. In addition, the effect of changing the citrate concentration and the manganese sulphate concentration of solution six was investigated. These are also detailed on Table 3-4.

| Solution 6 | 0.2 mol dm$^{-3}$ zinc sulphate  
0.6 mol dm$^{-3}$ nickel sulphate  
0.4 mol dm$^{-3}$ manganese sulphate  
0.4 mol dm$^{-3}$ sodium citrate  
10 cm$^3$ dm$^{-3}$ Tween™  
10 cm$^3$ dm$^{-3}$ anti-foaming agent  
40 g dm$^{-3}$ boric acid  
40 g dm$^{-3}$ ascorbic acid  
80 cm$^3$ dm$^{-3}$ hydrochloric acid  
$pH = 1$  
Temperature = 20- 40°C |
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Factors varied</td>
<td>Manganese sulphate</td>
</tr>
<tr>
<td>Concentrations investigated</td>
<td>0.3, 0.4 and 0.6 mol dm$^{-3}$</td>
</tr>
</tbody>
</table>
| Solution 7 | 0.2 mol dm$^{-3}$ zinc sulphate  
0.6 mol dm$^{-3}$ nickel sulphate  
0.4 mol dm$^{-3}$ manganese sulphate  
1.2 mol dm$^{-3}$ TRIS (see Table 3-3)  
$pH = 6.5$  
Temperature = 20°C |

Table 3-4 Zinc-nickel-manganese electroplating solutions

3.4.2 Bath configurations

A number of different bath configurations were used to produce electroplated samples.

The first bath configuration used for tank electroplating of zinc-nickel onto aluminium 2014-T6 and steel samples is shown in Figure 3-1. This bath configuration has been designated bath configuration 1.
Steel or aluminium alloy 2014-T6 coupon or connector shell

Inert carbon anode

Anode bag

Electroplating solution, volume 500 cm³ (1000 cm³ for configuration 2)

Figure 3-1 Bath configuration 1 used for zinc-nickel electroplating (bath configuration 2 was the same but with a solution volume of 1000 cm³)

Further tank electroplating of zinc-nickel was undertaken using a larger solution volume (1000 cm³) and this has been designated configuration 2. For brush electroplating of zinc-nickel and zinc-nickel-manganese onto steel the bath configuration (bath configuration 3) shown in Figure 3-2 was used.

Cathode

Sample

Anode bag saturated with electroplating solution

Carbon anode

Figure 3-2 Bath configuration 3 used for brush or selective electroplating
Experimental techniques

Two other bath configurations used for zinc-nickel-manganese electroplating are shown in Figure 3-3. These configurations were used with Solution 6 detailed in Table 3-4. These are designated bath configurations 4 and 5 respectively.

![Diagram of bath configurations 4 and 5](image)

Figure 3-3 Bath configurations 4 and 5 (configuration 4 on left, 5 on right) used for electroplating of zinc-nickel-manganese using Solution 6 detailed in Table 3-4

3.4.3 Cyclic voltammetry

Several solutions were investigated using cyclic voltammetry; zinc-nickel, nickel-manganese, zinc-manganese and zinc-nickel-manganese solutions. The solutions were tested initially, after 2, 3, 4, and 5 weeks. The compositions of the solutions used are given in Table 3-5. Boric acid was added to help stabilise the pH. A schematic of the cell used is given in Figure 3-4.
### Experimental techniques

#### Solution Composition

<table>
<thead>
<tr>
<th>Solution</th>
<th>Composition</th>
</tr>
</thead>
</table>
| Zinc-nickel               | 0.1 mol dm\(^{-3}\) NiSO\(_4\).7H\(_2\)O \[0.3\] \ mol dm\(^{-3}\) ZnSO\(_4\)
|                           | 0.15 mol dm\(^{-3}\) (NH\(_4\))\(_2\)SO\(_4\)
|                           | 10 cm\(^3\) dm\(^{-3}\) tween\(^{\text{TM}}\) \[40\] \ g dm\(^{-3}\) boric acid |
| Nickel-Manganese          | 0.1 mol dm\(^{-3}\) NiSO\(_4\).7H\(_2\)O \[0.25\] \ mol dm\(^{-3}\) MnSO\(_4\)
|                           | 0.15 mol dm\(^{-3}\) (NH\(_4\))\(_2\)SO\(_4\)
|                           | 0.3 mol dm\(^{-3}\) sodium citrate \[10\] \ cm\(^3\) dm\(^{-3}\) tween\(^{\text{TM}}\) \[40\] \ g dm\(^{-3}\) boric acid |
| Zinc-Manganese            | 0.3 mol dm\(^{-3}\) ZnSO\(_4\)
|                           | 0.25 mol dm\(^{-3}\) MnSO\(_4\)
|                           | 0.15 mol dm\(^{-3}\) (NH\(_4\))\(_2\)SO\(_4\)
|                           | 0.3 mol dm\(^{-3}\) sodium citrate \[10\] \ cm\(^3\) dm\(^{-3}\) tween\(^{\text{TM}}\) \[40\] \ g dm\(^{-3}\) boric acid |
| Zinc-Nickel-Manganese     | 0.1 mol dm\(^{-3}\) NiSO\(_4\).7H\(_2\)O \[0.25\] \ mol dm\(^{-3}\) MnSO\(_4\)
|                           | 0.15 mol dm\(^{-3}\) (NH\(_4\))\(_2\)SO\(_4\)
|                           | 0.3 mol dm\(^{-3}\) sodium citrate \[10\] \ cm\(^3\) dm\(^{-3}\) tween\(^{\text{TM}}\) \[40\] \ g dm\(^{-3}\) boric acid |

*Table 3-5 Compositions of solutions used for cyclic voltammetry*

The electrode area was 1 cm\(^2\) and the volume of plating solution was 300 cm\(^3\). Cyclic voltammograms were carried out at overpotentials from -2.5 to 2.0 V. They were facilitated using a Solatron 1280 Electrochemical Measurement Unit (Potentiostat) and accompanying Solatron software. Five cycles were carried out for each experiment with the fifth cycle used for undertaking comparisons with time. Sweeps were undertaken at room temperature (20°C), with no additional agitation.

The effect of varying the nickel content of the zinc-nickel, nickel-manganese and zinc-nickel-manganese solutions was also investigated using cyclic voltammetry, with concentrations of 0.2, 0.3 and 0.4 mol dm\(^{-3}\) of nickel sulphate. The rest of the concentrations of these solutions were kept as in Table 3-5.
Figure 3-4 Schematic of cell used for electrochemical measurements

3.4.4 DC and pulse electroplating conditions

Electroplating was undertaken either using a current pulse generator supplied by CGC Technology Ltd connected to a TGA 1230 30 MHz synthesised arbitrary waveform generator, or using an Axel Akerman AS Galvanic Rectifier Type 36S-100/50-F, depending on the maximum current required. The current pulse generator had a maximum voltage output of 20 V and a current limit of 10 A. The unit was designed to control the current while the voltage varied. The Axel Akerman Rectifier had a maximum voltage of 100 V and a maximum current output of 50 A and was used to electroplate larger coupons for corrosion testing. Both units were capable of supplying either direct current or pulse waveforms. The Axel Akerman unit was computer controlled while the current pulse generator was capable of being controlled either by computer or by using the front face function keys. In this work the latter gave sufficient control of the pulse conditions to negate the use of the computer. Simple square wave pulses were used as in Figure 2-3a. The values of $t_c$ and $t_d$ were varied.
Details of the applied electroplating current density and pulse conditions used are given in sections 4 (zinc-nickel coatings) and 5 (zinc-nickel-manganese coatings).

3.4.5 Experimental design techniques
Most experimentation was undertaken using classical methods detailed in Section 2-11-1. However, some experimentation was also carried out using Robust design methods (section 2-11-1). Robust design was only used to investigate the effect of solution variables in zinc-nickel-manganese electroplating on the composition of alloy produced. (Section 5, Table 5-5).

3.5 Analysis of coatings

3.5.1 Calculation of current efficiency
In order to assess the current efficiency of the electroplating process all samples were weighed before and after electroplating and the mass change calculated. The current efficiency of the electroplating process was calculated assuming that manganese was a two-electron process like zinc and nickel using the formula [52]:

\[
CE(\%) = \frac{g_a}{g_t} \times 100
\]

*Equation 3-1*

Where \(CE\) = current efficiency (\%), \(g_a\) = actual deposit weight, and \(g_t\) = theoretical deposit weight.

The theoretical deposit weight was calculated from the formula;

\[
g_t = \frac{I \cdot t \cdot W_a}{F}
\]

*Equation 3-2*

where \(I\) = current in Amps, \(t\) = time of electroplating, \(F\) = Faradays constant and \(W_a\) = electro-chemical equivalent. For a ternary alloy \(W_a\) is given by the formula;
Experimental techniques

\[
W_a = \frac{W_1' W_2' W_3'}{F_1' W_2' W_3' + F_2' W_1' W_3' + F_3' W_1' W_2'}
\]

Equation 3-3

For a binary alloy \( W_a \) is given by the formula:

\[
W_a = \frac{W_1 W_2}{F_1 W_2 + F_2 W_1}
\]

Equation 3-4

where \( W_1, W_2, \) and \( W_3 \) are equivalent weights of metals 1, 2 and 3 respectively and \( F_1, F_2 \) and \( F_3 \) are the fractions of metals 1, 2 and 3 in the alloy. \( F_1 + F_2 + F_3 = 1 \) and \( F_1 + F_2 = 1 \) for a binary alloy.

3.5.2 Scanning electron microscopy

Scanning electron microscopy was undertaken on a Cambridge Stereoscan Scanning Electron Microscope with ISIS software. Micrographs were taken at various magnifications at 20 KeV and a working distance of normally 25 mm. Coupons were mounted horizontally in the chamber.

3.5.3 X-ray energy dispersive analysis (EDAX)

X-ray energy dispersive analysis was also undertaken on the Cambridge Stereoscan scanning electron microscope using a SiLi Microspec WDX detector at 20 K eV and a working distance of 25 mm. The ISIS software was calibrated at the same magnification of the X-ray scan using a copper standard. The count rate was maintained to give less than 20% dead time over a scan length of 100 seconds.

3.5.4 Optical microscopy

Optical microscopy was undertaken on sectioned connector shells coated with cadmium and other electroplates to ascertain the deviation in thickness at several points on the connector shell (50 readings were taken around the circumference of each connector shell). The optical microscopy was carried out using an Olympus optical microscope at various magnifications. A graduated eye piece was used which was calibrated using a calibrated graticule CS906 from Graticules Ltd, Tonbridge, Kent.
Experimental techniques

Optical microscopy was also carried out on sectioned coatings on 2014-T6 aluminium, which had been corrosion tested in a neutral salt fog, to determine the depth and distribution of pits.

3.5.5 Thickness measurements

For steel substrates, coating thickness measurements were carried out using a Fischer Dualscope MP4C with EGAB 1.3 Fe probe. Ten readings were taken on each sample excluding the extreme edges in about the same positions. The mean, minimum, maximum, standard deviation and number of reading were recorded for each sample. The standard deviation of the measurements was used to determine the uniformity of the coating.

3.6 Corrosion testing

3.6.1 Potential-time monitoring

Monitoring of the corrosion potential with time in 3.5% sodium chloride solution was undertaken using a Grant Squirrel multi channel meter/ logger, 1000 series with potential readings being taken automatically every hour throughout the duration of the test. The cell configuration used is detailed in Figure 3-5. Samples for potential monitoring were cut on a guillotine to give an approximate exposed area of 1 cm² from the centre of the sample. Contacts were then attached to the rear of the samples using silver loaded epoxy adhesive. The contact area was then protected using two part epoxy resin. The contact wire was threaded through a glass rod. This was joined to the rear of the sample again using two part epoxy resin. The tag electrode thus produced was then lacquered on the back and edges with TURCO lacquer (Turcomask, TFM S45) leaving an exposed area of approximately 1 cm² in the centre to allow for any inconsistencies of the electroplate at the edges of the sample.
Experimental techniques

3.6.2 Galvanic compatibility

The current between the electroplated coatings and various different substrate materials was monitored over a time period to ascertain the galvanic compatibility of the electroplated coatings. A five channel ACM Instruments Galvanogil zero resistance ammeter and accompanying software was used to monitor the current. Coupons for testing were guillotined from the electroplated samples and the substrate material to give a sample with approximate dimensions of 7 cm x 1.5 cm. Contacts were attached to the rear of the samples using silver loaded epoxy adhesive. The majority of the sample was then protected using green protective, chemically resistant tape (3Ms pressure sensitive tape type #8403 HD 9270-01) to give an exact exposed area of 1 cm². The very edges of the exposed area was additionally protected from solution ingress by TURCO lacquer (Turcomask, TFM S45). The configuration of the sample cell is shown in Figure 3-6.
Experim ental techniques

Electrodes were 5 cm apart in 250 cm³ of solution. Cell lid was designed to make electrodes parallel to each other.

3.5% sodium chloride solution

Figure 3-6 Schematic of cell used for galvanic compatibility tests

3.6.3 Marine exposure

The atmospheric marine exposure trials were conducted at DERA Bincleaves, Weymouth, UK. The samples were located on exposure racks approximately 150 m from the open sea at an angle of 45⁰ to the horizontal, facing due south according to ASTM G50 [195]. The test coupons were protected on the rear and edges using green adhesive weatherproof tape (3Ms pressure sensitive tape type #8403 HD 9270-01).

3.6.4 Alternate immersion

Alternate immersion tests were undertaken using a modified ASTM G44 testing procedure [168]. Test coupons were immersed for 10 minutes in every hour in a 0.5% sodium chloride solution in an environmentally controlled room maintained at 45±6% relative humidity at 27±1°C. The rear and edges of the test coupons were protected with green, chemically resistant tape (3Ms pressure sensitive tape type #8403 HD 9270-01) and the coupons were suspended in the salt solution using non-conducting nylon cord.
3.6.5 Neutral salt fog corrosion testing

Neutral salt fog corrosion testing was undertaken in accordance with ASTM B117 [167] using a C&W SF/4 salt fog cabinet. The flat samples were located within the cabinet at 30° to the horizontal, spaced so that no sample received drips from any other sample. The rear and edges of each sample were protected using green, chemically resistant adhesive tape (3Ms pressure sensitive tape type #8403 HD 9270-01). The non-flat aluminium alloy connector shell samples were suspended using nylon cord inside the cabinet. The connector shells were not protected with green tape prior to exposure. The samples were subjected to continuous 5% salt fog solution at 35°C for the duration of the test. For the steel coupons this was time to 5% red rust in most cases. The amount of white rust was also recorded. For the aluminium alloy substrates the time of exposure was preset and the samples were ranked after exposure for level of staining or pitting. In some cases the samples were sectioned after exposure and the number and depth of pits evaluated using optical microscopy (see sub-section 3.5-4).

3.6.6 Linear polarisation resistance

Linear polarisation resistance measurements were carried out using an EG & G Potentiostat / Galvanostat Model 263A and accompanying EG & G software. The cell configuration is shown in Figure 3-4. Testing was undertaken in 3.5% sodium chloride solution. Sweeps were carried out at 20 mV either side of E_{corr} at a scan rate of 0.166 mV s^{-1} with the cell being allowed to stabilise for 30 minutes prior to test. The potential was monitored during the stabilisation period.

3.6.7 Double polarisation

Double polarisation tests were also undertaken using the EG & G Potentiostat / Galvanostat Model 263A and accompanying EG & G software. The cell configuration was as shown in Figure 3-4. Testing was undertaken in 3.5% sodium chloride solution. The cell was allowed to stabilise for 30 minutes prior to testing. While the cell was stabilising the potential was monitored. Scans were then undertaken starting at 250 mV negative of E_{corr}. The potential was then scanned at a rate of 0.5 mV s^{-1} to a point 250 mV positive of E_{corr}. The scan direction was then reversed back through E_{corr} to a point 250 mV negative of the original E_{corr}. In this way information on the possible passivation of the coating was obtained. A threshold limit of 0.01 A cm^{-2} was
placed on the cell. This meant that if the current reached this limit the scan would reverse.

3.7 Other tests

3.7.1 Porosity
The porosity of a number of samples was investigated visually by the use of chemical means [177]. A solution of $40 \text{ g dm}^{-3} \text{ K}_3\text{Fe(CN)}_6$ and $2 \text{ g dm}^{-3} \text{ NaCl}$ was used to anodically treat several zinc-nickel-manganese electroplated samples using selective anodising at $4 \text{ V}$ for 5 minutes at room temperature. The anodising was undertaken using a CGC Technology Ltd current pulse generator under DC conditions, adjusting the current supplied to give a voltage of 4 V.

This solution develops a deep blue colouration on the sample in the presence of Fe ions (i.e. at points of through coating porosity). It only works for ferrous substrates and could not therefore be used for zinc-nickel coatings on aluminium alloy.

3.7.2 Hardness testing
Micro-hardness testing was undertaken using a Buehler Micromet II digital micro-hardness tester. The micro-hardness tester was calibrated using a standard of known hardness. Five measurements were then undertaken on each sample using a load of 200 g. This load was the same as that used for the calibration standard. The average micro-hardness was then calculated.

3.7.3 Electrical conductivity
Electrical conductivity measurements were carried out using the method outlined in [190]. Here the conductivity of a coating was measured by measuring the voltage drop across a set distance when a current of 1 Amp was applied. This method allows for the contact resistance between the voltmeter and the sample, and for any resistances due to the connecting leads. A CGC Technology Ltd current pulse generator was used to provide the steady current of 1 Amp. The voltage was measured using a Thurlby digital voltmeter. A schematic of the circuit used for the measurement is given in Figure 3-7. Initially the two contacts were connected together and the voltage drop measured, this made allowance for the resistance of the measurement circuit. The
voltage drop across the sample was then measured. The resistance per linear cm was then calculated.

![Circuit configuration for conductivity tests](image)

**Figure 3-7 Circuit configuration for conductivity tests**

3.7.4 Adhesion tests

Cross hatch adhesion tests were undertaken as outlined in [178] using an individual square size of 1 mm and a grid width of 10 x10. Adhesive tape was applied to the cross cut and pulled off. The level of adhesion was then assessed visually using the reported ranking system in [178].

3.8 Summary

A summary of the experimental techniques used is given in Table 3-6.
<table>
<thead>
<tr>
<th>Title</th>
<th>Sub-title</th>
<th>Sub-section</th>
<th>Related Table or Figure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pre-treatment</td>
<td>For steel</td>
<td>3-3-1</td>
<td>Table 3-1</td>
</tr>
<tr>
<td></td>
<td>For aluminium</td>
<td>3-3-2</td>
<td>Table 3-2</td>
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<td></td>
<td>For detached coatings</td>
<td>3-3-3</td>
<td></td>
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<tr>
<td>Electroplating</td>
<td>Solutions</td>
<td>3-4-1</td>
<td>Tables 3-3, and 3-4</td>
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<td>Bath configurations</td>
<td>3-4-2</td>
<td>Figures 3-1, 3-2, and 3-3</td>
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<td>Cyclic voltammetry</td>
<td>3-4-3</td>
<td>Table 3-5, Figure 3-4</td>
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<td>DC and Pulse conditions</td>
<td>3-4-4</td>
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<tr>
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<td>Experimental techniques</td>
<td>3-4-5</td>
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<td>Analysis of coating</td>
<td>Calculation of current efficiency</td>
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<td>Potential monitoring</td>
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<td>Galvanic compatibility</td>
<td>3-6-2</td>
<td>Figure 3-6</td>
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<td>Marine exposure</td>
<td>3-6-3</td>
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<td>3-6-4</td>
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<td>Linear polarisation resistance</td>
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<td>Double polarisation</td>
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<td>Other tests</td>
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<td>Electrical conductivity</td>
<td>3-7-3</td>
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<td>Adhesion tests</td>
<td>3-7-4</td>
<td></td>
</tr>
</tbody>
</table>

*Table 3-6 Summary of experimental technique sub-sections*
4 Production of zinc-nickel coatings- results and discussion

4.1 Introduction
The aim of this Section was to investigate the possibility of depositing compositionally modulated zinc-nickel alloy layers onto 2014-T6 aluminium and steel. It was aimed to deposit between 0-14% nickel containing zinc-nickel alloy from a single tank by modifying the applied current density. On achieving single layer deposits with predictable compositions within this range, the process was then extended to produce dual layers (with two different nickel contents) on 2014-T6 aluminium alloy and steel. On the latter substrate the effect of electroplating parameters on the resultant coating, both in terms of composition and morphology were also studied.

The electroplating of non-flat (i.e. connector shells) samples with predictable zinc-nickel alloy contents was then undertaken to assess the suitability of the solution for this type of substrate.

Corrosion testing was then carried out on the single and dual layers on aluminium alloy and also on the actual connector shells to assess the possible advantages of using dual layer zinc-nickel coatings as replacements for cadmium electroplate.

On steel, corrosion testing of the resultant coatings was again undertaken both to determine the effect of using a steel rather than aluminium alloy substrate, and the effect of the different electroplating techniques, namely selective or brush electroplating and tank electroplating, on the corrosion properties of the resultant coatings. Results of corrosion tests are given in section 6.

Detached coatings of zinc-nickel of various compositions were also produced to investigate the electrochemical properties of the zinc-nickel without the interference obtained from the substrate. This was to obtain a more complete picture of the compatibility of the zinc-nickel with aluminium alloy 2014-T6 and also to produce a more complete understanding of the corrosion process of the alloy with time.
A short summary is given at the end of the Section.

4.2 Experimental

4.2.1 On aluminium alloy and aluminium alloy connector shells

The pre-treatments used for the 2014-T6 aluminium alloy coupons and electrical connectors are detailed in Section 3-3-2.

Initially an electroplating bath based on zinc and nickel sulphates with boric acid was investigated. Two different bath compositions were used, one without surfactant, the other with. The solutions used are detailed in Table 3-3, solutions 1 and 2, in Section 3-4-1.

Both direct current and pulse electroplating were used. Details of the DC and pulse conditions are given in Section 3-4-4. Electroplating was undertaken using a range of current densities, from 0.02 to 0.8 A cm\(^{-2}\) using bath configuration 1 detailed in Figure 3-1, Section 3-4-2. Pulse electroplating was carried out with \(t_c = 2\) ms and \(t_d = 4\) ms using a simple square wave as shown in Figure 2-3a.

However, the appearance of the samples was very poor, with a lot of unplated areas and spotting of the coating. The use of ultrasonic cleaning prior to electroplating slightly improved the appearance of the coating [90]. Hence it was possible to electroplate zinc-nickel alloys from solutions 1 and 2 but the appearance was very poor.

The use of an alternate zinc-nickel electroplating solution was therefore evaluated. The composition of the alternate electroplating solution is given in Table 3-3, solution 3. The main reasons for using TRIS as a complexing agent within the bath was to stabilise the solution and improve its throwing power [31], thus making it more useful for the electroplating of connectors. The added advantage of using TRIS was that a more neutral electroplating solution could be used. DC electroplating was undertaken over the current density range 0.02 to 0.3 A cm\(^{-2}\) to produce single layer coatings.
Dual layer coatings were prepared using solution 3 according to the parameters given in Table 4-1. Each layer was electroplated to give nominally 4 µm thickness onto 2014-T6 aluminium. The compositions given in Table 4-1 are the expected values obtained from the previous work on single layer coatings.

<table>
<thead>
<tr>
<th>Applied plating current density / A cm(^{-2})</th>
<th>Expected composition / % (At) Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>1(^{st}) layer</td>
<td>2(^{nd}) layer</td>
</tr>
<tr>
<td>0.02</td>
<td>0.1</td>
</tr>
<tr>
<td>0.05</td>
<td>0.1</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Series 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.02</td>
</tr>
<tr>
<td>0.05</td>
</tr>
<tr>
<td>0.1</td>
</tr>
</tbody>
</table>

*Table 4-1 Electroplating conditions for dual layer coatings*

Aluminium alloy electrical connector shells were electroplated from solution 3 detailed in Table 3-3 to give nominal compositions of 5, 7.5, 10 and 14% nickel. The coating was bright to semi-bright at the lower nickel contents, however, at the higher nickel contents (higher applied current density) the coatings were blackened on high current density areas at the edges and corners. A different bath configuration was therefore investigated to reduce the variance between the high current density and low current density regions when electroplating at high nominal current density i.e. to increase the throwing power of the bath. The different bath configuration used is detailed in Section 3-4-2, figure 3-1 bath configuration 2. A dual layer coating was electroplated from this bath configuration with nominal composition of 5, 14% Ni.

Further attempts were then made to improve the appearance and throwing power [151] of the bath by increasing the electrolyte conductivity whilst keeping the metal ion concentration the same. This was achieved by the addition of sodium chloride. Details of the solutions used are given in Table 3-3 solutions 4 and 5.

After electroplating all samples were rinsed and dried. The current efficiency of the process was then determined from the mass change according to Section 3-5-1. The composition of the resultant alloy coating was calculated using EDAX and the microstructure of the resultant coating analysed using SEM. Details of the SEM and EDAX techniques are found in Sections 3-5-2 and 3-5-3 respectively. The single and dual layer coatings produced from solution 3 (Table 3-3) were then subjected to
neutral salt fog corrosion testing, detailed in Section 3-6-5, in the case of the single layer coatings for a period of 2 weeks, and for the dual layer coatings for periods of 1, 2 and 4 weeks. The corroded samples were sectioned and polished and the depth and distribution of pits measured using optical microscopy detailed in Section 3-5-4. Unplated 2014-T6 coupons were also tested. The zinc-nickel and standard cadmium electroplated connector shells were also subjected to neutral salt fog testing for 4 weeks. As with the single and dual layer coatings the connector shells were sectioned and the depth and distribution of pits evaluated using optical microscopy.

In addition to the previous tests, some un-corroded electroplated connector shells were sectioned and their thickness distribution around the shell measured to give an indication of the throwing power of the cadmium electroplating bath. The zinc-nickel coated connector shell thickness distribution was compared to the commercial cadmium electroplated connector shells.

Linear polarisation resistance measurements in 3.5% NaCl and potential-time monitoring were also undertaken on the single and dual layer coatings to help to clarify the corrosion process. Potential time monitoring was undertaken as in Section 3-6-1 and LPR measurements as in Section 3-6-6.

The galvanic compatibility of the coatings with 2014-T6 aluminium and cadmium electroplate was evaluated by measuring the corrosion current between equal area couples of the coating and either 2014-T6 aluminium or cadmium electroplate in 3.5% NaCl solution. The galvanic compatibility with cadmium electroplate was only determined for the dual layer coatings. Detail of the method is given in Section 3-6-2. A schematic of the cell configuration is given in Figure 3-6.

For the dual layer coatings, micro-hardness testing, electrical resistance measurements and cross hatch adhesion testing were also undertaken to give a more complete picture of the coating properties. Micro-hardness testing was carried out as in Section 3-7-2, electrical resistance measurements as in Section 3-7-3 using the circuit detailed in Figure 3-7, and cross hatch adhesion tests as in Section 3-7-4.
4.2.2 On steel

In all cases the pre-treatment used was as detailed in Table 3-1, HCl pickle. Electroplating was undertaken from solution 3 (Table 3-3), using tank electroplating (Figure 3-1, bath configuration 2) and selective or brush electroplating (Figure 3-2, bath configuration 3). An inert carbon anode was used for both the selective and tank electroplating. Single and dual layer coatings were electroplated to give an approximate thickness of 8 μm overall, using DC electroplating detailed in Section 3-4-4 and an applied charge of 30 C. The electroplating conditions used are detailed in Table 4-2.

<table>
<thead>
<tr>
<th>Applied current density /A cm$^{-2}$</th>
<th>Target Ni content in alloy /atomic %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>Single layers</td>
<td></td>
</tr>
<tr>
<td>0.02</td>
<td>5</td>
</tr>
<tr>
<td>0.05</td>
<td>7.5</td>
</tr>
<tr>
<td>0.1</td>
<td>10</td>
</tr>
<tr>
<td>0.15</td>
<td>12</td>
</tr>
<tr>
<td>0.21</td>
<td>14</td>
</tr>
<tr>
<td>Dual layers</td>
<td></td>
</tr>
<tr>
<td>Layer 1</td>
<td>Layer 2</td>
</tr>
<tr>
<td>0.02</td>
<td>0.1</td>
</tr>
<tr>
<td>0.02</td>
<td>0.21</td>
</tr>
<tr>
<td>0.1</td>
<td>0.21</td>
</tr>
</tbody>
</table>

Table 4-2 Electroplating conditions for steel substrates

To assess the effect of the electroplate thickness on the corrosion performance of the zinc-nickel coated steel for brush electroplating a series of experiments undertaken at different values of electroplating charge were carried out, to give an electroplate thickness variation of between 4 and 25 μm. These are detailed in Table 4-3. The electroplating solution used was solution 3 detailed in Table 3-3 and the bath configuration was configuration 3 detailed in Figure 3-2 in Section 3-4-2. The steel samples were prepared for electroplating using the HCl pickle detailed in Table 3-1 in Section 3-3-1.

<table>
<thead>
<tr>
<th>Applied current density /A cm$^{-2}$</th>
<th>Total electroplating charge /C</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.05</td>
<td>15,30,45,60,90</td>
</tr>
<tr>
<td>0.21</td>
<td>15,30,45,60,90</td>
</tr>
</tbody>
</table>

Table 4-3 Experimentation undertaken to determine the effect of electroplating charge on the corrosion resistance of zinc-nickel electroplated from solution 3 using bath configuration 3
Again, after electroplating mass change was used to calculate the efficiency of the electroplating process (see Section 3-5-1). Thickness measurements using an eddy current probe were carried out as detailed in Section 3-5-5 for steel samples.

Composition of the alloy coatings was evaluated by EDAX and the micro-structure of the coatings produced using the different methods assessed by SEM as in Sections 3-5-3 and 3-5-2 respectively.

Accelerated corrosion testing was undertaken on the resultant coatings according to the methods detailed in Section 3. Neutral salt fog, LPR, double polarisation, galvanic compatibility and potential-time monitoring were all carried out.

4.2.3 Detached zinc-nickel coatings

Detached coatings of zinc-nickel were obtained by electroplating from solution 3 (Table 3-3) using bath configuration 2 (Figure 3-1). Experimental details are given in Table 4-4. All electroplating was undertaken using DC as detailed in Section 3-4-4. Details of the method used to produce detached coatings are given in Section 3-3-3.

<table>
<thead>
<tr>
<th>Applied electroplating current density /A cm$^{-2}$</th>
<th>Total electroplating charge /C</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.02</td>
<td>200</td>
</tr>
<tr>
<td>0.05</td>
<td>400</td>
</tr>
<tr>
<td>0.10</td>
<td>400</td>
</tr>
<tr>
<td>0.15</td>
<td>400</td>
</tr>
<tr>
<td>0.21</td>
<td>600</td>
</tr>
</tbody>
</table>

*Table 4-4 Experimental details used to produce detached zinc-nickel coatings*

Linear polarisation resistance measurements as detailed in Section 3-6-6 were undertaken, along with double polarisation measurements as in Section 3-6-7. The galvanic compatibility of the detached coatings with 2014-T6 aluminium was then determined using the method in Section 3-6-2. The monitoring of the potential of the detached coatings with time was also carried out as in Section 3-6-1.

4.3 Experimental summary

A short summary of the substrates used, the electroplating solutions, the plating conditions, bath configurations and testing undertaken on the resultant coatings is given in Table 4-5.
Production of zinc-nickel coatings - results and discussion

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Solution used</th>
<th>Plating conditions and current density range /A cm⁻²</th>
<th>Number of layers</th>
<th>Bath</th>
<th>Testing undertaken</th>
</tr>
</thead>
<tbody>
<tr>
<td>2014-T6 aluminium coupons</td>
<td>1&amp;2 DC and pulse 0.02-0.8</td>
<td>1</td>
<td>1</td>
<td>SEM, EDAX, current efficiency</td>
<td></td>
</tr>
<tr>
<td>3 DC 0.02 - 0.3</td>
<td>1</td>
<td>Current efficiency, SEM, EDAX, neutral salt fog with optical microscopy, LPR, potential monitoring and galvanic compatibility</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3 DC 0.02 - 0.21</td>
<td>2</td>
<td>As single layer &amp; micro-hardness, electrical resistance &amp; adhesion testing</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aluminium alloy connector shells</td>
<td>3,4,5 DC 0.02 - 0.21</td>
<td>1&amp;2</td>
<td>1&amp;2</td>
<td>Current efficiency, SEM, EDAX, neutral salt fog with optical microscopy &amp; thickness distribution using optical microscopy</td>
<td></td>
</tr>
<tr>
<td>Steel</td>
<td>3 0.02 - 0.21 DC &amp; variation of total applied charge</td>
<td>1&amp;2</td>
<td>2&amp;3</td>
<td>Current efficiency, SEM, EDAX, neutral salt fog, thickness measurements, LPR, potential monitoring, double polarisation (0.02 &amp; 0.21 A cm⁻² only), galvanic compatibility</td>
<td></td>
</tr>
<tr>
<td>Detached</td>
<td>3 0.02 - 0.21 DC</td>
<td>1</td>
<td>2</td>
<td>SEM, EDAX, LPR, double polarisation, galvanic compatibility, potential monitoring</td>
<td></td>
</tr>
</tbody>
</table>

Table 4-5 Summary of experiments undertaken in the production of zinc-nickel coatings

4.4 Calculation of Current efficiency

The aim of this sub-section is to investigate the relationship between applied electroplating current density and current efficiency for the five different solutions, deposited onto three different substrates. The calculation of current efficiency for the detached coatings was not undertaken as some coating was lost on detaching from the aluminium foil substrate.
The change in current efficiency with applied electroplating current density for electroplated 2014-T6 aluminium produced from solutions 1 and 2 is shown in Figure 4-1. In Figure 4-2 the change in current efficiency for both steel and aluminium 2014-T6 alloy electroplated from solution 3 is given. As can be seen the way in which the current efficiency changes with applied electroplating current density is very different for each solution used. For solution 1 the current efficiency increases as the applied current density increases. For solution 2 the current efficiency also increases but at a slightly slower rate. In addition the maximum current efficiency is lower when pulse electroplating is used in the presence of surfactant and antifoaming agent. The decrease in the height of the maximum for pulse electroplating is probably due to the inhibitor effect of the anti-foaming agent and surfactant being stronger for pulse electroplating than for DC. This is known to occur for pulse electroplating [124], where the concentration of additives is normally reduced to about 1/10th to allow for the different adsorption, re-absorption kinetics of the additive in pulse electroplating.

![Figure 4-1 Change in current efficiency with applied electroplating current density for 2014-T6 aluminium alloy coupons electroplated from solutions 1 and 2, using bath configuration 1](image-url)
The maximum current efficiency for DC electroplating appears to be in some cases greater than 100%. This could be due to the formation of hydroxides on the surface and has been observed by others [52].

For coupons electroplated from solution 3, which contained a complexing agent, the current efficiency decreases as the applied current density increases (Figure 4-2). The current efficiency is lower with solution 3, which contains complexants than for DC electroplating of solutions 1 and 2 (Figure 4-1), especially at high values of electroplating current density. This is common in complexed solutions [31]. When similar bath configurations are used i.e. configurations 1 and 2, the change in current efficiency with current density follows nearly the same trend. This is independent of the substrate used. When configuration 3 is used for electroplating (brush or selective electroplating) the rate of change of current efficiency with applied electroplating current density is less.

![Figure 4-2 Change in current efficiency with current density for coupons electroplated from solution 3 onto steel except when otherwise stated](image-url)
When solution 3 is used for electroplating the maximum current efficiency is reduced. Solution 3 contains a complexing agent while solutions 1 and 2 do not. The complexant is likely to reduce the maximum current density by inhibiting the electroplating reaction. The effect of the inhibition is more noticeable as the current density is increased. From Figures 4-1 and 4-2 it can be seen that the maximum current density, which can be used to electroplate from solution 3, is lower than for solutions 1 and 2. This represents a shift in the limiting current density of the bath due to the effect of the complexing agent inhibiting the reaction.

The change in current efficiency with electroplating current density for electroplated aluminium alloy connector shells produced from solutions 3, 4 and 5 using bath configurations 1 and 2 is shown in Figure 4-3. The current efficiency decreases as the applied current density increases. The trend in all cases is similar to that observed in Figure 4-2 for electroplating from solution 3 using bath configuration 2 onto either steel or 2014-T6 aluminium alloy coupons.

![Graph showing change in current efficiency with applied electroplating current density for aluminium alloy connector shells electroplated from solutions 3, 4 and 5 using bath configuration 2 unless noted otherwise.](image)

Figure 4-3 Change in current efficiency with applied electroplating current density for aluminium alloy connector shells electroplated from solutions 3, 4 and 5 using bath configuration 2 unless noted otherwise.
This similarity between solutions 3, 4 and 5 show that it is the complexing agent which is causing the differences in the way in which the current efficiency changes for solutions 1, 2 and 3. The addition of sodium chloride to the solution to try and improve the throwing power does not have the same inhibiting effect on the electroplating as the use of the complexing agent, TRIS.

The use of a different bath configuration has a slight effect on the way in which the current efficiency changes with current density. This can be seen in Figure 4-3 by comparing the red and blue trend lines. The fact that the bath configuration has an effect on the slope of the current efficiency/current density graph was seen previously in Figure 4-2 for the steel samples electroplated using bath configuration 2 and 3.

A summary of the trends in current efficiency with increasing electroplating current density is given in Table 4-6.

<table>
<thead>
<tr>
<th>Solution</th>
<th>Effect of applied electroplating current density on current efficiency</th>
<th>Possible reason given for effect</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Increase in current efficiency with increasing applied current density</td>
<td>Formation of more hydroxides on the surface as the current density is increased</td>
</tr>
<tr>
<td>2</td>
<td>Increase in current efficiency for DC with increasing current density. Pulse electroplating, lower current efficiency</td>
<td>High current efficiency due to hydroxide formation on surface for DC. Pulse electroplating current efficiency lower due to increased effect of additives on electroplating kinetics for pulse electroplating</td>
</tr>
<tr>
<td>3</td>
<td>Decrease in current efficiency with increasing applied current density. Bath configuration has a slight effect on slope of graph</td>
<td>Effect of complexant inhibiting the electroplating reaction as the current density is increased towards the limiting current density. The addition of sodium chloride in solutions 4 and 5 does not have the same inhibitory effect as the complexant</td>
</tr>
</tbody>
</table>

*Table 4-6 Summary of effect of applied electroplating current density on the current efficiency of the electroplating reaction for solutions 1, 2, 3, 4, and 5*
4.5 Composition

The aim of this sub-section was to investigate the way in which the nickel content of zinc-nickel changes with applied electroplating current density.

Again, the five solutions used are as detailed in Table 3-3. Firstly, the effect of applied current density for solutions 1 and 2 onto flat 2014-T6 aluminium alloy will be investigated, followed by the nickel content variation with applied electroplating current density for solution 3, using both a fresh and aged solution.

The effect of applied current density on the nickel content for coatings on aluminium alloy connector shells electroplated from solutions 3, 4 and 5 will then be presented. The effects of a different bath configuration and substrate (steel) on the way in which the nickel content changes with applied electroplating current density will then be evaluated. Finally this sub-section will look at the effect of increasing the thickness of electroplate has on the way in which the nickel content changes with an increase in applied electroplating current density, both for detached coatings and coatings produced on steel using solution 3.

The overall aim of obtaining a change in nickel content with applied electroplating current density was to enable the possible deposition of multilayer coatings of different nickel contents from a single bath by controlling the electroplating conditions, in this case applied electroplating current density.

The nickel content change with applied electroplating current density for zinc-nickel coatings electroplated on to 2014-T6 aluminium alloy from solutions 1 and 2 using bath configuration 1 is shown in Figure 4-4. The nickel content was determined using EDAX according to sub-section 3-5-3. In all cases there is an increase in nickel content with an increase in applied electroplating current density. As there are equal molarities of zinc and nickel in the electroplating solution and nickel is more noble, if the deposition was normal there would be more nickel than zinc in the coating [31]. The electroplating is therefore anomalous with zinc being deposited preferentially over the whole current density region. The electroplating is similar to region III in Figure 2-2. The pulse electroplating trend line is slightly shifted with a small flat
region (as region II in Figure 2-2) being seen at low values of current density. This shift in the composition line represents the differences between pulse and DC electroplating i.e. the thinner diffusion zone affecting the anomalous co-deposition and shifting the composition line to the right.

Figure 4-4 Variation of nickel content determined by EDAX with applied electroplating current density for 2014-T6 aluminium alloy coupons, electroplated using bath configuration I and solutions 1 and 2.

The change in nickel content with applied current density for solution 3 on 2014-T6 coupons is shown in Figure 4-5. More than 1 sample was electroplated at each value of current density and the resulting coatings examined using EDAX. This was to ascertain the consistency of the zinc-nickel composition obtained from solution 3. Again, the electroplating is anomalous over the whole current density range studied. For solution 3 the region of electroplating is again region III as shown in Figure 2-2. There is also a shift for the aged solution (two weeks old) to the right with possibly some of region II from Figure 2-2 being included. This shows the effect on the composition line of deterioration of the electroplating solution.

There was a variation of about 4% between the different samples electroplated at the same values of current density. However, EDAX is not the most accurate of
Production of zinc-nickel coatings - results and discussion

Techniques so the true variation between samples electroplated using the same conditions may not be quite as great as this. This variation in composition between samples was consistent at low values of current density (0.035 A cm⁻²) and at a higher value of current density (0.24 A cm⁻²).

![Graph showing variation of nickel content determined by EDAX with current density for zinc-nickel electroplate produced from solution 3, using bath configuration 1, onto 2014-T6 aluminium coupons.](image)

**Figure 4-5** Variation of nickel content determined by EDAX with current density for zinc-nickel electroplate produced from solution 3, using bath configuration 1, onto 2014-T6 aluminium coupons

In Figure 4-6 the change in nickel content with current density for aluminium alloy connector shells electroplated using solutions 3, 4 and 5 from bath configuration 2 is shown. The addition of sodium chloride (solutions 4 and 5) has the effect of reducing the change in nickel content over the applied current density range investigated.

The effect of changing the bath geometry from configuration 1 (see Figure 3-1) to configuration 2 is small, with a slight increase in nickel content at high values of current density being observed for configuration 2 as compared to configuration 1. There is also a small decrease in nickel content at low values of current density for configuration 2 compared to configuration 1. However, EDAX is not the most accurate of techniques with the condition of the surface strongly influencing the composition reading obtained [196]. At best therefore, EDAX should be used as a
Production of zinc-nickel coatings: results and discussion

semi-quantitative method. The differences observed between the two bath configurations in Figure 4-6 may hence be within experimental error.

![Graph showing nickel content vs current density](image)

**Figure 4-6** Change in nickel content with applied electroplating current density for zinc-nickel electroplated aluminium alloy connector shells using bath configuration 2 except when otherwise stated

The graph of change in nickel content for electroplated zinc-nickel coated onto steel using bath configurations 2 and 3 from solution 3 is shown in Figure 4-7. The change in nickel content with current density is approximately linear for the zinc-nickel coatings produced using bath configuration 2 and varies from 3 to 14% over the current density range investigated. The nickel content-current density curve for bath configuration 3 is not linear and is shifted towards a lower nickel content for a given applied electroplating current density. This clearly shows anomalous co-deposition and corresponds to the end of region II and the start of region III in Figure 2-2, with the curve for bath configuration 3 being shifted into region II. The range of compositions obtained for the coatings electroplated onto steel in Figure 4-7 is similar to that obtained for solution 3 in Figure 4-5 and 4-6 showing that the changing of the substrate from 2014-T6 aluminium to aluminium alloy connector shells to steel has only a very small effect on the composition of zinc-nickel.
The change in nickel content for the detached coatings with applied electroplating current density is shown in Figure 4-8. On comparing Figures 4-7 and 4-8 there can be seen to be a slight change in the slope of the composition/current density trend line. The nickel content of the detached coatings is higher at low values of current density and slightly lower at high values. The electroplating is still anomalous and corresponds to region III in Figure 2-2. The slight shift in the composition line may be due to the increased thickness of electroplate used for the detached coatings. Also shown in Figure 4-8 is the effect of the variation in applied charge or thickness on the composition of zinc-nickel electroplated using bath configuration 3 from solution 3 onto steel. Here it can be seen that the thickness of electroplate appears to have an effect on the nickel content especially at high values of current density. In all cases for the electroplated coatings on steel the composition of nickel is slightly reduced compared to the detached coatings. This reduction in nickel content has been seen previously for samples electroplated using bath configuration 3 in Figure 4-7. The
composition of the thin coating electroplated using configuration 3 (brush electroplating) and solution 3 at 0.15 A cm\(^{-2}\) for 15 C is much lower than expected. This could be due to incomplete coverage of the coating. This is likely as the EDAX analysis of this coating showed a significant percentage of iron (5%) indicating incomplete coverage. The range of compositions obtained for the detached coatings (see Figure 4-7 and 4-8) are similar to those obtained for zinc-nickel coatings on other substrates (EDAX is only a semi-quantitative technique [196]), showing again that the composition of the zinc-nickel is not dependent on the substrate used.

![Graph showing nickel content variation](image)

*Figure 4-8 Variation of nickel content with applied electroplating current density for coatings produced onto steel and for detached coatings produced using solution 3*

A summary of the results from this sub-section is given in Table 4-7. As can be seen the nickel content varied from 1 to 28%, with the majority of solutions giving a range of approximately 3 to 14% Ni. This is a useful range of nickel contents as 10 to 15% nickel is reported to give the best corrosion resistance without becoming non-sacrificial to the substrate [66,67], for zinc-nickel electroplated onto steel.
Production of zinc-nickel coatings - results and discussion

<table>
<thead>
<tr>
<th>Solution</th>
<th>Bath configuration</th>
<th>Substrate</th>
<th>Effect of applied electroplating current density on the nickel content</th>
<th>Region of anomalous co-deposition (see Figure 2-2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>2014-T6 aluminium alloy flat coupons</td>
<td>Increase in nickel content as applied electroplating current density increases</td>
<td>III (4 to 28% Ni)</td>
</tr>
<tr>
<td>2</td>
<td>1 pulsed</td>
<td></td>
<td></td>
<td>II to III (1 to 11% Ni)</td>
</tr>
<tr>
<td>3</td>
<td>1 aged</td>
<td></td>
<td></td>
<td>III (3 to 20% Ni)</td>
</tr>
<tr>
<td>3</td>
<td>1 and 2</td>
<td>Aluminium alloy connectors</td>
<td></td>
<td>II to III (3 to 14%)</td>
</tr>
<tr>
<td>4</td>
<td>2</td>
<td>Steel</td>
<td></td>
<td>III (2 to 20% Ni)</td>
</tr>
<tr>
<td>5</td>
<td></td>
<td></td>
<td></td>
<td>III with inhibition of nickel reaction (1 to 5% Ni)</td>
</tr>
<tr>
<td>3</td>
<td>3</td>
<td>Steel</td>
<td></td>
<td>III (3 to 14% Ni)</td>
</tr>
<tr>
<td>3</td>
<td>2</td>
<td>Detached</td>
<td></td>
<td>II to III (2 to 13% Ni)</td>
</tr>
<tr>
<td>3</td>
<td>3 different applied charge</td>
<td>Steel</td>
<td></td>
<td>III (4 to 12% Ni)</td>
</tr>
<tr>
<td>3</td>
<td></td>
<td></td>
<td></td>
<td>III (II at low applied charge 3 to 6% Ni)</td>
</tr>
</tbody>
</table>

Table 4-7 Summary of results of composition analysis of zinc-nickel coatings produced using the five different solutions onto the four different substrates

4.6 Thickness

The aim of this sub-section is to investigate the way in which the thickness of the coating, measured using a magnetic probe (see Section 3-5-5), changes with increase in electroplating current density. Taken in conjunction with the current efficiency measurements this will then give useful information on any variation in physical density, which may occur. For all current densities, electroplating was carried out for the same charge, hence if there is no significant change in thickness with applied electroplating current density, but there is a significant shift in current efficiency, there must be a variation in physical density.

An accurate knowledge of the thickness of electroplate is also important when subsequent corrosion testing is undertaken especially neutral salt fog exposure, where time to red rust is determined. The time to red rust will be strongly influenced by the thickness of electroplate tested especially for sacrificial coatings [28]. Hence, an understanding of thickness variation is important.
Initially the way the thickness of electroplate varied over the specimen surface with applied electroplating current density is investigated. The variation in the standard deviation of the thickness with applied current density is then analysed. All coupons were measured in ten different areas and the standard deviation of the measurement calculated. This was to give an indication of the consistency of electroplate across the surface, which has a bearing on the throwing power of the electroplating bath. The consistency of electroplate should also vary with different bath configurations as the primary, secondary and ternary current distribution within the bath will be different. It should also change with shape of substrate being electroplated and with the throwing power of the electroplating solution.

The thickness distribution of connector shells, electroplated from solutions 3, 4 and 5 were then evaluated and compared to the thickness distribution of commercially cadmium electroplated connector shells. A short summary completes the sub-section.

The change in thickness with applied electroplating current density for steel samples electroplated from solution 3 using bath configurations 2 and 3 is shown in Figure 4-9. As can be seen there is a general downward trend in the thickness with increasing current density. Configuration 3 shows a larger decrease in thickness with applied electroplating current density than configuration 2. This is in contrast to the trend in current efficiency with current density observed in Figure 4-2. Here the steel samples electroplated using configuration 3 showed a smaller decrease in current efficiency over the current density range studied. The downward trend in thickness can, in part, be accounted for by the decrease in current efficiency observed in Figure 4-2. However, it cannot explain why the decrease in current efficiency for the steel samples electroplated using configuration 2 was significantly greater than the decrease in thickness observed over the same current density range. This must mean that the density of the coating is changing as the current density increases. This may be due to differences in morphology but is more likely to be due to an increase in porosity as the current density is raised. This will be discussed further in the subsections on morphology and corrosion testing using neutral salt fog exposure.
The average standard deviation of the thickness measurements is plotted against the applied electroplating current density in Figure 4-10 (measurements were undertaken in about the same positions on all flat coupons). This was to give an indication of the uniformity of the coating across the surface. As can be seen the thickness variation of the coupons electroplated using bath configuration 3 is on average worse than that of samples electroplated using bath configuration 2. Bath configuration 3 is selective or brush electroplating (see Figure 3-2). Brush electroplating suffers more from operator variance [197]. This could account for the larger variance in the standard deviation of the thickness measurements across the coupons. The dual layer coatings show no significant improvement in their thickness uniformity than the single layer coatings with the selectively electroplated dual layers (configuration 3) still being less uniform than the tank electroplated dual layers (configuration 2).
From Figure 4-10 it can also be seen that there appears to be a slight improvement in uniformity with increasing electroplating current density except for the dual layer coatings produced using bath configuration 3. This improvement is only very small, especially for the coupons electroplated using bath configuration 3 (selective electroplating), and could be within the measurement error (±0.5µm).

The electrical connector shells were sectioned to determine the coating distribution. The results of the standard deviation of the thickness measurements are shown in Figure 4-11. In total 40 measurements were taken around both the inside and outside of each connector shell. For commercial electroplated cadmium connector shells the standard deviation was measured in the same manner, however, the actual applied electroplating current density was not known, therefore the commercial cadmium plated connector shells are represented by a straight line over the whole current density region in Figure 4-11. It should also be noted that the value obtained for the standard deviation also included thickness measurements taken on the inside of the
connector shell. The cadmium electroplated connector shells were of a slightly different geometry and as such would be expected to have a lower standard deviation. Two different dual layered connectors were measured, this was to give an indication of the sample variation obtained from the same electroplating bath. Both results are represented by a straight line in Figure 4-11 (again the value of current density used can not be shown as the dual layer coatings were produced using two different values of current density).

![Graph](image)

Figure 4-11 Thickness distribution expressed as a percentage versus applied electroplating current density for aluminium alloy connector shells using solutions 3, 4 and 5, and bath configuration 2 except when otherwise stated

As can be seen the addition of sodium chloride did not significantly improve the standard deviation at low values of current density, but seemed to show some improvement at higher values of current density. The standard deviation of the thickness on commercial cadmium electroplated connector shells was better than the deviation for the Zn-Ni coatings over the whole current density range. However, the standard deviation at medium values of applied electroplating current density for
samples produced from solution 3 and at high values of current density for those produced from solution 5 was similar to the commercial cadmium electroplated connectors. The dual layer coatings were not quite as even (higher standard deviation), but were similar to those obtained at higher values of current density using solution 3. The spread of results was high, this can be seen in Figure 4-11 when the two dual layer coated connector shells are compared. However, due to the experimental technique employed the accuracy of the standard deviation was probably of the order of $\pm 2.5 \mu m$ (a lower magnification was used to determine both the thickness and deviation than used for pit depth analysis in Section 6). If the different geometry of the cadmium connector shells is taken into account, the zinc-nickel coating can be seen to possibly have a thickness deviation similar to the commercial cadmium electroplate.

A summary of the conclusions drawn from this sub-section is given in Table 4-8.

| Thickness     | Zinc-nickel coatings on steel | Thickness decreased with increasing electroplating current density. This follows the same trend as current efficiency
|               |                              | Thickness decreases more rapidly for electroplating using bath configuration 2. This indicates a decrease in density with increasing electroplating current density. Especially noticeable for the dual layer coatings produced using bath configuration 2
| Variation of thickness | On steel | Configuration 3 more uneven than configuration 2. No improvement in variation for dual layer coating
|               | On aluminium alloy connector shells | Some variation with electroplating current density, but not consistent
|               |                              | Not as consistent as cadmium electroplate
|               |                              | No significant improvement in distribution using solution 4 or 5

*Table 4-8 Summary of results for zinc-nickel coatings obtained from measurements of thickness and of variation of thickness across samples*

### 4.7 Morphology

This sub-section will aim to investigate the effect of the different solutions, substrates, bath configurations and applied electroplating current densities on the morphology and appearance of the coatings. A selection of micrographs are given to show the general trends in morphology obtained.
By examining the morphology and appearance of the coatings at this stage it is hoped to get an indication of any significant changes in the morphology, which may affect the corrosion performance and other coating properties.

Firstly the morphologies of coatings produced on 2014-T6 aluminium alloy flat coupons from solutions 1,2 and 3 are presented, followed by those of dual layer coatings produced from solution 3 onto 2014-T6 aluminium alloy. The results of the morphological analysis of single and dual layer coatings electroplated onto steel using solution 3 and bath configurations 2 and 3, namely tank and brush electroplating are then given. The appearance of aluminium alloy connector shells electroplated from solutions 3,4 and 5 are then investigated, followed by a morphological study. The results of the SEM analysis of the detached coatings then follows.

Finally, this sub-section investigates the way in which the morphology of the coatings is related to the nickel content of the alloy. A brief look at the density of the coatings is also undertaken as this has a direct impact on the observed morphology. A summary of the important points learnt from this sub-section is given in conclusion.

The morphology of the coatings electroplated onto 2014-T6 aluminium using solution 1 and configuration 1, using SEM analysis is shown in Figure 4-12. The micrographs are featureless or almost featureless at low values of electroplating current density. There is, however, some indication of porosity and “spotting” on the coatings. At the highest value of applied electroplating current density the morphology is considerably more uneven with clear evidence of burning in some areas. There is also evidence of considerable porosity.
The morphology of coatings electroplated from solution 2 using bath configuration 1 and DC electroplating onto 2014-T6 aluminium is also shown in Figure 4-12. Again, at the lowest value of applied electroplating current density the coating is nearly
featureless. There is again evidence of some porosity and spotting on the surface. As the electroplating current density is increased the morphology becomes more noticeable. The morphology is uneven with some nearly featureless areas and some areas of distinct small rounded grains, with evidence of porosity and spotting of the surface. On further increasing the value of the applied electroplating current density the morphology becomes even more pronounced. There are more uneven areas and surface defects. As the applied electroplating current density is increased to a value of 0.4 $\text{A cm}^{-2}$ the morphology becomes even more uneven, with small distinct rounded grains being visible. This corresponds to a higher nickel content of 13%. At the highest value of electroplating current density (0.6 $\text{A cm}^{-2}$), corresponding to the highest nickel content of 28% the morphology becomes even more uneven with large areas of small round grains clumped together. The number of surface defects and the level of porosity also increases. From Figure 4-12 it can therefore be seen that the nickel content of the coatings produced seems to have an effect on the microstructure, with an increase in nickel content leading to a more distinct grain structure, more surface defects and more porosity.

Micrographs of the coatings produced from solution 2 using pulse electroplating and bath configuration 1 onto 2014-T6 aluminium alloy coupons are given in Figure 4-13. Again, as the nickel content is increased the level of surface features also increases. The highest nickel content achieved using pulse electroplating was 11% nickel. On comparing this micrograph in Figure 4-13 with the micrograph in Figure 4-12 for 13% nickel it can be seen that the microstructure is more uneven for the pulse electroplated coating produced from solution 2. The 1% nickel coating pulse electroplated from solution 2 in Figure 4-13 also has more features than the corresponding direct current electroplated coating of 1% nickel in Figure 4-12. However, there does seem to be some refinement of the grain structure using pulse electroplating. This is reported elsewhere for pulse electroplating [126].

Micrographs of coatings produced from fresh solution 3 onto 2014-T6 aluminium alloy coupons using bath configuration 1 are also given in Figure 4-13. As can be seen the number of surface defects increases as the applied electroplating current density increases, with the coatings produced at 0.24 $\text{A cm}^{-2}$, corresponding to the highest nickel content of 17%, showing considerable surface defects and porosity. SEM
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Micrographs of coatings produced from an aged solution 3 using bath configuration 1 onto 2014-T6 aluminium alloy coupons are also shown in Figure 4-13. On comparing the coatings from the aged and fresh solutions it can be seen that there is some refinement of the grain structure in the coatings produced from the aged bath. The level of surface defects and porosity, apparent at the higher current density value, is also reduced for the aged bath.

SEM micrographs of dual layer coatings produced onto 2014-T6 aluminium using bath configuration 1 are given in Figure 4-14. Again, an aged bath was used. As can be seen the dual layer produced using current densities of 0.02 and 0.1 A cm\(^{-2}\) with 0.1 A cm\(^{-2}\) being used for the top layer shows a small rounded grain structure. The dual layer produced with a higher value of applied electroplating current density for the top layer is more featureless. However, some surface defects and inclusions can still be observed. On comparing the single layer coating produced from the aged bath (Figure 4-13) with the dual layer coating with the top layer produced at the same value of applied current density it can be seen that there is considerable refinement of the microstructure for the dual layer with less porosity and surface inclusions being present.
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0.1 A cm$^{-2}$, solution 2, pulsed, configuration I, 2014-T6 aluminium coupon, single layers, corresponding to 1% nickel

0.8 A cm$^{-2}$, solution 2, pulsed, configuration I, 2014-T6 aluminium coupon, single layers, corresponding to 11% nickel

Single layer, electroplated at 0.02 A cm$^{-2}$ corresponding to 4% Ni, solution 3, configuration I, 2014-T6 aluminium alloy coupons, un-aged solution

Single layer, electroplated at 0.24 A cm$^{-2}$ corresponding to 17% Ni, solution 3, configuration I, 2014-T6 aluminium alloy coupons, un-aged solution

Current density = 0.02 A cm$^{-2}$ solution 3 (5% Ni), configuration I, 2014-T6 aluminium alloy coupons, aged solution

Current density = 0.21 A cm$^{-2}$ solution 3 (14% Ni), configuration I, 2014-T6 aluminium alloy coupons, aged solution

Figure 4-13 Micrographs of coatings produced from solution 2 using pulse electroplating and bath configuration I onto 2014-T6 aluminium alloy coupons and single layer coatings produced from aged and un-aged solution 3 using DC electroplating again onto 2014-T6 aluminium alloy

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Current density = 0.02 A cm\(^{-2}\) first layer, second layer = 0.1 A cm\(^{-2}\), solution 3, configuration 1, 2014-T6 aluminium alloy coupons, aged solution, dual layer

Current density = 0.02 A cm\(^{-2}\) first layer, second layer = 0.21 A cm\(^{-2}\), solution 3, configuration 1, 2014-T6 aluminium alloy coupons, aged solution, dual layer

Figure 4-14 Micrographs of dual layer coatings produced from solution 3, using bath configuration 1 onto 2014-T6 aluminium alloy coupons

SEM micrographs of single layer coatings produced from solution 3, using bath configurations 2 and 3, onto steel are shown in Figure 4-15. The coatings produced using bath configuration 2 all show a fairly uneven round nodular structure, with many surface inclusions and porosity holes being present. The amount of defects increases as the current density is increased. This was also seen for the coatings produced using solution 3 onto 2014-T6 aluminium alloy coupons. However, the number of surface inclusions and defects apparent at the lower values of applied electroplating current density is higher than for the coatings produced on aluminium alloy. This may have been due to the different substrate used, or due to the different
bath configuration with the coatings produced on steel being produced using bath configuration 2 and those on flat aluminium alloy coupons being produced using bath configuration 1.

The largest difference in morphology, however, is observed in Figure 4-15 when the type of electroplating is changed to bath configuration 3 (selective or brush electroplating). Even at high values of applied electroplating current density, the morphology is almost featureless and the steel coupons appeared bright to semi bright after electroplating. This suggests that the bath configuration, rather than the change of substrate, is the primary cause of the difference between the low nickel content coatings produced using bath configuration 2 onto steel (Figure 4-15) and those produced onto 2014-T6 aluminium alloy coupons (Figure 4-13).
Dual layer coatings produced on steel using solution 3 and bath configurations 2 and 3 are shown in Figure 4-16. Again the considerable difference between the two electroplating configurations can be clearly seen, with the coatings produced using configuration 3 (selective electroplating) producing almost featureless morphologies.

The level of surface defects, inclusions and porosity for the dual layers produced using bath configuration 2 are similar to those for the single layers.

Figure 4-16 Micrographs of dual layer Zn-Ni coatings electroplated onto steel using bath configurations 2 and 3 and solution 3

Pictures of the aluminium alloy connector shells electroplated from solutions 3, 4 and 5 using bath configuration 1 and 2 are shown in Figure 4-17. As can be seen the
majority of the connectors are bright to semi-bright at low values of applied electroplating current density when solution 3 is used. As the applied current density is increased the appearance of the coatings gets less bright with areas of uneven porous plate being present. The appearance using configuration 2 is improved at higher values of electroplating current density when compared to bath configuration 1. Using solution 4 containing 1 mol dm\(^{-3}\) of sodium chloride improves the appearance of the electrical connectors at all values of applied electroplating current density. However, there are still areas of uneven, almost burnt, electroplate on the areas of connector which obtained the highest current when the highest electroplating applied current density is used. Any improvement in coating appearance is then lost when solution 5, containing more sodium chloride, is used, except at the highest value of applied current density. This suggests that there was no large increase in the uniformity and coverage of the electroplate with the addition of sodium chloride. This observation is supported by the thickness distribution obtained in Figure 4-11. The thickness distribution was found to slightly improve at higher values of applied electroplating current density when solutions 4 and 5 were used. This supports the slight improvement observed in the appearance using solutions 4 and 5 at high values of applied electroplating current density. There was no such improvement in throwing power or thickness distribution and appearance at lower values of current density.

It should also be noted that the addition of sodium chloride caused the composition of the resultant electroplate to change (see Figure 4-6) resulting in alloy coatings with lower nickel contents at higher values of current density. The improvement observed in the thickness distribution and appearance at high applied current electroplating for solutions 4 and 5 could therefore be related to the change in nickel content observed.

The appearance of a dual layer electroplated zinc-nickel coating obtained using solution 3 and bath configuration 2 is shown in Figure 4-18. The appearance of the dual layer electrical connector shell can be seen to be improved when compared to the single layer electroplated coatings produced at the highest value of applied electroplating current density. The top layer of the dual layer electrical connector shell was produced using the same value of applied current density as the highest applied electroplating current density used for the single layers. From Figure 4-11, which shows the thickness distribution around the connector shell, it can be seen that at the
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A high value of current density the thickness distribution of the dual layer coating is improved when compared to the single layers. This supports the observation that an increase in the uniformity of the appearance is an indication of an improvement in the thickness distribution i.e. the throwing power of the solution or in this case an improvement in the distribution due to the use of dual rather than single layers.

Electrical connector shells, bath configuration 1, solution 3, lowest applied current density (nickel percentage) on left

Electrical connector shells, bath configuration 2, solution 3, lowest applied current density (nickel percentage) on left

Electrical connector shells, bath configuration 2, solution 4, lowest applied current density (nickel percentage) on left

Electrical connector shells, bath configuration 2, solution 5, lowest applied current density (nickel percentage) on left

Figure 4-17 Single layer Zn-Ni electrical connector shells

Dual layer Zn-Ni electrical connector shell, bath configuration 2, solution 3, 1st layer electroplated at 0.02 A cm⁻² approximately 5% Ni, 2nd layer electroplated at 0.08 A cm⁻² corresponding to approximately 14% Ni

Figure 4-18 Dual layer Zn-Ni electrical connector shell after electroplating with Zn-Ni, using bath configuration 2 and solution 3

SEM micrographs of the single layer coatings electroplated onto connector shells using solution 3 and bath configuration 1 are shown in Figure 4-19. The morphology of the coatings can be related directly to the appearance of the coatings in Figure 4-17.
The lowest electroplating current density, corresponding to a nickel content of 5%, produced a small rounded compact grain structure corresponding to a semi-bright electroplate. The zinc-nickel electroplated connector shell electroplated at 0.05 A cm$^{-2}$ had a more uneven microstructure with numerous inclusions and surface defects. The more uneven nature of the electroplated coating produced at a higher value of electroplating current density can be clearly seen in Figure 4-17. The morphologies of the coatings become increasingly more uneven as the current density used for electroplating is raised. This can be seen in Figure 4-19 and can be directly related to the visual appearance of the electroplated connector shells shown in Figure 4-17.
SEM micrographs of the coatings produced from solution 3 using bath configuration 2 over a range of applied electroplating current densities are shown in Figure 4-20. Again, the morphology of the coating produced at the lowest value of electroplating current density is the most even with the smallest amount of inclusions and surface defects. Small rounded grains can just be observed. As the current density is increased the morphology becomes very different to that observed previously for electroplated coatings produced using bath configuration 1. Both coatings produced at 0.05 and 0.1 A cm$^{-2}$ using bath configuration 2 show a very distinct three dimensional structure with numerous porosity holes and grain boundaries. The grains are rounded in appearance. As the applied electroplating current density is further raised to 0.125 A cm$^{-2}$ the morphology changes becoming less defined and crazed in nature as though burning has occurred, due to the level of applied electroplating current density.

This burnt, uneven morphology agrees well with the visual observations in Figure 4-17 for single layer coatings electroplated from solution 3 using bath configuration 2.

The morphology of a dual layer coating produced from solution 3 using bath configuration 2 onto a aluminium alloy connector shell is shown in Figure 4-21. Although the applied current density of the top layer was fairly high (0.08 A cm$^{-2}$), the surface appearance of the coating shows slightly less surface inclusions and porosity than the single layer coatings produced at 0.05 and 0.1 A cm$^{-2}$ in Figure 4-20. The extended three-dimensional structure is not as prominent. The grain size of the rounded grains is also significantly reduced when compared to the single layers.
<table>
<thead>
<tr>
<th>Current Density</th>
<th>Nickel Content</th>
<th>Connector Configuration</th>
<th>Solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.02 A cm(^{-2})</td>
<td>2%</td>
<td>2, 3</td>
<td></td>
</tr>
<tr>
<td>0.05 A cm(^{-2})</td>
<td>11%</td>
<td>2, 3</td>
<td></td>
</tr>
<tr>
<td>0.1 A cm(^{-2})</td>
<td>15%</td>
<td>2, 3</td>
<td></td>
</tr>
<tr>
<td>0.125 A cm(^{-2})</td>
<td>20%</td>
<td>2, 3</td>
<td></td>
</tr>
<tr>
<td>0.125 A cm(^{-2})</td>
<td>20%</td>
<td>2, 3</td>
<td></td>
</tr>
</tbody>
</table>

*Figure 4-20 SEM micrographs of aluminium alloy electrical connectors configuration 2, solution 3*

There is also no sign of a cracked, burnt morphology corresponding to an area of too high an applied electroplating current density. The improvement in morphology obtained for the dual layer coating is substantiated by the improvement in visual appearance observed on comparing Figure 4-17 and 4-18.
Dual layer Zn-Ni electrical connector shell, bath configuration 2, solution 3, 1st layer electroplated at 0.02 A cm\(^{-2}\) approximately 5% Ni, 2nd layer electroplated at 0.08 A cm\(^{-2}\) corresponding to approximately 14% Ni

<table>
<thead>
<tr>
<th>Figure 4-21 SEM micrograph of dual layer Zn-Ni electrical connector shell, electroplated from solution 3 using bath configuration 2</th>
</tr>
</thead>
</table>

SEM micrographs of zinc-nickel coatings produced on aluminium alloy connector shells using bath configuration 2 and solution 4 are shown in Figure 4-22. There is some improvement in the consistency of the morphology of the coatings electroplated using low values of applied current density. However, as the applied electroplating current density is raised this improvement is lost. At the highest value of current density used the strongly three-dimensional rounded grained structure shown in Figure 4-20 for solution 3 is again visible. Again the morphology observed agrees well with the visual observations made in Figure 4-17.

From Figure 4-22 it can also be seen that the nickel content of the alloy is reduced compared to solution 3, this is also illustrated in Figure 4-6. The improvement in appearance of the morphology of the connector shells electroplated using solution 4 could therefore be due to the reduction in nickel content rather than any improvement in the throwing power and levelling ability of the electroplating bath. This is further supported by Figure 4-11 where the thickness distribution around the connector shells for the different electroplating solutions is evaluated. Here no improvement in the throwing power of solution 4 was observed.
Production of zinc-nickel coatings - results and discussion

The morphology of the zinc-nickel coatings on aluminium alloy connector shells produced using solution 5 and bath configuration 2 is shown in Figure 4-23. The coatings produced using the lower values of applied electroplating current density show a more defined grain structure than those produced at the lower values of current density from solution 4 (Figure 4-22). This agrees well with the lack of brightness observed visually in Figure 4-17 for solution 5 at the lower values of applied electroplating current density.
The coating produced at 0.05 A cm\(^{-2}\) electroplating current density shows the strongly defined three-dimensional rounded grain structure observed previously for solution 4 and 3 in Figures 4-22 and 4-20. However, the applied electroplating current density is considerably lower. The composition of the resultant coating also contains less nickel. This shows that the addition of sodium chloride to solution 3 has had the effect of both shifting the composition/ current density curve and shifting the morphology of the coatings to the left creating a strongly three-dimensional coating morphology at a lower nickel content, using a lower applied electroplating current density.

![SEM micrographs](image)

**Figure 4-23 SEM micrographs of single layer coating produced from solution 5 using bath configuration 2 onto aluminium alloy connector shells**

As the applied electroplating current density is increased the morphology of the coatings in Figure 4-23 become more uneven with more surface inclusions and porosity being present. At the highest value of electroplating current density used, the
Production of zinc-nickel coatings - results and discussion

morphology is again that of well defined round grains although the three dimensional appearance is lost. All these observations on the morphology explain the lack of bright to semi-bright deposits seen in Figure 4-17 for connector shells electroplated from solution 5.

SEM micrographs of the detached coatings produced using solution 3 and bath configuration 2 are given in Figure 4-24. In all cases the morphology is more three-dimensional than the non-detached coatings seen previously. This is due to the longer electroplating times used, which produced thicker coatings. As the electroplating process is undertaken for longer, any preferential electroplating due to high current density regions will be intensified creating a more three-dimensional structure. The increase in porosity observed for the non-detached coatings with increase in applied electroplating current density can again be observed for the detached coatings in Figure 4-24.

The small compact rounded grain morphology is better defined at the lower values of applied electroplating current density corresponding to the lower nickel contents. As the nickel content increases the grain structure becomes less well defined, however, it is still apparent. None of the detached coatings were bright or semi-bright in appearance. This presence of the small rounded grain morphology supports this observation. Previously an almost featureless morphology was seen to correspond to bright to semi-bright coatings. This can be seen on comparing Figure 4-17 with the appropriate SEM micrographs.

To ascertain whether the increase in porosity and surface inclusions seen for all single layer zinc-nickel coatings on all substrates using bath configurations 1 and 2 were due to the increase in nickel content seen as the applied electroplating current density was raised, SEM micrographs were arranged according to their nickel content. This is illustrated in Figure 4-25. The use of bath configuration 3, selective electroplating was not included as the surface morphologies of these coatings were very different and distinct in comparison to the other bath configurations used. Dual layer coatings were also not included as there tended to be a significant reduction in porosity and surface inclusions for all dual layer coatings. Also not included were the pulse electroplated coatings produced from solution 2 using bath configuration 1, as these again showed a
difference in morphology due to the pulse conditions rather than the nickel content. The detached coatings were also excluded as their morphologies were again significantly different due to the increase in electroplate thickness required to produce free standing coatings.

<table>
<thead>
<tr>
<th>Image</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1.png" alt="Image" /></td>
<td>Detached zinc-nickel coating produced from solution 3 using bath configuration 2 and 0.02 A cm$^{-2}$ electroplating current density corresponding to 5% nickel</td>
</tr>
<tr>
<td><img src="image2.png" alt="Image" /></td>
<td>Detached zinc-nickel coating produced from solution 3 using bath configuration 2 and 0.1 A cm$^{-2}$ electroplating current density corresponding to 11% nickel</td>
</tr>
<tr>
<td><img src="image3.png" alt="Image" /></td>
<td>Detached zinc-nickel coating produced from solution 3 using bath configuration 2 and 0.21 A cm$^{-2}$ electroplating current density corresponding to 12% nickel</td>
</tr>
</tbody>
</table>

*Figure 4-24 Micrographs of detached zinc-nickel coatings produced from solution 3 using bath configuration 2*
Overall there can be seen to be an increase in surface inclusions and porosity as the nickel content increases. There are, however, some exceptions, these being mainly the coatings produced from solutions 4 and 5 onto aluminium alloy connector shells using bath configuration 2. This agrees with the observation made previously that the addition of sodium chloride to solution 3 has shifted both the composition and the morphology, giving rise to more three-dimensional highly defined microstructures at lower nickel contents.

Coatings with the lower nickel contents tended to give more featureless morphologies with less porosity and surface inclusions. At the highest values of nickel content the coatings all tended to show distinct features with numerous surface inclusions and in some cases significant micro-cracking and burnt uneven deposits.

The change in nickel content therefore seems to be mainly responsible for the increase in porosity. However, in all cases as the nickel content increases the applied electroplating current density required also increases. For each solution using each bath configuration and substrate, the position of the composition versus applied electroplating current density curve is slightly different. This is illustrated in Figures 4-4 to 4-8. The cause of the apparent change in morphology with increasing nickel content could therefore be the position of the coating in relationship to the composition current curve. At higher current densities and nickel contents the amount of hydrogen evolution on electroplating will be higher. This causes a reduction in the current efficiency, which is observed in Section 4-4. The level of hydrogen evolution will be different for each solution and each bath configuration and each substrate. The hydrogen reaction is given in Equation 2-6. This change in amount of hydrogen evolution could therefore be the cause of the increase in porosity observed as the nickel content is increased. A schematic representing the different morphologies apparent for different nickel contents and applied electroplating current densities is given in Figure 4-26 (all different substrates were included as the morphology was relatively independent of substrate and depended more on the nickel content). Here it can be seen that the featureless morphology only occurs at low values of both applied electroplating current density and nickel content. The extent of the small round grained region is larger, extending upwards to about 10% nickel content and across to
much higher electroplating current densities. The region of porosity and surface defects occupies the highest nickel content area of the graph, where the applied electroplating current density is also highest.

<table>
<thead>
<tr>
<th>Increasing nickel content</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image" alt="Image of coating morphology" /></td>
</tr>
</tbody>
</table>

The figures represent the nickel content /atomic%. Nickel content increases from left to right and down the rows. When there is any significant difference in the morphology at a given nickel content, all micrographs at that content are shown.

*Figure 4-25 Change in morphology of coatings with increase in nickel content of alloy. For the zinc-nickel coatings on aluminium alloy electrical connectors, where there is a difference in the morphology due to solution changes, the solution used is shown under the appropriate micrograph.*
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Figure 4-26 Morphological diagram showing the regions of different surface morphology for zinc-nickel coatings produced using solutions 3, 4 and 5, bath configurations 2 and 3 onto mild steel, 2014-T6 aluminium, aluminium alloy connector shells and detached coatings

To further confirm this, electroplating current efficiency was plotted against density of electroplate. The result is shown in Figure 4-27. The level of scatter in Figure 4-27 is due to the average thickness being used in conjunction with the mass change and area electroplated to calculate the density. The use of the average thickness to calculate density has lead to a larger level of scatter in Figure 4-27 for samples produced using configuration 3 (selective electroplating) as these were not as uniform as coatings produced using configuration 2 (see Figure 4-10). As the current efficiency increases the density of the electroplate also increases. This confirms that at low values of current efficiency more hydrogen is trapped in the electroplate leading to a lower density and hence more porosity.

To combat this increase in porosity caused by hydrogen evolution during electroplating, the relative position on the composition/current density curve would need to be changed, to allow the required composition of zinc-nickel to be produced at lower values of applied electroplating current density. This could be achieved by
increasing the nickel content of the electroplating bath. However, in all cases the electroplating is anomalous. A significant increase in nickel concentration within the bath may therefore be required to shift the composition current density to the left. This would require further experimentation. Another way of shifting the composition current curve to reduce the level of hydrogen evolution would be to increase the pH of the electroplating bath. This may cause the bath to become unstable leading to precipitation of the complexant present in the bath, and eventually the metals themselves.

![Graph](image)

*Figure 4-27 Density of electroplate versus electroplating current efficiency for zinc-nickel on steel produced using bath configurations 2 and 3 and solution 3*

The position of the composition current curve could also be shifted by increasing the level of agitation within the bath. This may also reduce the grain size and improve the morphology [85], but is, however, difficult to control and quantify especially if air agitation is used. There is also an increased likelihood of producing more zinc and less nickel as the level of agitation is raised, as zinc is normally mass transport controlled and nickel is unlikely to be. Hence, as the agitation level increases, the
double layer decreases and a higher proportion of zinc is incorporated into the coating.

Except for the coatings produced using bath configuration 3 (brush electroplating) the morphology of the coatings was more related to the nickel content of the alloy rather than the substrate, bath configuration used or applied electroplating current density.

As the nickel content increased, the level of porosity and surface defects increased. This has been shown to be due to a reduction in electroplate density, due to increased hydrogen evolution as the current efficiency decreased. This could have serious implications for the corrosion resistance of the resultant coating with a possibility that 10-15% nickel would not show the expected improvement in corrosion performance when compared to 5% nickel because of increased levels of porosity. The increase in porosity would only cause a significant change in corrosion performance if the coating is also becoming non-sacrificial to the substrate with exposure. This possibility will be investigated further in section 6.

A short summary of the main conclusions from this sub-section is given in Table 4-9.

<table>
<thead>
<tr>
<th>Bath configuration 3, brush electroplating</th>
<th>More uniform than other electroplating bath configurations with significantly less surface features</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dual layers</td>
<td>On 2014-T6 and aluminium alloy connectors a reduction in level of porosity and surface inclusions</td>
</tr>
<tr>
<td></td>
<td>On steel no significant difference observed</td>
</tr>
<tr>
<td>Nickel content</td>
<td>The morphology found to be related to the nickel content. Increase in porosity and surface inclusions as nickel content increases. Caused by hydrogen evolution increasing as current efficiency decreases as nickel content increases. May have implications on corrosion resistance of alloys</td>
</tr>
</tbody>
</table>

Table 4-9 Summary of observations of the appearance and morphology of zinc-nickel coatings
5 Production of zinc-nickel-manganese coatings - results and discussion

5.1 Introduction
The aim of this section of experimental work is to investigate the possibility of producing ternary zinc-nickel-manganese alloy coatings as a possible replacement for cadmium. It is known that ternary zinc-nickel-manganese coatings can be produced from sulphate baths to produce alloys with very low percentages of manganese [115]. The addition of a complexant to the bath may increase the manganese content of the coating. This is investigated. The corrosion resistance of the resultant coatings is examined to ascertain whether the addition of manganese improves the corrosion performance, especially the formation of white rust, to make these coatings more suitable for use on electrical connectors as a replacement for cadmium.

Firstly, the solutions used to produce zinc-nickel, nickel-manganese and zinc-nickel-manganese are investigated by undertaking cyclic voltammetry on the solutions. This will give an indication of the feasibility of using a complexant to produce zinc-nickel-manganese from a sulphate bath. Cyclic voltammograms were undertaken in accordance with Section 3-4-3 using the solutions detailed in Table 3-5 and the cell configuration given in Figure 3-4.

Two different complexing agents are then examined, the use of sodium citrate as a complexant as this is known to function well in the production of zinc-manganese coatings, and the complexant TRIS, which was used for the production of the zinc-nickel coatings detailed in Section 4. Details of the solutions used are given in Section 3-4-1 and Table 3-2.

Various different corrosion tests are then undertaken on the resultant coatings, to give an understanding of the way in which the manganese influences the corrosion resistance.

This section details the experimental work undertaken. The results of the cyclic voltammetry are firstly given. The experiments using the two different zinc-nickel-
manganese solutions are then detailed. A short summary completes the experimental section. The current efficiency, composition, thickness and morphology are then examined. Results of corrosion testing of zinc-nickel-manganese coatings are given in section 7.

5.2 Cyclic voltammograms

Cyclic voltammograms were undertaken by cycling the potential from -2.5 V of the open circuit potential, through $E_{\text{corr}}$ to a value 2.0 V positive of $E_{\text{corr}}$ and back to the original starting potential. This cycle was repeated five times with the fifth cycle being shown. All voltammograms were carried out with 2014-T6 aluminium alloy as the working electrode. In hindsight the recording of the first cycle would have given more information about the deposition process.

The aim of conducting cyclic voltammograms was to give an indication of the feasibility of producing ternary zinc-nickel-manganese from a citrate containing solution and to compare the nature of the trace obtained with than given for zinc-nickel and zinc-manganese. Although cyclic voltammetry can be used to give semi-qualitative information on simple systems, this is not as easy on complex electroplating solutions [198], therefore here it is just used as a comparative method to show the relative differences between the electroplating solutions [199]. Further mechanistic and semi-quantitative information can be obtained from cyclic voltammetry by undertaking sweeps at different values of starting potentials, varying the scan rate and observing differences between the first and subsequent scans. By performing cyclic voltammograms over a time range an indication of the stability of the electroplating solutions with time is also achieved.

The variations in the electrochemical reactions of the different solutions with time are shown in Figures 5-1 to 5-4. The solutions used were as detailed in Section 3-4-3, Table 3-5. The cell configuration used is detailed in Figure 3-4. Initially the response for zinc-nickel does not change with age of solution, it then changes abruptly after 14 days and the response at positive values of overpotential is significantly different. The potential of the reduction peak (in a simple reversible reaction this can be represented by Oxidised species + ne\(^-\) $\rightarrow$ Reduced species) stays at about the same value throughout the time investigated at about $-500 \text{ mV}$ overpotential with a slight shift to
more positive values with time. The value of \( E_{\text{plating}} \) for the solution can be taken as the point where the curve crosses zero current (assuming limited hydrogen evolution). In the case of zinc-nickel the value of \( E_{\text{plating}} \) did not change significantly with time and stayed at about \(-1100 \text{ mV}\) overpotential. On the return sweep for a deposition process the current trace will normally cross the forward trace leading to a difference in \( E_{\text{plating}} \) value between the forward and reverse scans, this corresponds to the overpotential required to give initial nucleation on the electrode surface. However, this is not shown in Figure 5-1, as the cycle given is not the first cycle but the fifth. Nucleation has already therefore taken place on the electrode surface. Initially both the forward and reverse sweeps cross the point of zero current at the same value of overpotential, representing a continuous deposition/stripping process. The stripping process does not occur as easily as metal deposition, this is shown by the lack of an oxidation peak on the reverse cycle indicating an irreversible reaction. However, as the solution ages there is a shift in the reverse cycle, with incomplete dissolution of the coating. This is probably due to the aggressive nature of the solution causing a competing reaction with the working electrode, leading to corrosion of the working electrode and incomplete dissolution of the electroplate and hence metal deposition on the working electrode. On removal of the 2014-T6 working electrode it was found that some metal had been deposited during the scans.

Other differences in the forward and reverse scans can be attributed to two factors. Firstly an increased surface area of the electrode after initial metal deposition, and secondly to hydrogen evolution [121]. The scans at 21, 28 and 35 days all showed a difference in forward and reverse scans, indicating that there is both some hydrogen evolution and some change in surface area. Whether the change in surface area is due only to metal deposition, or whether it is also caused by dissolution of the working electrode cannot be discerned without further scans over different potential ranges and at other scan rates for example a larger potential range of \( \pm 4.0 \text{ V} \) with a slower scan rate of \( 5 \text{ mV min}^{-1} \). By undertaking scans at different rates it may be possible to observe two separate peaks in the forward scan, one corresponding to hydrogen evolution the other to metal deposition.

The graph for nickel-manganese (Figure 5-2) on the other hand only shows a noticeable reduction peak after 0 days, with a very small reduction peak at 14 days,
Production of zinc-nickel-manganese coatings - results and discussion

after this time no peak is apparent. The peak at 0 days is at about an overpotential of 
$-1000 \text{ mV}$, while the small peak at 14 days has shifted slightly to about $-1200 \text{ mV}$
overpotential. It is hard to determine the value of $E_{\text{plating}}$ as the curve lies very close to
zero current over a large potential range, but it can be taken to be about $-1200 \text{ mV}$ at
zero days and $-1300 \text{ mV}$ overpotential at 14 days.

![Cyclic voltammogram showing the variation of zinc-nickel solution (see Table 3-5 for solution composition) response with time using a 2014-T6 aluminium alloy working electrode. Arrows represent the direction of scanning. For clarity only curves at 0, 21 and 35 days are shown.](image)

There is, however, in all cases a large difference in the point at which the forward and
reverse scans cross zero current. This indicates that even on the fifth cycle nickel-
manganese is slow to nucleate (any difference in forward and reverse cycles due to
nucleation is diminished as the number of cycles increases [198], showing that nickel-
manganese needs a larger applied overpotential in order to electroplate from a citrate
Production of zinc-nickel-manganese coatings- results and discussion

containing solution than zinc-nickel. The lack of reduction peak with ageing also shows the reluctance of nickel-manganese to electroplate from a complexed solution.

![Figure 5-2 Cyclic voltammogram showing the variation of nickel-manganese solution response with time (only the central part of the voltammogram is shown to enable the small reduction peaks to be observed). Solution details are given in Table 3-5. The working electrode was 2014-T6 aluminium alloy.](image)

The graph of zinc-manganese solution response with time (Figure 5-3) shows a very pronounced reduction peak at 0 days at -530 mV overpotential. The size and placement of this reduction peak then changes, getting smaller with time to an approximately steady size at 28 days, with an overpotential of -860 mV. The value of $E_{\text{plating}}$ on the other hand does not change much with time, remaining at about -1200 mV overpotential. This slightly more negative $E_{\text{plating}}$ value can be attributed to the effect of manganese when compared to the more positive value of $E_{\text{plating}}$ for zinc-nickel.
All cyclic voltammograms show evidence of a second reduction peak, which is probably due to hydrogen evolution which is known to occur in conjunction with zinc-manganese electroplating [87]. The second reduction peaks presence is more noticeable after 28 days. Like the nickel-manganese solution, there is a large difference between the point at which the forward and reverse scans cross zero current. The difference is not as great as that observed for nickel manganese. This shows that the rate of nucleation of zinc-manganese is greater than nickel-manganese but not as great as zinc-nickel.

![Graph showing cyclic voltammogram](image)

**Figure 5-3** Cyclic voltammogram showing the variation of zinc-manganese solution response with time (see Table 3-5). Only a portion of the scan is again shown for clarity (scanned from −2.5v to 2.0 v versus open circuit using a 2014-T6 aluminium alloy working electrode). The arrows represent the scan direction

Again the graph of zinc-nickel-manganese solution response with time in Figure 5-4 shows a very pronounced reduction peak at 0 days with a potential of −360 mV
overpotential. This response again gets smaller with time reaching a steady size at about 35 days, with an overpotential of -730 mV. The shape of the zinc-nickel-manganese graph is very similar to that of the zinc-manganese graph although the potentials are slightly less negative than zinc-manganese.

![Cyclic voltammogram showing the variation of zinc-nickel-manganese solution](image)

This shows that the response is mainly due to the interaction between the zinc, manganese and citric acid within the solution. The presence of nickel does not seem to affect the shape of the graph largely. It, however, shifts the potential at the minimum reduction peak by about 100 mV less negative. This has been reported to occur with nickel-iron electroplating [55] and hence shows the effect of the addition...
of nickel to zinc-manganese is to shift the potential of the reduction peak to more positive values. The value of $E_{\text{plating}}$ is again more positive than the zinc-manganese system, being about $-1100$ mV overpotential. This again shows the effect of the addition of nickel on the zinc-manganese system. The fact that the shape of the cyclic voltammograms are not significantly effected by the presence of nickel suggests that the production of zinc-nickel-manganese from an electroplating solution containing citrate ions is feasible, as zinc-manganese is known to deposit from a citrate based solution [89]. Although the presence of nickel in the electroplating solution has affected the cyclic voltammetry response, this does not necessarily mean that any nickel will be present in the deposit. Again, like zinc-manganese the presence of additional small reduction peaks probably due to hydrogen evolution and adsorption on the surface can be seen.

The difference in forward and reverse scans at the point of crossing zero current is not as great as for zinc-manganese and nickel-manganese showing that the rate of nucleation of the ternary alloy (if in fact a ternary alloy is produced) is greater than for zinc-manganese. The reduction in this difference is an indication that either the presence of nickel is activating the deposition of zinc, or manganese, onto the 2014-T6 aluminium alloy surface or that nickel is being co-deposited with the zinc-manganese.

The cyclic voltammograms looking at the effect of varying the nickel content of the solutions are shown in Figures 5-5 to 5-7.

The zinc-nickel response (Figure 5-5) does not vary greatly with an increase in the nickel content of the solution. The reduction peak stays at about the same level although it decreases slightly, and has an overpotential of $-480$ mV. The value of $E_{\text{plating}}$ again stays constant at $-1010$ mV overpotential. This insensitivity to the amount of nickel in solution gives an indication that the nickel is not preferentially deposited, i.e. anomalous co-deposition is occurring (see Section 2-5).

In all cases there is a difference in forward and reverse cycles showing the deposition of metal on the electrode surface. A deposit was again observed when the electrochemical cell was dismantled. The forward scan crosses the zero current line at
a lower potential than the reverse scan showing that there is no overpotential required for electroplating to continue (fifth cycle shown), as the deposit is growing on already nucleated sites. This shows that some of the metal deposit is remaining on the surface after each scan, and suggests that like Figure 5-1 some corrosion of the 2014-T6 working electrode must be occurring.

![Graph showing variation of zinc-nickel solution response with concentration of nickel](image)

*Figure 5-5 Variation of zinc-nickel solution response with concentration of nickel (solution detailed in Table 3-5), using a 2014-T6 aluminium alloy working electrode. Only the central part of the cyclic voltammogram is given for clarity. Arrows indicate the scan direction.*

The nickel-manganese response in Figure 5-6 on the other hand shows a significant difference in both the size and the placement of the reduction peak. Initially the reduction peak is small with an overpotential of -260 mV. The size of the peak then increases dramatically when the nickel concentration is 0.3 mol dm$^{-3}$. The potential of this peak also changes to 300 mV overpotential. On addition of another 0.1 mol dm$^{-3}$
of nickel the size of the peak reduces and the potential becomes less noble, being 130 mV overpotential. The value of $E_{\text{plating}}$ is consistent at $-830 \text{ mV}$. This is different to the value for $E_{\text{plating}}$ determined for nickel-manganese with 0.1 mol dm$^{-3}$ nickel at zero days. In the case of nickel-manganese the response is more sensitive to the amount of nickel present in solution, suggesting that the type of deposition is not anomalous.

The difference in potential between the forward and reverse scans at zero current shows that nucleation is still slow to occur, however, the rate is greater than that observed for nickel-manganese in Figure 5-2, with a lower solution concentration of nickel. This indicates that as the nickel solution content is raised, the rate of nucleation of metal deposition is increased, showing that an increased presence of nickel aids nucleation onto 2014-T6 aluminium alloy in the presence of citrate ions.

![Graph showing variation of nickel-manganese solution response with nickel concentration using a 2014-T6 aluminium alloy working electrode and solution as detailed in Table 3-5. For clarity only the central part of the voltammogram is shown (scan $-2.5 \text{ V} \text{ versus open circuit to } +2.0 \text{ V}$), arrows indicate direction of scan.](image)

*Figure 5-6 Variation of nickel-manganese solution response with nickel concentration using a 2014-T6 aluminium alloy working electrode and solution as detailed in Table 3-5. For clarity only the central part of the voltammogram is show (scan $-2.5 \text{ V} \text{ versus open circuit to } +2.0 \text{ V}$), arrows indicate direction of scan*
The zinc-nickel-manganese solution response (Figure 5-7) on addition of nickel is initially very similar as the nickel solution concentration is raised, with a reduction peak of about the same size and with an overpotential of \(-840\) mV. When the nickel concentration within the solution reaches \(0.4\) mol dm\(^{-3}\) the size of the peak increases dramatically. The value of the overpotential for the reduction peak becomes nobler with a value of \(-510\) mV. The value of \(E_{\text{plating}}\) stays constant throughout at \(-1060\) mV overpotential. This is very similar to that obtained for the \(0.1\) mol dm\(^{-3}\) nickel concentration solution. The zinc-nickel-manganese response is more sensitive to the nickel solution concentration than zinc-nickel but not as sensitive as nickel-manganese, this suggests that the anomalous co-deposition of zinc-nickel is being interfered with due to the presence of manganese, with the normal co-deposition of
manganese causing the interference. This observation shows that the solution must be capable of depositing manganese.

It is therefore likely that a ternary alloy containing manganese would be deposited from this solution. The presence of nickel in the deposit is also likely due to the mixed response of additions of nickel. There is a small variation in the size of the reduction peak when the nickel content is changed from 0.1 mol dm\(^{-3}\) to 0.2 mol dm\(^{-3}\), suggesting that at low nickel contents the deposition is dominated by the anomalous co-deposition of nickel, hence some nickel will be present in the alloy.

On comparing Figure 5-7 with Figure 5-4 it can be seen that there is again an indication of a second reduction peak possibly corresponding to hydrogen evolution, however, the separation of the peaks is more noticeable as the nickel content in the solution is raised. This suggests that perhaps as the nickel content in the solution is raised the level of hydrogen evolution associated with the process increases, indicating that the nickel in the solution may be aiding the deposition of manganese, which is associated with hydrogen evolution.

As the nickel concentration in solution is raised the difference in forward and reverse scans at zero current in Figure 5-7 initially increases and then decreases, suggesting that the presence of nickel has a complex effect on the nucleation rate. The nucleation rate with 0.4 mol dm\(^{-3}\) of nickel in solution is about the same as for 0.1 mol dm\(^{-3}\) nickel in Figure 5-4. More cyclic voltammograms at different scan rates and over different potential ranges would be needed to ascertain the true effect of an increase in nickel solution concentration on the ternary deposition of zinc-nickel-manganese. The limited cyclic voltammetry undertaken in this research has given an indication of the feasibility of producing zinc-nickel-manganese from a citrate solution. However, the possible alloy content cannot be determined from this amount of experimentation. Further investigation would be required to clarify the effect of nickel additions on the solution and the ageing characteristics of the solution.

5.3 Electroplating experimentation

Electroplating was undertaken using the solutions detailed in Table 3-4 in Section 3-4.1. All experimentation was carried out on mild steel coupons, prepared as detailed
in Section 3-3-1 and Table 3-1. Mild steel was used as the substrate to enable accurate thickness measurements to be undertaken, and also to enable time to red rust to be determined in neutral salt fog testing to facilitate the interpretation of results. Unless otherwise stated, all electroplating was undertaken to constant electroplating charge to give a nominal thickness of electroplate of 8 μm.

Initially solution 6, the citrate complexed solution was investigated. Bath configuration 4 was used. The bath configuration is detailed in Figure 3-3. Further examination of the solution and coating properties was then carried out using solution 6 and bath configuration 5 (Figure 3-3), to enable larger coupons to be tested using a variety of corrosion test methods. The experimental conditions used to initially investigate solution 6 are given in Table 5-1.

<table>
<thead>
<tr>
<th>Bath configuration (see Figure 3-3)</th>
<th>Pre-treatment (see Table 3-2)</th>
<th>Electroplating conditions</th>
<th>Current density /A cm⁻²</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>Abrade</td>
<td>DC</td>
<td>0.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.4</td>
</tr>
<tr>
<td></td>
<td>Pulsed te = 0.001 s, td = 0.002 s</td>
<td></td>
<td>0.4</td>
</tr>
<tr>
<td></td>
<td>HCl pickle</td>
<td>Pulsed te = 0.002 s, td = 0.004 s</td>
<td>0.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.8</td>
</tr>
</tbody>
</table>

Table 5-1 Initial experimental conditions used for investigating solution 6

A series of experiments looking at the effect of the different bath configuration, namely configuration 5 in Figure 3-3 was then undertaken. For these experiments the volume of solution used in the electroplating bath was kept consistent with that used previously (namely 1 litre used in configuration 4). The volume of electroplating solution was then increased to 4 litres for all subsequent experimentation. The experimental conditions used are given in Table 5-2.

The use of a nickel under-plate between the ternary zinc-nickel-manganese coating and the steel substrate was also investigated. Details of the nickel electroplating solution and the experimental parameters used are given in Table 5-3.
Production of zinc-nickel-manganese coatings - results and discussion

<table>
<thead>
<tr>
<th>Bath configuration</th>
<th>Volume of electroplating solution /litres</th>
<th>Pre-treatment</th>
<th>Electroplating conditions</th>
<th>Applied electroplating current density /A cm⁻²</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>1</td>
<td>Abrasion</td>
<td>Pulsed $t_c = 0.001$ s, $t_d = 0.002$ s</td>
<td>0.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>DC</td>
<td>0.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>HCl dip</td>
<td>Pulsed $t_c = 0.001$ s, $t_d = 0.002$ s</td>
<td>0.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Pulsed $t_c = 0.002$ s, $t_d = 0.004$ s</td>
<td>0.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Pickle</td>
<td>Pulsed $t_c = 0.001$ s, $t_d = 0.002$ s</td>
<td>0.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.8</td>
</tr>
<tr>
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<td></td>
<td></td>
<td></td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Pulsed $t_c = 0.002$ s, $t_d = 0.004$ s</td>
<td>0.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.4</td>
</tr>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>0.4</td>
</tr>
</tbody>
</table>

Table 5-2 Experimental conditions used to investigate solution 6 and bath configuration 5

<table>
<thead>
<tr>
<th>Nickel electroplating solution</th>
<th>120 g dm⁻³ NiSO₄·6H₂O</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>15 g dm⁻³ NH₄Cl</td>
</tr>
<tr>
<td></td>
<td>15 g dm⁻³ Boric acid</td>
</tr>
<tr>
<td></td>
<td>pH = 5.3</td>
</tr>
<tr>
<td></td>
<td>Temperature = 25°C</td>
</tr>
<tr>
<td></td>
<td>Current density = 0.02 A cm⁻²</td>
</tr>
<tr>
<td></td>
<td>Amount of applied electroplating charge = 5 C giving a thickness of about 0.5 µm</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Bath configuration</th>
<th>Pre-treatment</th>
<th>Electroplating conditions</th>
<th>Current density /A cm⁻²</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>Pickle</td>
<td>Pulsed $t_c = 0.002$ s, $t_d = 0.004$ s</td>
<td>0.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>DC</td>
<td>0.2</td>
</tr>
</tbody>
</table>

Table 5-3 Experimental parameters used to produce coatings of zinc-nickel-manganese over an under-plate of nickel
The effect of thickness of electroplate on the corrosion properties of the zinc-nickel-manganese coatings was examined as well. This was undertaken by electroplating for different values of applied electroplating charge. Details are given in Table 5-4. Electroplating was undertaken using bath configuration 5 detailed in Figure 3-3, using four litres of solution and pickling the steel prior to electroplating (see Section 3-3-1 and Table 3-2).

<table>
<thead>
<tr>
<th>Electroplating conditions</th>
<th>Applied electroplating current density /A cm²</th>
<th>Total applied charge /C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pulsed t_c = 0.002 s, t_d = 0.004 s</td>
<td>0.2</td>
<td>30, 60, 90, 120, 150</td>
</tr>
<tr>
<td>DC</td>
<td>1.0</td>
<td></td>
</tr>
<tr>
<td>DC</td>
<td>0.2</td>
<td></td>
</tr>
</tbody>
</table>

Table 5-4 Experimental conditions used to investigate the effect of thickness of electroplate

To investigate how the manganese and the citrate complexant interact within the solution a set of experiments examining the effect of increasing the sodium citrate and the manganese concentration was undertaken. This experimentation was carried out using a modified Taguchi L₈ orthogonal array (see Section 2-11-1). Two verification experiments were also performed. The array and the verification experiments are detailed in Table 5-5. Bath configuration 3 (selective or brush electroplating) was used as this enabled the use of smaller solution volumes. This helped to simplify the undertaking of the orthogonal array. The initial starting solution was based on solution 6 in Table 3-4, with the only differences being the sodium citrate and manganese sulphate concentrations. All electroplating was undertaken to the same value of applied electroplating charge to give nominally the same thickness of electroplate. As well as the citrate and manganese concentrations, the use of pulse electroplating as apposed to DC electroplating was investigated, along with the use of two different etch treatments. The parameters varied are given in Table 5-5.

To provide information on the electrochemical behaviour of zinc-nickel-manganese several detached coatings were produced using solution 6 and bath configuration 4. Like the production of zinc-nickel detached coatings the zinc-nickel-manganese coatings were initially deposited onto aluminium foil and then carefully peeled off.
Production of zinc-nickel-manganese coatings - results and discussion

<table>
<thead>
<tr>
<th>Experiment number</th>
<th>Amount of sodium citrate /mol dm$^{-3}$</th>
<th>Amount of manganese sulphate /mol dm$^{-3}$</th>
<th>Electroplating conditions</th>
<th>Pre-treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.4</td>
<td>0.4</td>
<td>DC</td>
<td>Pickle</td>
</tr>
<tr>
<td>2</td>
<td>0.6</td>
<td>0.6</td>
<td>Pulsed $t_c = 0.002$ s, $t_d = 0.004$ s</td>
<td>HCl dip</td>
</tr>
<tr>
<td>3</td>
<td>0.4</td>
<td>0.4</td>
<td>DC</td>
<td>HCl dip</td>
</tr>
<tr>
<td>4</td>
<td>0.8</td>
<td>0.6</td>
<td>Pulsed $t_c = 0.002$ s, $t_d = 0.004$ s</td>
<td>Pickle</td>
</tr>
<tr>
<td>5</td>
<td>0.8</td>
<td>0.6</td>
<td>DC</td>
<td>HCl dip</td>
</tr>
<tr>
<td>6</td>
<td>1.2</td>
<td>0.6</td>
<td>Pulsed $t_c = 0.002$ s, $t_d = 0.004$ s</td>
<td>Pickle</td>
</tr>
<tr>
<td>7</td>
<td>1.2</td>
<td>0.6</td>
<td>DC</td>
<td>HCl dip</td>
</tr>
<tr>
<td>Verification 1</td>
<td>0.4</td>
<td>0.4</td>
<td>Pulsed $t_c = 0.002$ s, $t_d = 0.004$ s</td>
<td>Pickle</td>
</tr>
<tr>
<td>Verification 2</td>
<td>1.2</td>
<td>0.6</td>
<td>DC</td>
<td>HCl dip</td>
</tr>
</tbody>
</table>

Table 5-5 Taguchi modified $L_8$ array and verification experiments used to investigate the effect of citrate and manganese concentrations

To investigate the use of TRIS as an alternative complexing agent, which would enable electroplating to be carried out in a more neutral solution, a short set of experiments using solution 7 detailed in Table 3-4 and bath configuration 3, selective electroplating were undertaken. The experimental conditions used are detailed in Table 5-6.

<table>
<thead>
<tr>
<th>Electroplating solution</th>
<th>Bath configuration</th>
<th>Electroplating conditions</th>
<th>Applied electroplating current density /A cm$^{-2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>3</td>
<td>DC</td>
<td>0.05</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.4</td>
</tr>
</tbody>
</table>

Table 5-6 Experimental conditions used to produce zinc-nickel-manganese coatings onto steel from solution 7

5.4 Zinc-nickel-manganese electroplate testing

All coatings produced were examined using optical microscopy, detailed in Section 3-5-2. EDAX was used to determine the composition of the resultant coatings. Details of the EDAX method are given in Section 3-5-3. The current efficiency of the coating process was calculated by weighing all test coupons before and after electroplating.
Details of the current efficiency calculations are given in Section 3-5-1. The thickness of the resulting electroplate was measured using an eddy current probe, details of which are given in Section 3-5-5.

All coatings on steel were subjected to neutral salt fog corrosion testing to 5% red rust. Details of the neutral salt fog exposure testing procedure are given in Section 3-6-5. Potential monitoring as described in Section 3-6-1 was undertaken on a number of test samples to investigate the way in which the addition of manganese affected the change in potential with time. Potential monitoring was also performed on steel coupons, 2014-T6 aluminium alloy coupons, and cadmium electroplated onto steel.

Galvanic compatibility tests in accordance with Section 3-6-2 were carried out on a number of coating compositions, again to further investigate the effect of additions of manganese to zinc-nickel. To further clarify the role of manganese in the sacrificial nature of the coatings, galvanic tests on pure manganese coatings electroplated onto steel were undertaken. The galvanic compatibility of cadmium electroplated steel was also investigated as a control.

To further investigate the corrosion mechanism, double polarisation measurements were carried out. The method used is detailed in Section 3-6-7. As well as investigating selected zinc-nickel-manganese coatings on steel, detached zinc-nickel-manganese was investigated along with manganese electroplate on steel.

Alternate immersion tests and marine exposure trials were undertaken on coatings produced from solution 6 using bath configuration 5. Details of the method used for undertaking alternate immersion tests are given in Section 3-6-4 and for marine exposure trials in Section 3-6-3.

Porosity testing in accordance with the method described in Section 3-7-1 was also carried out on a number of coatings to give a qualitative indication of its level and the way in which it changed with coating composition.
Hardness testing, according to the method described in Section 3-7-2, was undertaken as well along with electrical conductivity measurements as shown in Section 3-7-3 and Figure 3-7.

### 5.5 Experimental summary

A short summary of the experimentation performed to investigate zinc-nickel-manganese electroplating is given in Table 5-7. For details of the experimental conditions used, solutions, pre-treatments, bath configurations and subsequent testing see Section 3.

<table>
<thead>
<tr>
<th>Cyclic voltammograms</th>
<th>With time</th>
<th>Zn-Ni</th>
<th>Ni-Mn</th>
<th>Zn-Mn</th>
<th>Zn-Ni-Mn</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Change in forward and reverse scans</td>
<td>Reduction peak decreases rapidly, solution less active</td>
<td>More negative $E_{\text{plating effect of Mn}}$ (-1200 mV)</td>
<td>Similar to Zn-Mn but less negative $E_{\text{plating}}$ (-1100 mV). Shape due to citrate</td>
<td></td>
</tr>
<tr>
<td></td>
<td>metal deposited</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>With nickel solution concentration</td>
<td>Zn-Ni</td>
<td>Ni-Mn</td>
<td>Zn-Ni-Mn</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Not sensitive to nickel additions, anomalous co-deposition</td>
<td>Very sensitive to nickel additions, normal co-deposition</td>
<td>Mixed response, both nickel and manganese should be co-deposited with zinc</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

#### Electroplating

<table>
<thead>
<tr>
<th>Solutions investigated</th>
<th>6 and 7</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solution volumes investigated</td>
<td>1 and 4 litres</td>
</tr>
<tr>
<td>Bath configurations</td>
<td>3, 4 and 5</td>
</tr>
<tr>
<td>Pre-treatments</td>
<td>Abrade, HCl dip, HCl pickle</td>
</tr>
<tr>
<td>Solution parameters investigated</td>
<td>Change in Mn concentration from 0.4 to 0.6 mol dm$^{-3}$, change in citrate concentrations from 0.4 to 1.2 mol dm$^{-3}$</td>
</tr>
<tr>
<td>Substrates</td>
<td>Steel, detached, nickel underlayer</td>
</tr>
<tr>
<td>Thickness of electroplate</td>
<td>Varied by changing applied electroplating charge from 30 C to 150 C</td>
</tr>
<tr>
<td>Pulse conditions</td>
<td>DC and pulsed using 2 different values of $t_c$ and $t_d$</td>
</tr>
<tr>
<td>Applied electroplating current densities</td>
<td>Varied from 0.05 to 1.0 A cm$^{-2}$</td>
</tr>
<tr>
<td>Analysis</td>
<td>EDAX, SEM, thickness and current efficiency calculations</td>
</tr>
<tr>
<td>Corrosion testing</td>
<td>Neutral salt fog, potential monitoring with time, galvanic compatibility, double polarisation, alternate immersion and marine exposure</td>
</tr>
<tr>
<td>Other tests</td>
<td>Porosity, hardness and electrical conductivity</td>
</tr>
</tbody>
</table>

*Table 5-7 Summary of investigation into zinc-nickel-manganese electroplating*
5.6 Variation of current efficiency with applied electroplating current density

The way in which the calculated current efficiency varies with increasing applied electroplating current density for zinc-nickel-manganese coatings produced using solution 6, the citrate complexed solution, and bath configuration 4 is shown in Figure 5-8. For details of the experimental conditions reference should be made to Section 3.

![Graph showing variation of current efficiency with applied electroplating current density](image-url)

**Figure 5-8** Variation of current efficiency with applied electroplating current density for zinc-nickel-manganese coatings produced from solution 6 using bath configuration 4 onto steel

The current efficiency of the electroplating process can be seen to be very low in all cases, being lower than those observed for zinc-nickel electroplating (see Figures 4-1 to 4-3). The current efficiency then decreases as the applied electroplating current density is increased. For the DC electroplated coatings the current efficiency is lower at a given value of applied electroplating current density than for coatings produced using pulse electroplating. The nature of the pulse and the pre-treatment both seem to influence the resulting current efficiency at a given value of applied electroplating current density. Whether it is the change of pre-treatment to acid pickle or the change in pulse conditions to longer pulse lengths is unclear, this will be investigated further for solution 6 using bath configuration 5. In hindsight significantly more data points would be required to clarify the relationship.
The cause of the low values of current efficiency compared with zinc-nickel electroplating, from a complex bath, could be due to the different complexant used, the influence of the manganese or the effect of the bath pH which was very low to prevent the precipitation of manganese citrate which occurs at higher values of pH. The low pH used will increase the rate of hydrogen evolution and hence reduce the current efficiency of the process. At a low pH more H\(^+\) ions are present, hence the hydrogen reaction rate increases (see equation 2-6). The deposition of manganese is also associated with hydrogen evolution, hence any deposition of manganese will also increase the rate of the hydrogen evolution reaction and so reduce the current efficiency of the process. The use of a different complexant will also have an effect depending on how strong the inhibitory effect of the complexant is. The effect of the complexant may not be as large as the effect of the reduction in pH or the simultaneous deposition of manganese [51], but this is dependent on how strongly it complexes the three metals in solution.

The way in which the calculated current efficiency varies with the applied electroplating current density for zinc-nickel-manganese coatings produced from solution 6 using bath configuration 5 and one litre of electroplating solution is illustrated in Figure 5-9. Again, there can be seen to be a decrease in calculated current efficiency with increasing applied electroplating current density. The use of DC as opposed to pulse electroplating again has the effect of reducing the current efficiency at a given value of applied electroplating current density. Both the coatings produced using acid pickle pre-treatment and using a longer pulse period show a slight increase in calculated current efficiency. This shows the change observed in Figure 5-8 between the pulse electroplated coatings to be due to both the nature of the pre-treatment and the length of the pulse period.
The change in the calculated current efficiency with applied electroplating current density for coatings produced from solution 6 using bath configuration 5 and 4 litres of solution is shown in Figure 5-10. There is again a reduction in current efficiency with increase in applied electroplating current density. The use of DC rather than pulse electroplating again reduces the current efficiency at a given value of applied electroplating current density. The use of a longer pulse period can also be seen to increase the calculated current efficiency. The use of a nickel underlayer does not, however, have a significant effect on the current efficiency, with a slight increase in current efficiency being observed at low values of applied electroplating current density and a slight decrease at high values.
Figure 5-10 The variation in calculated current efficiency with applied electroplating current density for coatings produced from solution 6 using bath configuration 5 and 4 litres of electroplating solution onto steel and a nickel underlayer.

The thickness of electroplate does not influence the calculated value of current efficiency. This is illustrated in Figure 5-11, and shows that the current efficiency is consistent throughout the thickness of electroplate, suggesting that the alloy composition will also be consistent as the current efficiency of the process is known to be related to the manganese content.
Figure 5-11 Change in current efficiency with total applied electroplating charge for zinc-nickel-manganese coatings produced from solution 6 using bath configuration 5 onto steel.

The effect of the different factors varied on the calculated current efficiency for the Taguchi L₈ array used to investigate the effect primarily of citrate and manganese solution concentration is given in Figure 5-12.

Initially increasing the concentration of sodium citrate has a positive effect on the current efficiency, however, as the concentration of sodium citrate is further raised the current efficiency of the process decreases. This may be due to an increase in the manganese content of the resultant alloy and will be discussed further in the section on composition change.

The amount of manganese sulphate in the solution has a small positive effect on the current efficiency. However, the effect is very small and may be within the error of measurement (certainly within the standard deviation of the spread of results).
Changing the electroplating conditions from DC to a long period pulse increases the current efficiency of the process. This has already been observed in Figures 5-8, 5-9, and 5-10 for electroplating undertaken using bath configurations 4 and 5 rather than configuration 3, which was used for this experimental set.

Decreasing the applied electroplating current density also has the effect of increasing the current efficiency of the electroplating process. This has again been observed for solution 6 using both bath configuration 4 and 5.

Changing the type of pre-treatment from HCl dip to HCl pickle (HCl pickle higher temperature for longer, see Table 3-1) seems to, however, have an opposite effect on the current efficiency of the process than observed previously. This change in current efficiency is only very small and is within the experimental deviation.
The way in which the current efficiency of the electroplating process changes with applied electroplating current density for solution 7 is illustrated in Figure 5-13. Here it can again be seen that there is a decrease in current efficiency with increase in applied electroplating current density. The values of current efficiency for the solution containing TRIS rather than citrate ions (solution 7 rather than solution 6) are similar to those seen previously for the citrate solutions. The reason for the large decrease in the current efficiency of the process compared to electroplating of zinc-nickel is therefore unlikely to be the low pH of solution 6, giving rise to an increase in the hydrogen evolution reaction and hence decreasing the current efficiency. Solution 7 still shows a reduction in current efficiency when compared to the zinc-nickel electroplating solution. Both solution 3, used for electroplating zinc-nickel and solution 7, used for the zinc-nickel-manganese deposition, contain the same complexant at the same pH. The nature of the complexant is therefore unlikely to be the cause of the reduction in current efficiency of the process. The co-deposition of manganese with its high associated hydrogen reaction is therefore the cause of the reduction in current efficiency between the zinc-nickel and zinc-nickel-manganese solutions.

Figure 5-13 Variation of calculated current efficiency with applied electroplating current density for zinc-nickel-manganese coatings produced onto steel using solution 7 and bath configuration 3 (selective electroplating)
A summary of the main conclusions from this sub-section is given in Table 5-8.

<table>
<thead>
<tr>
<th>Factor varied</th>
<th>Effect on calculated current efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td>Increasing applied electroplating current</td>
<td>Decreases</td>
</tr>
<tr>
<td>density</td>
<td></td>
</tr>
<tr>
<td>Changing from DC to pulse electroplating</td>
<td>Increases</td>
</tr>
<tr>
<td>Increasing pulse period</td>
<td>Increases</td>
</tr>
<tr>
<td>Effect of pre-treatment</td>
<td>Increases for HCl pickle</td>
</tr>
<tr>
<td>Increasing sodium citrate concentration</td>
<td>Decreases</td>
</tr>
<tr>
<td>Changing bath configuration</td>
<td>No significant effect</td>
</tr>
<tr>
<td>Changing thickness of electroplate</td>
<td>No effect</td>
</tr>
<tr>
<td>Changing complexant</td>
<td>No effect</td>
</tr>
<tr>
<td>Changing pH</td>
<td>No significant effect</td>
</tr>
<tr>
<td>Overall</td>
<td>Lower than zinc-nickel TRIS solution</td>
</tr>
<tr>
<td></td>
<td>(solution 3) due to co-deposition of</td>
</tr>
<tr>
<td></td>
<td>manganese</td>
</tr>
</tbody>
</table>

Table 5-8 Summary of results from undertaking current efficiency calculations on zinc-nickel-manganese coatings electroplated onto steel

5.7 Thickness measurements

Thickness measurements were undertaken in accordance with the method described in Section 3-5-5. The way in which the thickness varies with applied electroplating current density should mirror the variation in current efficiency with applied electroplating current density. Any deviation would suggest that there is a change in the density of electroplate, and hence either a change in the level of porosity or a change in the microstructure of the coating.

The results of carrying out thickness measurements on zinc-nickel-manganese coatings produced using solution 6 (see Table 3-4) and bath configuration 4 (see Figure 3-3) are given in Figure 5-14. For the corresponding graph of variation in current efficiency (see Figure 5-8), there is, in all cases, a general downward trend in efficiency with increasing applied electroplating current density. The rate of decrease in current efficiency is rapid at first for the coatings produced using DC electroplating. This is not shown by the thickness measurements, nor is the general downward trend shown in Figure 5-8. In fact there is an increase in thickness with increasing applied electroplating current density for the coatings produced using an acid pickle pre-treatment and the longer pulse period electroplating. The rate of decrease of thickness with increase in applied electroplating current density is not as great for DC electroplating as the rate of decrease of current efficiency (Figure 5-9).
There must therefore be some change in the morphology or level of porosity as the current density is increased. It could possibly be a morphological change as the coatings produced using the shorter pulse and abrasion as a pre-treatment do not exhibit the same deviation from the expected pattern. This will be investigated further in the section on morphology.

Figure 5-14 Variation of thickness with applied electroplating current density for zinc-nickel-manganese coatings produced from solution 6 using bath configuration 4 onto steel substrate

The change in thickness with applied electroplating current density for coatings produced from solution 6 using bath configuration 5 and 1 litre of solution is shown in Figure 5-15. Again, there is a difference in the way in which thickness changes with increase in current density when compared to the current efficiency variation shown in Figure 5-9. There can be seen to be a slight upward trend in thickness with increasing applied electroplating current efficiency for coatings produced using abrasion and the shorter pulse period, and a larger upward trend at high applied electroplating current density for coatings produced using the longer pulse period. This upward trend in thickness with applied electroplating current density was also observed in Figure 5-14 for coatings produced from solution 6 using bath configuration 4 and the longer pulse period with an acid pickle pre-treatment.
However, there is no such upward trend for coatings produced using the shorter pulse period and HCl pickle in Figure 5-15. This suggests that the cause of the change in density of the coatings at higher values of applied electroplating current density is not the pickle but rather the length of the pulse period used.

![Graph showing the variation in thickness with applied electroplating current density for coatings produced using solution 6 and bath configuration 5 with 1 litre of electroplating solution](image)

The order of thickest to thinnest coatings is also different than the order shown for current efficiency in Figure 5-9, with the HCl pickle and shorter pulse, and the HCl dip and longer pulse giving the lowest thickness but the highest current efficiencies. The HCl dip and DC coatings also show a significant reduction in expected thickness. This suggests that both the use of a longer pulse period and HCl dip or pickle have a significant effect on the morphology giving rise to more compact higher density coatings at low values of applied current density. This will be investigated further in the section on morphology (Section 5-9).

The variation in thickness with applied electroplating current density for coatings produced using 4 litres rather than 1 litre of solution 6, using bath configuration 5 is given in Figure 5-16. On comparing Figure 5-16 with Figure 5-10 the corresponding
Production of zinc-nickel-manganese coatings - results and discussion

Graph for change in current efficiency, there can again be seen some differences. Firstly the thickness of the DC electroplated coatings increase as the current density rises while the current efficiency decreases with a rise in applied current density. For DC electroplating it was only possible to electroplate at two values of current density, however, more than one sample at each value of current density was obtained and the values averaged to obtain the DC data points in Figures 5-15 and 5-16. This shows that there is a change in density of the DC electroplated coatings as the current density used for electroplating is changed. This has already been observed for other coatings (see Figures 5-14 and 5-15). The increase is only small suggesting a small decrease in density with increasing applied electroplating current density.

Again the order from thickest to thinnest coating when compared to the order from highest to lowest current efficiency in Figure 5-10 is different. In this case the coatings produced using the longer pulse show a reduction in their expected thickness when compared to their current efficiency. This is consistent with the observation from Figure 5-15, which suggested that the use of a longer pulse period increased the density of the coatings produced.

Figure 5-16 The variation in thickness with applied electroplating current density for coatings produced from solution 6 using bath configuration 5 and 4 litres of electroplating solution onto steel and a nickel underlayer
The way in which the applied electroplating charge influences the thickness of electroplate produced is shown in Figure 5-17. There is a general upward trend in thickness with increase in applied charge, this is linear as expected as the current efficiency of the electroplating process does not vary with increase in charge (see Figure 5-11). The 0.2 A cm\(^{-2}\) peak current, pulsed coatings produced the greatest thickness for an equivalent applied electroplating charge. This is as expected from Figure 5-11, which showed the 0.2 A cm\(^{-2}\) pulsed coating to have the highest current efficiency. There is a slight reduction in the gap between the thickness of the DC and 1.0 A cm\(^{-2}\) pulsed coating compared to their differences in current efficiency shown in Figure 5-11. This shows the 1.0 A cm\(^{-2}\) pulsed coating to have a lower density. This is consistent with coatings produced using a high current density and the longer pulse period in Figure 5-15, which showed a decrease in density at high values of applied current density.

![Figure 5-17 Change in thickness with total applied electroplating charge for zinc-nickel-manganese coatings produced from solution 6 using bath configuration 5 onto steel](image)

The influence of changing the sodium citrate and manganese sulphate concentration, the electroplating conditions, current density and pre-treatment of coatings produced from solution 6 using bath configuration 3 (selective electroplating see Figure 3-2) on
the thickness of electroplate produced is illustrated in Figure 5-18. On comparing Figure 5-18 with the corresponding graph for current efficiency of the process it can be seen that the change in thickness with the various factors follows the same trends as the change in current efficiency. This is as expected, showing no significant change in density. This lack of change in the density of electroplate shows that the pulse period, which was not varied here is the cause of the majority of density changes observed previously.

![Graph](image)

Figure 5-18 Influence of citrate, manganese concentration, electroplating variables, current density and pre-treatment on the thickness of zinc-nickel-manganese coatings produced onto steel using solution 6 and bath configuration 3 (selective electroplating)

The thickness variation with applied electroplating current density for coatings produced from solution 7 using bath configuration 3 and DC electroplating is given in Figure 5-19. On comparing Figure 5-19 with the corresponding figure for current efficiency variation (Figure 5-13), it can be seen that the downward trend with increasing current density is the same. The slope for the change in thickness with increasing current density is, however, not as steep. This shows that there is a slight
decrease in density of electroplate with increase in applied electroplating current density.

![Graph showing variation of thickness with applied electroplating current density](image)

**Figure 5-19** Variation of thickness with applied electroplating current density for zinc-nickel-manganese coatings produced onto steel using solution 7 and bath configuration 3 (selective electroplating)

To further investigate the role of the applied electroplating current density in the change in morphology or density of the coating, density of electroplate was plotted against applied electroplating current density. The result is shown in Figure 5-20.

In all cases the density of electroplate decreased with an increase in the electroplating current density. The longer pulse period used produced the densest coatings for a given value of applied electroplating current density. This increase in density for the coatings produced using the longer pulse period agrees with the findings of Figures 5-9 and 5-10. There is also a larger decrease in density when using the longer pulse at the higher values of electroplating current density. This again agrees with the findings of Figure 5-9. The DC electroplated coatings showed the lowest density. This reduction in density for the DC electroplated coatings again agrees with Figure 5-10.
**Figure 5-20** Change in density of electroplate with increase in applied electroplating current density for zinc-nickel-manganese coatings produced from solution 6 onto mild steel

The reduction in density with increase in applied electroplating current density may be due to an increase in hydrogen evolution as the current density is raised, causing an increase in the amount of hydrogen trapped within the coating, and hence a reduction in density. Solution 7 operates at a higher pH value (see Table 3-4), it therefore is likely to show a reduction in the amount of hydrogen evolution. This is obviously partly the case as coatings produced from solution 7 do not show as large a decrease in density with increase in applied electroplating current density. This is also illustrated in Figure 5-20. This will be investigated further in the section on morphology of the coating. The decrease in electroplate density may also be due to an increase in the amount of manganese within the coating, causing a change in morphology due to the size of the manganese ion, which is considerably different to both zinc and nickel ions and so may distort the metallic lattice [200]. The possible increase in the manganese content with increase in applied electroplating current density will be examined in the following section, where the composition of the coatings is investigated.
A summary of the main conclusions from this sub-section is given in Table 5-9.

<table>
<thead>
<tr>
<th>Variable</th>
<th>Effect on thickness</th>
<th>Effect on density</th>
</tr>
</thead>
<tbody>
<tr>
<td>Increase electroplating current density</td>
<td>Decreases</td>
<td>Decreases</td>
</tr>
<tr>
<td>Using DC electroplating</td>
<td>Lower thickness</td>
<td>Lower density than pulsed</td>
</tr>
<tr>
<td>Using longer pulse period</td>
<td>Decreases</td>
<td>Increases</td>
</tr>
<tr>
<td>Increasing sodium citrate concentration</td>
<td>Decreases</td>
<td>No change</td>
</tr>
<tr>
<td>Increasing manganese solution concentration</td>
<td>No effect</td>
<td>No effect</td>
</tr>
<tr>
<td>Increasing electroplating charge</td>
<td>Linear increase</td>
<td>No change</td>
</tr>
<tr>
<td>Changing from solution 6 (low pH) to solution 7 (higher pH)</td>
<td>About the same</td>
<td>Does not decrease at the same rate with increase in applied electroplating current density</td>
</tr>
</tbody>
</table>

Table 5-9 Summary of conclusions obtained from undertaking thickness measurements.

5.8 Composition of coatings

Compositional analysis of the zinc-nickel-manganese coatings was carried out according to the procedure given in Section 3-5-3. The variation in composition with applied electroplating current density for coatings produced using solution 6 and bath configuration 4 (detailed in Table 3-4 and Figure 3-3) is shown in Figure 5-21. Like the zinc-nickel coatings produced using solution 3 (see Figure 4-7), which also contained a complexant, there is an increase in nickel content with increasing electroplating current density. For DC electroplating the nickel content increases from 1% to 11% over the current density region studied. The manganese content also increases for DC electroplating with increase in applied electroplating current density by about the same order of magnitude. However, nickel is the more noble metal and as such would be expected to deposit preferentially. Anomalous co-deposition of nickel is therefore occurring. The change in nickel content with increasing current density corresponds to region III in Figure 2-2. The change in manganese content is not due to anomalous co-deposition corresponding to region III as manganese is the least noble metal. Hence manganese is undergoing normal co-deposition over the whole current density range studied.
For coatings produced using pulse electroplating there is also a rise in nickel content with increasing applied electroplating current density. However, the rise is dependent on the length of pulse period used, with the longer times producing more of a change in nickel content over the region studied. The deposition is still anomalous with nickel deposition being inhibited, with the level of inhibition dependant on the pulse period length, the shorter the pulse period length the less nickel is deposited for a given value of applied electroplating current density.

![Graph showing variation of composition with applied electroplating current density for zinc-nickel-manganese coatings produced from solution 6 using bath configuration 4 onto steel.](image)

Figure 5-21 Variation of composition with applied electroplating current density for zinc-nickel-manganese coatings produced from solution 6 using bath configuration 4 onto steel

The composition change with applied electroplating current density for zinc-nickel-manganese coatings produced from solution 6 using bath configuration 5 is shown in Figure 5-22. Here it can be seen that the effect of changing the bath configuration is to change the effect of the different variables such as pulse length and pre-treatment on the composition of the resultant coating. With bath configuration 4 in Figure 5-21, the longer pulse period gave a higher nickel content than the shorter pulse period ($t_c = 0.001\ s$, $t_d = 0.004\ s$). With bath configuration 5 the effect is the opposite, with the shorter pulse period giving a higher nickel content and the longer pulse period giving
Production of zinc-nickel-manganese coatings - results and discussion

a lower nickel content. The different trend is also apparent for the manganese contents, with bath configuration 4 giving a higher manganese content for the shorter pulse period and bath configuration 5 giving a lower manganese content for the shorter pulse.

The change in the effect of the pulse period on the nickel and manganese composition must be due to the different primary, secondary and ternary current distributions within the two different baths. These will affect the double layer in a different way depending on the pulse length, hence perhaps causing the variation in trends shown in Figures 5-21 and 5-22.

![Figure 5-22](image.png)

Figure 5-22 Graphs showing the variation in composition with applied electroplating current density for coatings produced using solution 6 and bath configuration 5 with 1 litre of electroplating solution onto steel

When the volume of electroplating solution is increased to four litres the trend in nickel contents is still the same, with the shorter pulse period producing a higher nickel content than the longer pulse. This is illustrated in Figure 5-23. As for Figure 5-21, the use of DC electroplating produces higher nickel and manganese contents for a given value of applied electroplating current density. The nickel content of the coatings electroplated onto a nickel underlayer is higher than expected. This is due to
the nickel underlayer influencing the EDAX results obtained. It can therefore be concluded that a change in electroplating solution volume has a smaller effect on the composition of the ternary alloy than the use of a different anode, cathode arrangement i.e. a different bath configuration. DC electroplating is less affected by a change in bath geometry than pulse electroplating.

Figure 5-23 The variation in composition with applied electroplating current density for coatings produced from solution 6 using bath configuration 5 and 4 litres of electroplating solution onto steel and a nickel underlayer

The effect of changing the concentration of complexant and other factors on the nickel and manganese contents in the resultant coatings is given in Figure 5-24. Like the other bath geometries used there is an increase in the nickel and manganese content as the applied electroplating current is increased. There is also a decrease in both the nickel and manganese contents with changing from DC to pulse electroplating. This again is consistent with other bath configurations used in Figures 5-21, 5-22 and 5-23. The use of different pre-treatments has a very small effect on the manganese content and no effect on the nickel content. This again agrees with results already obtained for the other bath configurations used. Changing the molarity of
manganese within the electroplating bath has a small effect on the nickel content and a slightly larger effect on the manganese content.

Figure 5-24 Influence of citrate, manganese concentration, electroplating variables, current density and pre-treatment on the composition of zinc-nickel-manganese coatings produced onto steel using solution 6 and bath configuration 3 (selective electroplating)

However, the increase in the molarity of complexant within the electroplating bath has the largest effect on the manganese content in the resultant coating. It has a much smaller effect on the nickel content. This is as expected as the complexant will influence the rate of the manganese electroplating process to a much higher degree than the nickel process, because the complexant is added primarily to increase the manganese content within the coating and is primarily associated with the manganese ions in solution.

The variation of composition with applied electroplating current density for coatings produced from solution 7 using bath configuration 3 (selective electroplating), is shown in Figure 5-25. Here it can be seen that the manganese content increases as the
applied electroplating current is increased. The manganese content is greater than seen for solution 6. However, the molarity of the TRIS used in solution 7 was greater than that used to produce the majority of coatings from solution 6. When the molarity of the citrate complexant is also increased to 1.2 mol dm$^{-3}$ the manganese content also increases to about the same as that obtained for solution 7 (see Figure 5-24).

The nickel content, however, is significantly greater when electroplating is undertaken from solution 7, especially at low values of applied electroplating current density. The nickel content in the coatings produced from solution 7 does not vary significantly over the applied electroplating current density range studied, but is still anomalous with respect to nickel. Both solution 6 and solution 7 contained the same molarity of nickel ions. The change in nickel content observed for solution 7 could therefore be related to the use of the different complexant namely TRIS. But when TRIS is used in a solution, which does not contain manganese ions, namely solution 3 in Table 3-3, the result is different. In this case the nickel content varied from 3 to 13 atomic % (see Figure 4-7), for zinc-nickel electroplated onto steel using solution 3 and bath configuration 3 (selective electroplating). The way in which the nickel anomalous co-deposition is occurring must therefore be influenced by the presence of manganese either as ions in the solution or as metal in the electroplate. It may be that the presence of manganese in solution shifts the value of $E_{\text{plating}}$ to a more negative value, which causes more nickel to be deposited for a given value of applied electroplating current density. This has been illustrated for zinc-nickel-manganese solutions containing citrate as the complexant in Figures 5-4 and 5-7, where the cyclic response of citrate containing solutions were compared, giving a value of $E_{\text{plating}}$ of $-1100$ mV for zinc-nickel-manganese and $-1010$ mV for zinc-nickel. The only way in which a negative shift in the value of $E_{\text{plating}}$ could cause an increase in nickel content would be if the nickel electroplating became more anomalous as the electroplating potential became more negative. If nickel was being co-deposited normally a negative shift in $E_{\text{plating}}$ would lead to a decrease in nickel content as nickel is more noble with a less negative rest potential than either zinc or manganese.
A short summary of the important results from this sub-section on composition is given in Table 5-10.

<table>
<thead>
<tr>
<th>Electroplating solution and bath configuration</th>
<th>Effect on composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solution 6, bath configuration 4</td>
<td>Increasing applied electroplating current density increases nickel and manganese content, dependant on pulse conditions. A longer pulse period gives an increase in the change in nickel content. DC produces more nickel and manganese for a given applied electroplating current density</td>
</tr>
<tr>
<td>Solution 6, bath configuration 5</td>
<td>As configuration 4 except effect of pulse period. A shorter pulse period leads to an increase in nickel content change</td>
</tr>
<tr>
<td>Changing sodium citrate solution 6 concentration using bath configuration 3</td>
<td>Significant increase in manganese content. No increase in nickel content. Rest same as for solution 6, bath configuration 4</td>
</tr>
<tr>
<td>Solution 7, bath configuration 3</td>
<td>Higher nickel content than solution 6. Higher nickel content than solution 3 (Zn-Ni TRIS solution). Comparable manganese contents with high molarity citrate solution. Presence of manganese influencing ( E_{\text{plating}} ) and hence amount of nickel in coating</td>
</tr>
</tbody>
</table>

Table 5-10 Summary of compositional analysis results for zinc-nickel-manganese coatings
**5.9 Morphology of coatings**

The morphology of the coatings was examined according to the method described in Section 3-5-2. By examining the morphology of the zinc-nickel-manganese coatings it was hoped to get an indication of the way in which the nature of the electroplating, the composition of the coating and the electrolyte used effected the nature of the microstructure. The coating morphology may then be related to other properties of the coating, such as composition and porosity.

**5.9.1 DC versus pulse electroplating**

Firstly the use of DC and pulse electroplating was investigated. The results for solution 6 are shown in Figure 5-26. All the coatings produced using solution 6 tended to show an uneven grain shape, rather than small rounded grains, with evidence of porosity being present especially at higher nickel and manganese contents corresponding to a higher applied electroplating current density. The level of increase in porosity is especially apparent for the DC electroplated coatings. This significant increase in observed porosity can account for the difference in electroplate density observed for DC electroplating when the applied electroplating current density is raised in Figure 5-20.

There is an increase in grain size as the pulse period is lengthened for low nickel and manganese contents (nominally 0%), which could be causing the increase in density observed for these coatings in Section 5-7. A larger grain size could be the result of more compaction of the grains, causing the grains to clump together, giving a higher coating density with a larger grain size. This increase in grain size does not occur at higher values of nickel and manganese content (9% Ni, 5% Mn).
<table>
<thead>
<tr>
<th>Solution</th>
<th>Nickel %</th>
<th>Manganese %</th>
<th>Pulse Period</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>1%</td>
<td>0%</td>
<td>t_c = 0.001 s, t_d = 0.002 s</td>
</tr>
<tr>
<td>6</td>
<td>1%</td>
<td>0%</td>
<td>t_c = 0.002 s, t_d = 0.004 s</td>
</tr>
<tr>
<td>6</td>
<td>9%</td>
<td>5%</td>
<td>t_c = 0.001 s, t_d = 0.002 s</td>
</tr>
<tr>
<td>6</td>
<td>9%</td>
<td>5%</td>
<td>t_c = 0.002 s, t_d = 0.004 s</td>
</tr>
<tr>
<td>6</td>
<td>3%</td>
<td>2%</td>
<td>DC electroplating</td>
</tr>
<tr>
<td>6</td>
<td>10%</td>
<td>6%</td>
<td>DC electroplating</td>
</tr>
</tbody>
</table>

**Figure 5-26** Influence of the type of electroplating used on the morphology of zinc-nickel-manganese coatings, electroplated onto steel using bath configurations 4 and 5.
Production of zinc-nickel-manganese coatings - results and discussion

As the nickel and manganese content of the coating is increased, the refinement in grain structure observed for the shorter pulse period coatings is lost, with the longer pulse period coatings producing a slightly smaller grain size. The corresponding DC electroplated coating shows considerable porosity, with an open grain structure. The actual size of the grains is not changed by increasing the nickel and manganese content of the coating for DC electroplating, whereas it is when a pulse waveform is used. The shorter pulse period leads to an increase in grain size as the nickel and manganese content is raised, whereas the longer pulse period leads to a decrease in grain size. This reduction in grain size as the nickel and manganese content of the coatings is increased (corresponding with an increase in applied electroplating current density, see Section 5-8) may be the cause of the reduction in density of the longer pulse period coatings observed in Section 5-7 as the applied electroplating current density is raised.

5.9.2 Influence of substrate

The way in which the size of the grains changes for the longer pulse period, when electroplating is undertaken over a thin nickel underlayer is illustrated in Figure 5-27. Again, there can be seen to be a decrease in grain size and an increase in porosity with increasing nickel and manganese content within the coating. This increase in porosity of the coatings is the likely cause of the decrease in density observed as the applied electroplating current density is increased in Section 5-7 along with the change in microstructure from large compact grains to smaller, less compact grains.

The grain size of the low nickel, manganese content coating produced onto a nickel underlayer using solution 6 is larger than that observed for a low nickel, manganese coating electroplated directly onto steel in Figure 5-26 (the slight change in measured composition between 1 and 2% nickel could be inside the error of determination of composition as EDAX is only semi-quantitative). The use of nickel underlayer is therefore leading to an increase in observed grain size and hence a slightly more compact coating. However, this is not causing the expected increase in density due to a parallel increase in porosity of the coatings on nickel. This can be seen by comparing the higher nickel, manganese content coatings in Figures 5-26 and 5-27. The shape of the grains is still similar to those observed for electroplating directly onto steel, with an uneven swirly grain shape.
5.9.3 Influence of electrolyte

The use of solution 7 as an electroplating solution has a large influence on the nature of the grain structure and morphology of the coatings. This is shown in Figure 5-28, where two comparable composition coatings produced using the two different solutions, namely solution 6 and solution 7 are compared. Here it can be seen that the uneven nature of the grain shape is lost when solution 7 is used rather than solution 6, with small quite round grains being produced with solution 7. The grain size is comparable with that produced from solution 6, however, there is a large spread in the size of the grains.

The overall morphology of the coating produced from solution 7 is more even and less erratic than that produced from solution 6, although DC rather than pulse electroplating was used. However, the coatings produced using solution 7 were electroplated using bath configuration 3 (selective electroplating). For zinc-nickel electroplated coatings produced from TRIS containing solution 3, there was seen to be a considerable improvement and refinement of the grain structure when bath configuration 3 rather than bath configuration 2 was used. This is illustrated in Figure 4-16. The refinement in the grain structure observed for solution 7 could therefore be due to the influence of the bath configuration.
5.9.4 Influence of electroplating bath configuration

Coatings electroplated using bath configuration 3 and solution 6 are shown in Figure 5-29. Although the same type of electroplating was used as for solution 7 (namely DC electroplating), no improvement in the morphology of the coatings can be seen, with uneven grain shapes still dominating the morphology. The improvement in the morphology of the coatings produced from solution 7 in Figure 5-28, giving more rounded grains, is therefore not due to the nature of the bath configuration used.
5.9.5 The effect of the composition on the morphology

The influence of the nickel and manganese content within the alloy coatings was then investigated. This is illustrated for a change in manganese content in Figure 5-30. Here it can be seen that for solution 7, an increase in the manganese content while keeping the nickel alloy content about the same, leads to a slightly more pronounced grain structure (this is clearer at higher magnification where the coating with 0% manganese becomes hard to resolve but the other coating with 10% manganese does not), but with the same grain shape and size. For solution 6, although there is also a more pronounced grain structure as the manganese content is increased, there is also a significant reduction in grain size, with the higher manganese content coating producing smaller grains.

![Figure 5-30 Influence of manganese content and electroplating solution on the morphology of zinc-nickel-manganese coating](image)
The uneven swirly nature of the grains is also not as apparent as the manganese content is increased. This reduction in grain size as the manganese content is increased for solution 6 is partly the cause of the reduction in density observed in Section 5-7 as the applied electroplating current density and hence manganese content is raised. On examination of Figure 5-20 it can be seen that the use of solution 7 does not cause as large a decrease in density as solution 6. The cause of the decrease in density is hence the change in microstructure to a smaller less compact grain size. Therefore, the use of solution 6 has a large influence on the morphology of the coating produced and the density of the electroplate as the manganese content is increased, whereas the use of solution 7 does not cause such a change in both morphology and density with increased manganese content.

The way in which the morphology of the coatings produced is influenced by the nickel content for both solutions is illustrated in Figure 5-31. Here it can be seen that there is little change in the morphology of the coatings produced from solution 6 when the nickel content is increased, whereas there is a significant change in the morphology of the coatings produced from solution 7 as the nickel content is increased (by a smaller amount than solution 6).

For solution 7 there is an increase in grain size as the nickel content in the coatings is increased. There is also a reduction in porosity as the nickel content is increased. This suggests that the grains are clumping together as the nickel content increases, reducing the porosity and leading to a larger grain size. This improvement in morphology is not apparent for solution 6, although there are some signs of a reduction in porosity with increase in nickel content.
The influence of the two different complexing agents on the electroplating processes occurring within the two different solutions must therefore be very different. The use of solution 6 gives a significant change in morphology when the manganese content is raised, whereas the use of solution 7 gives a significant change in morphology when the nickel content is raised and only a small change in the morphology when the manganese content is changed. This difference in the effect of the complexing agent has already been observed with the grain shape. The change in the grain shape with the different electroplating solutions also suggests that the use of the different complexant is effecting the morphology of the coating. When TRIS is used as a complexant in zinc-nickel electroplating, there is no irregular swirly grain pattern apparent (see Figure 4-25). The production of the swirly irregular shaped grains must therefore be due to the presence of the citrate complexant.
The citrate ion is slightly larger than the TRIS ion (tris (hydroxymethyl)methylamine) and is more reactive hence some of the carbon present in the citrate could be more easily incorporated within a coating and have a detrimental effect on the morphology. The presence of incorporated carbon would lead to irregular deposition of the metal ions causing the swirly irregular pattern seen (the co-deposition of carbon is observed with cyanide electroplating [20]). The adsorption of the complexing agent or its decomposition products can sometimes lead to improved coating properties [31] but can also have a detrimental effect on the coating morphology with some organic compounds being so strongly adsorbed by the deposit that they produce brittle and cracked deposits. This is especially true for higher molecular weight organic complexants such as citrate. As the manganese content is increased more carbon or decomposition product would be incorporated within the coating, as the citrate ion is predominantly complexed with the manganese ion. This increase in co-deposition of part of the complexant would lead to a less compact, less dense structure, and prevent clumping together of the metal ions causing a reduction in both density and grain size. This does not occur to the same extent for the slightly smaller less reactive TRIS ion, hence the morphology of the zinc-nickel-manganese produced from solution 7 stays about the same although the manganese content is increasing. Structures of the citrate and TRIS ions are given in Figure 5-32.

This change in morphology associated with the presence of decomposed citrate ions within the coating does not occur to the same extent for an increase in nickel content as the nickel ions are not associated with citrate to the same level as with manganese. Hence, an increase in nickel content will not lead to a significant increase in incorporated carbon and hence no change in morphology is observed.

Further EDAX or other determination method looking for carbon or other decomposition products would be required to support the hypothesis that citrate ions or their decomposition products are being incorporated whereas the TRIS ions are not.
Figure 5-32 Structures of citrate and TRIS ions

A short summary of the main points from this sub-section is given in Table 5-11.

| Solution 6 | Irregular, swirly shaped grains. Evidence of porosity increasing with nickel and manganese content increase. Increase in manganese content leads to less compact smaller grains causing a reduction in density. Increase in nickel content no decrease in grain size |
| Length of pulse period used | Change in morphology observed. Longer pulse period produced larger, more compact grains at low nickel, manganese contents explaining increase in density observed previously |
| Solution 7 | Round even grains. Morphology not due to type of electroplating bath configuration used. No change in morphology with increase in manganese content. Some change in morphology with increase in nickel content |
| Conclusions | Part of the decomposed citrate ion is being incorporated into the coating causing strange, swirly morphology and a reduction in grain size and density. As manganese content increases more carbon is incorporated |

Table 5-11 Summary of the investigation into the morphology of zinc-nickel-manganese coatings
6 Corrosion of zinc-nickel coatings- results and discussion

6.1 Introduction

The results within this section were all obtained using the experimental techniques detailed in Section 3. A summary of Section 3 is given in Table 3-7.

In order to present the results, the section will be divided into a number of subsections, these will assess the corrosion resistance of the coatings using a variety of techniques, namely neutral salt fog exposure, linear polarisation resistance measurements, potential monitoring with time, galvanic current measurements and double polarisation sweeps thus giving an extensive insight into the coating properties. Micro-hardness, electrical resistance and adhesion will then be evaluated.

A summary of the important points and conclusions from this section will be given at the end. Further discussion on the corrosion and other properties of zinc-nickel will be given in Section 8, where results from the experimental work undertaken in Sections 4-8 will be reviewed. This will give a greater understanding of the properties of binary zinc-nickel and ternary zinc-nickel-manganese coatings, especially in terms of their suitability as replacements for cadmium on electrical connectors and fasteners.

In total five different electroplating solutions were investigated, two without complexants and based on the solution investigated by [52]. The other three solutions all contained the complexant TRIS (see Section 4), with different levels of sodium chloride added in an attempt to improve the throwing power of the solution.

In all, four different substrates were investigated, namely mild steel, 2014-T6 flat aluminium alloy coupons, aluminium alloy connector shells and detached coatings. The detached coatings were produced in order to investigate electrochemical corrosion properties of the zinc-nickel coatings without interference from the attached substrate.
6.2 Neutral salt fog exposure

Neutral salt fog corrosion testing was undertaken according to the method described in Section 3-6-5. For the steel substrates time to 5% red rust was determined along with the amount of white rust present. For the coatings electroplated onto 2014-T6 aluminium alloy coupons and onto aluminium alloy connector shells the coatings were exposed for a pre-determined time, removed, sectioned and polished. The pit depth and distribution was then determined using optical microscopy.

The results of neutral salt fog corrosion testing of the zinc-nickel electroplated coating using a steel substrate, bath configurations 2 and 3 and solution 3 are shown in Figure 6-1. The results of undertaking identical testing on commercial zinc-nickel (10-12% Ni) are also shown and are slightly better but comparable with the best results for the experimental zinc-nickel coatings on steel. The spread of results for the coatings is also shown (duplicate samples). This shows one of the major drawbacks of neutral salt fog testing, namely reproducibility of data with some coatings giving over 100 hours difference in time to 5% red rust for identical nickel contents.

Figure 6-1 Time to 5% red rust for zinc-nickel coated steel, produced using bath configurations 2 and 3 from solution 3 versus nickel content
There is a decrease in time to 5% red rust with increase in nickel content except for the 6% nickel coatings, which showed on average longer times to 5% red rust than any of the other coatings. This is contrary to results reported elsewhere for zinc-nickel coatings on steel [48,52,63,64], tested using neutral salt fog exposure. However, as mentioned in Section 4-7, there is a decrease in density of the electroplate as the applied electroplating current density is increased and the current efficiency decreases. This decrease in density may be causing the reduction in the time to red rust as the applied electroplating current density is increased (nickel content increased). To confirm this the time to red rust for the zinc-nickel coatings on steel were divided by the density of electroplate and plotted against the nickel content. The result is shown in Figure 6-2.

![Figure 6-2 Time to red rust in neutral salt fog testing versus nickel content taking into consideration the density of the coating for single layer zinc-nickel coatings on steel produced using bath configurations 2 and 3 and solution 3](image)

As can be seen from Figure 6-2 when the reducing density of the electroplate is considered there is an increase in the time to red rust for both electroplating bath configurations with increasing nickel content. This is as expected from the literature
There is, however, a large spread of results. This may be due to the average thickness of electroplate being used to calculate the density, without consideration being made of the variation of thickness across the surface.

The coverage of white rust produced by the zinc-nickel coatings on steel after neutral salt fog testing is shown in Figure 6-3. As can be seen there is a decrease in the amount of white rust being produced with increase in nickel content of the alloy. This is as expected as one of the advantages of using zinc-nickel rather than zinc is a reduction in amount of white rust. This reduction is advantageous for use on electrical connector shells. However, there is still a fairly significant amount of white rust present even at 14% nickel. The amount of white rust is reduced for high nickel contents when configuration 3 is used rather than configuration 2. This may be related to the different microstructure of the coatings produced using the different electroplating configurations.

![Figure 6-3 Coverage of white rust after neutral salt fog testing versus nickel content of coating for zinc-nickel electroplated onto steel using bath configurations 2 and 3 and solution 3, single layer coatings](image-url)
Corrosion of zinc-nickel coatings - results and discussion

The effect of different thickness of electroplating on the time to 5% red rust was determined for zinc-nickel coatings produced using bath configuration 3 and solution 3 at two different electroplating current densities. The results are given in Figure 6-4. As the thickness of electroplate increases the time to red rust increases. This is expected, as a thicker coating will take longer to corrode when the coating is acting sacrificially to the substrate. A higher electroplating current density corresponding to a higher nickel content in the alloy gives a slightly longer time to 5% red rust for an equivalent thickness of electroplate. This would support the finding of other research, which shows an improvement in resistance to neutral salt fog exposure as the nickel content of the alloy increases [48,52,63,64].

![Figure 6-4: The effect of thickness of electroplate on time to 5% red rust for zinc-nickel electroplated onto steel using bath configuration 3 and solution 3, single layer coatings](image)

When undertaking neutral salt fog testing on 2014-T6 aluminium alloy substrates, the equivalent of time to red rust for the steel could not be determined. Instead, the coupons or connector shells were exposed to neutral salt fog for a set time. The coupons were then sectioned, mounted and polished, and the number and depth of pits determined using optical microscopy as detailed in Section 3-5-4.
The results of the pit depth analysis for flat 2014-T6 aluminium alloy coupons with single layer zinc-nickel coatings deposited from fresh solution 3 using bath configuration 1 are shown in Figure 6-5. The coupons were exposed for two weeks (336 hours).

![Variation of number and depth of pits for single layer coatings, electroplated onto 2014-T6 aluminium alloy using solution 3 after 2 weeks exposure to neutral salt fog](image)

Each point on the graphs shown in Figure 6-5 was obtained by using the cumulative number of pits i.e. the total number of pits less than for example 70 \( \mu \text{m} \) is equal to the sum of the number of pits between 0 and 70 \( \mu \text{m} \) and not just the number of pits between 60 and 70 \( \mu \text{m} \). The number of pits per mm was calculated to allow for any difference in measurement distance. The slope of the graphs between two data points represents the number of pits within that depth range. The steeper the slope therefore the more pits. On examining Figure 6-5 it can, hence, be seen that initially the number of shallow pits is large (steep slope initially), the slope then becomes less steep, with only a small number of deep pits. The total number of pits per mm can be seen to increase as the nickel content within the alloy increases. This observation holds for 4% nickel to 7% nickel and 10% nickel to 17% nickel. However, it does not for 7%
nickel to 10% nickel, with 7% nickel showing a larger total number of pits than 10% nickel. On looking at the slopes of the graphs, however, it can be seen that 7% nickel has far fewer deep pits. The level of corrosion damage for 10% nickel is therefore greater.

The pit depth analysis for dual layer zinc-nickel coatings produced from solution 3 using bath configuration 1 are given in Figure 6-6 for coupons exposed for one week to neutral salt fog exposure, and in Figures 6-7 and 6-8 for coupons exposed for two and four weeks respectively. Bare 2014-T6 aluminium alloy is also shown for comparison. The compositions shown are the nominal compositions expected for each layer. Again cumulative data is used to plot the graphs, with the number of pits per mm again being calculated as for Figure 6-5.

In Figure 6-6 the number of deep pits observed in all cases is lower than for the single layer coatings in Figure 6-5. However, the length of exposure to neutral salt fog was in these cases less. The total number of pits is also less. The largest total number of pits is obtained for the bare 2014-T6 aluminium alloy. On comparing the 5/10 dual layer coating (corresponding to a nominal layer composition of 5% nickel for the bottom layer and 10% nickel for the top layer) with the 7.5/10 dual layer coating it can be seen that, although the total number of pits is greater for the 5/10 dual layer, the number of deeper pits is slightly reduced.

The 5/14 dual layered coating had less total pits but again slightly more deep pits than the 7.5/10 coating. This trend is again repeated from 5/14 to 7.5/14 coatings with the 7.5/14 dual layered coating having significantly more deep pits. It also had more pits overall. The 10/14 coating, however, had slightly less deep pits but more pits overall than the 7.5/14 coating. The bare 2014-T6 coupons showed the least number of deep pits but the most shallow pits.
From Figure 6-7 it can be seen that the number of deep pits has increased for the dual layers as the length of exposure to neutral salt fog has increased from one to two weeks. This is not the case, however, for the bare 2014-T6 aluminium alloy, which showed no increase in depth or number of pits from one to two weeks exposure. The most significant increases in the number of deep pits were seen for the 7.5/10 and the 5/14 dual layer coatings, with 7.5/10 showing the largest increase in total pits but not in deep pits.
The 10/14 coating showed a decrease in the total number of pits but a very slight increase in the number of deep pits. The 7.5/14 coating showed a slight overall increase in total number of pits, with an increase in the number of medium pits.

On comparing Figures 6-5 and 6-7 the dual and single layer coatings exposed for two weeks neutral salt fog it can be seen that the single layer coatings produced significantly more pits but fewer deep pits at the lower values of nickel content than the dual layers. This may have been due to the use of dual layers or it may have been due to the use of an aged bath to produce the dual layers with an un-aged bath being used for the single layers. This is likely as the morphology of the coatings produced from the aged bath was significantly less porous and contained less surface inclusions than the morphology of the un-aged bath (see Figure 4-13). The porous morphology of the coatings produced from the un-aged bath would lead to more corrosion pits being started if the coatings became non-sacrificial to the substrate. The sacrificial behaviour of the coatings will be investigated further in Section 6-5. Less porosity
would lead to a small number of pits dominating the corrosion process if the coating became non-sacrificial producing a small number of significantly deeper pits. This would indeed seem to be occurring for the dual layer coatings.

The theory that the dual layer coatings corrosion performance in neutral salt fog is being dominated by non-sacrificial coatings, with the porous nature causing a small number of deep pits is further upheld when Figure 6-8, the results of the pit depth analysis after four weeks exposure, is considered. In all cases there is a significant increase in the number of pits. There is also, for most of the dual layer coatings an increase in the number of deep pits. The bare 2014-T6 does not show this increase in deep pits although there is a slight increase in total number of pits.

On examining the shapes of the pits from the zinc-nickel coatings and from the bare 2014-T6 aluminium alloy, it was found that there was a significant difference in morphology. The shapes of the pits produced are represented schematically in Figure 6-9.

![Figure 6-8 Depth and number of pits after 4 weeks neutral salt fog exposure for dual layer coatings on 2014-T6 aluminium alloy coupons electroplated from solution 3 using bath configuration 1]
The bare 2014-T6 aluminium produced shallow flat pits with rounded bottoms, whereas the zinc-nickel coatings produced sharper, narrow pits, which spread as the coating was penetrated. The difference in pit shape is due to the different corrosion mechanisms involved, with the zinc-nickel coatings producing increased corrosion at the base of the pits as the substrate is exposed due possibly to the coatings becoming non-sacrificial to the substrate. The bare 2014-T6 does not suffer from non-sacrificial coatings, but contains inter-metallics, which cause anodic and cathodic areas on the surface leading to wide shallow pits.

The results of the pit depth and number analysis of sectioned, electroplated aluminium alloy connector shells are given in Figure 6-10 taken after four weeks neutral salt fog exposure. There are fewer deep pits present than for the zinc-nickel coatings on flat 2014-T6 aluminium coupons. This may be a result of the different geometry affecting the corrosion within the neutral salt fog test cabinet, with the rounded geometry of the connector shells leading to better run off of the salt fog causing less deep pitting.

The actual number of pits is similar to those observed in Figure 6-5 for single layer electroplated flat 2014-T6 substrates. Both the 11% and 15% nickel electroplated connector shells show an increase in level and depth of pitting when compared to the
2% and 20% nickel connector shells. This could again be related to the morphology rather than the nickel content, with both 11 and 15% nickel showing a strongly three-dimensional porous morphology (see Figure 4-20). The dual layer coating produced slightly less pitting than that observed for the 15% nickel content single layer electroplated onto connector shells. The dual layer coating did not show the strongly three dimensional morphology exhibited by this coating (see Figure 4-21) again suggesting the reason for the increase in the number and depth of pits for the 11 and 15% nickel coatings is the morphology.

![Graphs showing depth and number of pits for electroplated aluminium alloy connector shells exposed for 4 weeks to neutral salt fog. Zinc-nickel coatings produced using solution 3 and bath configuration 2.]

Commercially electroplated cadmium connector shells showed significantly less pitting after four weeks neutral salt fog than the single and dual zinc-nickel coatings. The cadmium electroplated also showed significantly less white rust and corrosion products than all the zinc-nickel coatings tested.

A summary of the results from this sub-section is given in Table 6-1.
Corrosion of zinc-nickel coatings - results and discussion

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Effect of Zn-Ni coating</th>
</tr>
</thead>
<tbody>
<tr>
<td>Steel</td>
<td>Because there is a decrease in density as the nickel content increases there is a decrease in time to 5% red rust as the nickel content increases</td>
</tr>
<tr>
<td>2014-T6 aluminium alloy coupon</td>
<td>For single layers the amount and depth of pits increases as the nickel content increases. The dual layers show fewer pits but have a larger percentage of deeper pits. Bare 2014-T6 aluminium alloy shows very different shaped pits and significantly fewer deep pits. The depth of pits suggests that the coatings may be becoming non-sacrificial with time of neutral salt fog exposure, causing the porosity to effect the corrosion resistance and the corrosion resistance to decrease as the nickel content increases.</td>
</tr>
<tr>
<td>Aluminium alloy connector shells</td>
<td>About the same number of pits as single layers on 2014-T6 aluminium alloy coupons, but slightly less due to different geometry in neutral salt fog. 11 and 15% nickel have more pits due to different morphology. All zinc-nickel coatings have significantly more white rust and pits than cadmium electroplated connector shells</td>
</tr>
</tbody>
</table>

Table 6-1 Summary of neutral salt fog corrosion results

6.3 Variation of potential with time

To further investigate the possibility of the zinc-nickel coatings becoming non-sacrificial with respect to the substrate, potential monitoring over time in 3.5% sodium chloride solution was undertaken. Potential monitoring was carried out as in Section 3-6-1, and Figure 3-5, on single and dual layer coatings electroplated onto both steel and 2014-T6 aluminium alloy coupons. Potential monitoring of detached coatings was also undertaken. In hindsight in order to draw firm conclusions from the potential data it would have been advisable to undertake duplicate testing.

The results obtained for zinc-nickel single coatings on steel are given in Figure 6-11. Here it can be seen that the potential initially ranges from -1.0 to -1.1 V; it then becomes more noble with immersion time, obtaining a consistent value after about 500 hours immersion of about -0.65 to -0.7 V with respect to SCE. The level of nickel within the alloy affects the rate of ennoblement, with the lower percentages nickel showing a slower rate of ennoblement. This is consistent for both electroplating bath configurations.
The results of the potential monitoring of dual layer coatings electroplated onto steel from solution 3 using bath configurations 2 and 3 are shown in Figure 6-12. Again, the initial potential is similar to that obtained for the single layer coatings, being between \(-1.0\) and \(-1.1\) V with respect to a SCE. Again, ennoblement of the coating occurs on immersion in 3.5% sodium chloride, with a stable potential of \(-0.65\) to \(-0.7\) V being obtained after about 400 to 600 hours immersion.

However, unlike the single layers there is a difference in the performance of the coatings produced using the two different bath configurations, namely configuration 2 and 3, corresponding to tank and brush electroplating. The dual layer coatings produced using bath configuration 2 show similar shaped curves to those obtained for the single layer coatings, with an initial rapid ennoblement of the alloy dependant on composition (the ennoblement is most rapid for the highest nickel content). The coatings produced using bath configuration 3 (brush or selective electroplating), show a smaller initial rapid ennoblement, the rate of ennoblement then slows down, reaching a stable potential after a longer time of immersion than the coatings produced using bath configuration 2. This may be related to the less porous nature of
the dual layer coatings produced using bath configuration 3 and will be investigated further in the sub-section on galvanic properties of the coatings.

Figure 6-12 Potential versus time for dual layer coatings on steel electroplated using solution 3, bath configurations 2 and 3 in 3.5% sodium chloride solution

Figure 6-13 shows the results of potential monitoring with time of zinc-nickel coatings produced onto 2014-T6 aluminium alloy coupons using solution 3 and bath configuration 1. Like the zinc-nickel coatings on steel an ennoblement of the alloy is observed with immersion time. There is again a difference in the rate of ennoblement depending on the nickel content, with the lower nickel content coatings not becoming noble as quickly as the high nickel content coatings. The difference in the rate of ennoblement between the lower nickel content coatings and the higher nickel content coatings is larger than for the coatings electroplated onto steel, with the lower nickel content coatings giving a longer time to reach a stable more noble potential. The final potential of the coatings is similar to those produced on steel being about -0.65 to -0.75 V with respect to SCE. The rate of ennoblement of the coatings in potential monitoring with time can be related to the number of deep pits obtained for the zinc-nickel coatings on 2014-T6 aluminium alloy. This can be seen on comparing Figure 6-5, which shows the level of pitting for single layer coatings with Figure 6-13. The number of deep pits in Figure 6-5 is greater for the 10 and 17% nickel coatings. From
Figure 6-13 it can be seen that the rate of ennoblement of these coatings with time of immersion is faster than for the lower nickel content coatings. This observation supports the suggestion that the deep pits observed on undertaking neutral salt fog testing are due to ennoblement of the coating, causing the coating to become non-sacrificial, which then leads to the formation of deep pits. The more rapid the ennoblement the deeper the pits.

![Graph showing potential versus time for 2014-T6 electroplated aluminium alloy coupons electroplated from solution 3 using bath configuration 1, single layer coatings in 3.5% sodium chloride solution.](image)

The results of potential monitoring with time for the dual layer coatings electroplated onto 2014-T6 aluminium alloy using solution 3 are given in Figure 6-14. Again, ennoblement of the coatings is seen to occur. The rate of ennoblement of the alloy is related to the nickel content of the coating with the dual layer coatings with nominally 10% nickel in their top layer having very similar potential curves. The 5/14% nickel coating on the other hand shows more rapid ennoblement, similar to that seen for the high nickel content single layer coatings. Again the rate of ennoblement of the coating can be related to the number of deep pits observed on neutral salt fog exposure. This
can be seen by comparing Figures 6-8 and 6-14, where the coating which suffered the highest rate of ennoblement (5/14% nickel) can be seen to have the largest number of deep pits. This again supports the theory that the deep pits are related to the sacrificial behaviour of the coating.

![Graph showing potential versus time for dual layer coatings, electroplated from solution 3 using bath configuration 1 in 3.5% sodium chloride solution.]

Figure 6-14 Potential versus time for dual layer coatings, electroplated from solution 3 using bath configuration 1 in 3.5% sodium chloride solution

The effect of the thickness of the electroplate is investigated in Figure 6-15, where the results of the potential monitoring of zinc-nickel coatings produced onto steel using solution 3, bath configuration 3 and different applied electroplating charges are shown. The smaller the total applied electroplating charge the thinner the coating.

As can be seen the thin coatings show an increase in the rate of ennoblement with immersion in 3.5% sodium chloride. An increase in the nickel content of the thicker coatings also leads to an increase in the rate of ennoblement. The initial and final stable potentials obtained for the different thickness coatings are similar to those seen previously in Figures 6-11, 6-12, 6-13 and 6-14. The time taken to reach a stable potential is longer for the thick coatings (90 C of applied charge corresponding to a
Corrosion of zinc-nickel coatings - results and discussion

thickness of about 20 μm), being about 800 hours. The time taken to reach a stable potential for the thin coatings (15 C applied electroplating charge corresponding to a thickness of about 4 μm) is less than 200 hours. This is less than the time taken to reach a stable potential for approximately 10 μm coatings on steel in Figure 6-11 of about 400 hours. The rate of reaching a stable potential is therefore related to the thickness of electroplate. This is as expected because the rate of ennoblement of the coating should be related to the amount of zinc-nickel coating present as well as to the nickel content. Initially, a sacrificial coating with corrode uniformly until a point when it becomes non-sacrificial (if de-zincification is occurring). Non-uniform corrosion or pitting will then result. This initial uniform corrosion is related both to the nickel content, which controls the initial corrosion rate and to the thickness of the coating, which controls the time taken for the coating to be all removed.

![Figure 6-15 Potential versus time for coatings of different thickness (electroplated for different amounts of applied charge), electroplated onto steel using solution 3 and bath configuration 3](image)

Also the thinner the coating the higher the possibility of any through thickness porosity being present. This increase in porosity would help to cause an increase in the ennoblement rate if the increase in porosity was leading to an increase in the number of cathodic sites. This would increase the rate of the rate determining cathodic
Corrosion of zinc-nickel coatings - results and discussion

oxygen reaction (equation 2-7) and hence increase the corrosion rate causing an increase in the rate of ennoblement.

The results of potential monitoring with immersion time in 3.5% sodium chloride for detached coatings of zinc-nickel are given in Figure 6-16. As can be seen there is no significant ennoblement with immersion time for the detached coatings. This is not similar to the results obtained for the zinc-nickel coatings on steel or on 2014-T6 aluminium alloy.

There is, however, a slight ennoblement over the test period, with the 5% nickel coating having changed in potential from about –1.05 volts to about –1.02 volts over a time period of 1300 hours. This shows there is some ennoblement with time caused by de-zincification of the zinc-nickel coating. In general the higher the nickel content the more noble the potential of the coating (the 11% and 12% coatings are approximately the same composition as EDAX is only a semi-quantitative technique). This is expected as nickel is more noble than zinc and would hence give a higher potential if present in larger amounts.

The cause of the rapid ennoblement of the zinc-nickel coatings on both steel and 2014-T6 aluminium must therefore be the presence of the substrates. The substrate would only affect the potential seen if there was through thickness porosity (or enough porosity to lead to substantially thinner areas of coating) present. This has indeed been observed for these coatings (see Section 4-7). The porosity must therefore also be affecting the rate of the corrosion causing increased ennoblement in a shorter time. This would only occur for a sacrificial coating if the rate determining cathodic reaction on the substrate was increasing, hence, increasing the anodic corrosion reaction of the coating causing accelerated ennoblement. This will be investigated further in the following sub-sections, on polarisation, linear polarisation resistance and galvanic compatibility. The fact that the lack of substrate or nature of substrate affects the rate of ennoblement explains the differences observed in the ennoblement rate for the steel and aluminium alloy substrates.
Corrosion of zinc-nickel coatings - results and discussion

The change in the rate of the cathodic reaction which causes the increase in rate of ennoblement of the coating is related to the amount of through thickness porosity, and would explain the difference between the two different bath configuration ennoblement rates observed in Figure 6-12. As seen previously (sub-section 4-7), the morphology of the coatings produced using the different bath configurations is significantly different, with bath configuration 3 (brush electroplating) producing significantly less porous coatings, explaining the reduction in the rate of ennoblement of the dual layer coatings produced using bath configuration 3 in Figure 6-12.

A summary of the important observations from this sub-section on potential monitoring is given in Table 6-2.

Figure 6-16 Potential versus time for detached, electroplated using solution 3 and bath configuration 2 coatings in 3.5% sodium chloride solution
Corrosion of zinc-nickel coatings - results and discussion

<table>
<thead>
<tr>
<th>Observation</th>
<th>Significance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rate of ennoblement dependent on nickel content, increases with increase in nickel content</td>
<td>Possibly causing the coating to become non-sacrificial with exposure time leading to an increase in pitting levels with increase in nickel content</td>
</tr>
<tr>
<td>Number of deep pits related to the rate of ennoblement</td>
<td>Coating is becoming non-sacrificial</td>
</tr>
<tr>
<td>Rate of rapid ennoblement dependant on substrate, does not occur for detached coatings</td>
<td>Presence of substrate is causing an increase in the rate determining cathodic reaction due to presence of porosity, this increase is dependent on the nature of the substrate and the amount of porosity present</td>
</tr>
<tr>
<td>For dual layers on steel the rate of ennoblement is dependent on the bath configuration used</td>
<td>The bath configuration used determines the level of porosity and morphology. Hence an increase in porosity leads to acceleration of ennoblement, due to acceleration of cathodic rate determining reaction</td>
</tr>
<tr>
<td>Rate of ennoblement dependant on thickness of coating</td>
<td>Coating is initially sacrificial. Reaction rate governed by amount of zinc-nickel coating present i.e. proximity of the substrate. Also thinner coatings have increased through coating porosity</td>
</tr>
</tbody>
</table>

Table 6-2 Summary of observations obtained from potential monitoring with time in 3.5% sodium chloride solution and their possible significance

6.4 Linear Polarisation Resistance (LPR)

Linear polarisation resistance measurements were undertaken in accordance with Section 3-6-6. The cell configuration in Figure 3-4 was used. By carrying out linear polarisation resistance measurements it was hoped to gain more information about the corrosion current present for the coatings on various substrates, to clarify the role of the substrate, the role that the nickel content has in the corrosion behaviour and the role of any porosity present. Zinc-nickel coatings electroplated onto steel and 2014-T6 aluminium alloy as well as detached coatings were investigated.

The results of the $E_{corr}$ measurements obtained from undertaking linear polarisation tests are given in Figure 6-17. As can be seen the value of $E_{corr}$ becomes more noble as the nickel content of the alloy increases. This would support the finding of the potential monitoring of detached coatings shown in Figure 6-16. The trend-lines for the data have similar slopes apart from the data obtained for the coatings produced using bath configuration 3, brush electroplating. The morphology of the brush electroplated coatings was significantly different from the morphology of the other coatings. This would suggest that the morphology as well as the nickel content has an effect on the instantaneous $E_{corr}$ value obtained. A difference in the potential
behaviour was seen previously for the coatings produced using bath configuration 3, when the change in potential with time was investigated. It is not therefore surprising that the different morphology also affects the instantaneous potential as well as the long term potential behaviour. The difference in the slope is, however, only small, so the morphology difference does not have such a large effect on the instantaneous potential as it has on the longer term potential behaviour.

![Graph showing Ecorr vs nickel content](image)

**Figure 6-17** Value of $E_{corr}$ obtained from linear polarisation resistance measurements versus nickel content of coating for zinc-nickel coatings electroplated onto steel, 2014-T6 aluminium alloy and detached coatings, using solution 3

Figure 6-18 shows the way in which $I_{corr}$, as measured using linear polarisation resistance, changes with nickel content for coatings electroplated onto steel using bath configurations 2 and 3. Here there is a more significant difference in the results obtained using the two different electroplating bath configurations.

The coatings electroplated using normal tank electroplating (bath configuration 2) show an increase in $I_{corr}$ value as the nickel content is increased. The $I_{corr}$ values obtained for these coatings are also significantly higher than those obtained using bath configuration 3 (brush electroplating). The morphology of the coatings could again be
the cause of this difference in $I_{\text{corr}}$ values obtained. The coatings electroplated using bath configuration 2 are known to increase in porosity as the nickel content increases. This increase in porosity is known to affect the time to red rust in neutral salt fog testing and also the rate of ennoblement of the coatings in potential time monitoring tests. The fact that porosity is the cause of the change in $I_{\text{corr}}$ seen in Figure 6-18 accounts for the level of scatter obtained. Any porous (or thinner) areas will dominate the $I_{\text{corr}}$ result leading to considerable scatter as the nickel content increases and the level of porosity increases. For each coating composition two different areas on each sample were measured. If inconsistent results were obtained, a further sample of the same composition was used to undertake repeat measurements. This increases the appearance of scatter in Figure 6-18 as all results are shown.

An increase in corrosion current would lead to an increase in corrosion reaction and hence an increased rate of ennoblement of the alloy in potential time monitoring. Hence, although the corrosion rate of zinc-nickel is supposed to decrease with increasing nickel content [66], in these cases this is not occurring due to the presence of significant porosity. The porosity is causing an increase in the rate determining cathodic reaction, which then leads to an increase in the value of $I_{\text{corr}}$, causing an increase in the rate of ennoblement (see Section 6-3). This perhaps causes the coating to become non-sacrificial, causing the substrate to corrode, hence leading to the formation of red rust in neutral salt fog testing (see Section 6-2).

The coatings electroplated using bath configuration 3 (brush electroplating), do not show as marked an increase in porosity with increase in nickel content. The level of porosity is also lower than the coatings produced onto steel using bath configuration 2. The value of $I_{\text{corr}}$ measured is therefore lower for all nickel contents and there is less scatter. It also does not increase in the same way as the nickel content increases as the cathodic rate determining reaction is not increased due to significantly more porosity being present (this also reduces the level of scatter for configuration 3). This leads to a reduction in the rate of ennoblement of the alloy in potential monitoring with time (see Section 6-3 Figure 6-12).
Results of linear polarisation resistance measurements of $I_{\text{corr}}$ on coatings produced on 2014-T6 aluminium alloy coupons and on detached zinc-nickel coatings are given in Figure 6-19. For the coatings electroplated onto 2014-T6 aluminium alloy, the value of $I_{\text{corr}}$ increases as the nickel content increases. This is the same as for the coatings electroplated onto steel using bath configuration 3 in Figure 6-18. However, the value of $I_{\text{corr}}$ is lower for a given nickel content. This would agree with the results of the potential time monitoring, which showed the coatings produced on 2014-T6 to have a reduction in the rate of ennoblement especially at low nickel contents. The reduction in $I_{\text{corr}}$ values obtained would lead to a reduction in the corrosion rate and hence a reduction in the rate of ennoblement observed in potential time monitoring. There is still, however, an increase in $I_{\text{corr}}$ value with increase in nickel content. Again this is due to the increase in porosity observed for the coatings on 2014-T6 aluminium alloy (see Section 4-7). The increase in porosity again leads to an increase in the rate determining cathodic reaction, and hence an increase in the $I_{\text{corr}}$ values. It would also
explain the increase in deep pits as the nickel content increases observed on neutral salt fog testing in Section 6-2, and the more rapid ennoblement at higher nickel contents observed when the potential was monitored. The lower values of $I_{\text{corr}}$ obtained for the coatings on 2014-T6 aluminium alloy are due to the different nature of the substrate, perhaps not providing as large a driving force for the corrosion reaction. This will be investigated further in the Section on galvanic compatibility.

![Graph showing corrosion current density values](image)

**Figure 6-19** Corrosion current density values obtained using linear polarisation resistance measurements versus nickel content for coatings electroplated onto 2014-T6 aluminium coupons and for detached coatings, all produced from solution 3

From Figure 6-19 it can also be seen that there is an increase in the $I_{\text{corr}}$ values for detached coatings with increase in nickel content. This is contrary to the results obtained for potential time monitoring, which showed no increase in ennoblement rate with increase in nickel content, and showed the substrate effect to be dominating the ennoblement and increase in $I_{\text{corr}}$ with nickel content observed.

Although there is no substrate present when testing the detached coatings, there is still signs of an increase in porosity as the nickel content of the detached coatings is increased (see Figures 4-24). This increase in porosity may be causing the increase in
$I_{corr}$ observed, especially if the sample configuration in Figure 3-4 is considered, along with the sample preparation for detached coatings used. Electrical contact for the detached coatings was made to the back of the detached coating using silver loaded epoxy. If any of the porosity present in the detached coatings went through the coating thickness, the use of silver loaded epoxy would then become significant. This would cause the contact area to act in the same manner as the substrates used for the other coatings, leading to an increase in cathodic reaction rate as the nickel content increases and hence a rise in $I_{corr}$. The use of an o-ring on a brittle detached coating to maintain a water tight seal (see Figure 3-4), would compound the problem, making it more likely that the silver loaded epoxy would affect the results of the polarisation resistance measurements, but not affect the results of the potential time monitoring to the same extent. A different means of attaching the contact to the sample would be needed to overcome this, and check that this was not adversely affecting the results obtained.

A summary of the results obtained from this sub-section on linear polarisation measurements is given in Table 6-3.

<table>
<thead>
<tr>
<th>Observation</th>
<th>Significance</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_{corr}$ becomes more noble as nickel content increases. There is a different slope for steel substrates electroplated using bath configuration 3</td>
<td>Nickel content related to $E_{corr}$, due to noble nature of nickel [202]. Morphology also affects $E_{corr}$ due to presence of substrate and porosity of the coating</td>
</tr>
<tr>
<td>$I_{corr}$ increases as the nickel content increases. Not in the case of steel substrates electroplated using bath configuration 3</td>
<td>Due to increase in porosity as nickel content increases, causing an increase in the rate determining cathodic reaction. Steel samples electroplated using bath configuration 3 do not show as large an increase in porosity, hence no increase in $I_{corr}$. Increase in $I_{corr}$ due to increase in porosity could explain the potential time results and the neutral salt fog results</td>
</tr>
</tbody>
</table>

Table 6-3 Summary of linear polarisation results

6.5 Galvanic compatibility

Galvanic compatibility tests were undertaken as in Section 3-6-2. The cell configuration used is given in Figure 3-6. The reasons for carrying out galvanic tests were to find out if the coatings were becoming non-sacrificial with respect to the
substrates with time of immersion, and to obtain an indication of the magnitude of the
current involved. By obtaining this information, the role that the substrate plays in the
corrosion mechanism can be further investigated, as well as the role of the coating.

The results obtained for detached zinc-nickel coatings coupled to 2014-T6 aluminium
alloy are given in Figures 6-20 and 6-21. Figure 6-20 shows the actual current
measurements and shows whether the coating is becoming non-sacrificial (negative
current readings show non-sacrificial behaviour). Figure 6-21 shows the calculated
total charge passed with time. This gives an indication of the magnitude of the
corrosion reaction.

![Figure 6-20 Galvanic corrosion current density](image)

*Figure 6-20 Galvanic corrosion current density (using a nominal area of 1 cm² as shown in Figure 3-6) measurements for detached coatings, immersed in 3.5% sodium chloride solution and coupled to 2014-T6 aluminium alloy over time*

From Figure 6-20 it can be seen that the detached coatings remain predominately
sacrificial to 2014-T6 aluminium. The highest nickel content coating shows a small
area of non-sacrificial behaviour after about 270 hours immersion. The coating then
becomes sacrificial again for the duration of the test. The way in which the corrosion
Corrosion of zinc-nickel coatings - results and discussion

Current changes with time for the three different nickel content detached coatings is very different and can be seen more clearly in Figure 6-21, which shows the total charge passed.

From Figure 6-21 it can be seen that initially the 5% nickel detached coating corrodes at a steady rate, the slope of the graph then becomes flatter indicating that the coating is becoming more passive. The 11% nickel coating starts with a flatter slope indicating initial passive behaviour after a small portion of active behaviour lasting for about 50 hours. The coating then becomes non-passive and corrodes at a faster rate than the 5% nickel coating (indicated by a large increase in the slope after 300 hours immersion). Toward the end of the test time the steepness of the slope for 11% nickel reduces indicating a partial return to more passive behaviour.

![Graph showing total charge passed over time for detached zinc-nickel coatings immersed in 3.5% sodium chloride solution and coupled to 2014-T6 aluminium alloy](image)

Figure 6-21 Total charge passed over time for detached zinc-nickel coatings immersed in 3.5% sodium chloride solution and coupled to 2014-T6 aluminium alloy

The 12% nickel detached coating on the other hand is initially active for a longer period than the 11% nickel and with a greater degree of activity, then becomes
slightly more passive. The slope of the graph then increases again indicating a return to non-passive behaviour. This return to non-passive behaviour occurs after the coating became non-sacrificial towards the 2014-T6 aluminium (see Figure 6-20).

EDAX is not the most accurate composition determination method, hence both the 11% and 12% nickel coatings could have essentially identical compositions. However, the 12% nickel coating was produced using a higher electroplating current density, which lead to a greater degree of porosity (see Figure 4-24). This rather than the compositional differences may be the cause of the change in galvanic behaviour observed.

Proposed mechanisms to explain the different corrosion behaviour of the detached coatings when coupled to 2014-T6 aluminium alloy are given in Figures 6-22, 6-23 and 6-24.

Low nickel (5%)

As can be seen from Figures 6-22, 6-23 and 6-24, the way in which the zinc-nickel corrodes when coupled to 2014-T6 aluminium is very dependent on the nature of the passive film, which forms. In all cases there will be some corrosion of the cathodic
(2014-T6) part of the couple due to alkaline induced corrosion but this is likely to be similar for all nickel contents and would only serve to reduce the value of current observed by about the same factor and has hence been excluded from the schematics for clarity. With the low nickel content alloy (low porosity) the passive film does not block the corrosion process as much as the medium nickel content alloy. This prevents one large anode site from dominating the corrosion process and prevents the removal of the passive film.

Medium nickel (11%)

![Diagram](image)

**Figure 6-23 Proposed mechanism for medium nickel content galvanic corrosion**
The medium nickel content process is more completely blocked except at anodic areas of activity, allowing corrosion to spread under the passive film causing the passive film to become detached from the alloy leading to a sudden increase in corrosion current. This increase in the level of passivation is likely to be caused by the increase in the nickel content of the alloy.

High nickel content (12%) or more porous film

![Diagram](image_url)

*Figure 6-24 Proposed corrosion mechanism for high nickel content zinc-nickel when coupled to 2014-T6 aluminium alloy*
With the high nickel content alloy the level of passivation is much lower. This may be due to the increase in porosity of this coating (see Section 4-7). The increase in porosity will allow a larger area of zinc-nickel to be exposed leading to a greater corrosion current, even although the nickel content has increased slightly. This increase in corrosion current causes accelerated de-zincification of the non-passivated region. This then means that the zinc-nickel becomes cathodic, causing the 2014-T6 aluminium to corrode and form an oxide layer. The oxide layer will be incomplete due to the presence of alloying elements within the 2014-T6 aluminium, but will be sufficient to change the potential of the 2014-T6, making it more noble and allowing the zinc-nickel to again become the anode.

The results of the galvanic current measurements on zinc-nickel coatings electroplated on 2014-T6 aluminium and coupled to 2014-T6 aluminium are shown in Figure 6-25. The total current passed with time for coatings produced on 2014-T6 aluminium and coupled to 2014-T6 aluminium is shown in Figure 6-26.

![Figure 6-25 Current density measurements for zinc-nickel coatings electroplated onto 2014-T6 aluminium alloy, immersed in 3.5% sodium chloride solution and coupled to 2014-T6 aluminium, produced from solution 3 using bath configuration 1](image)
From Figure 6-25 it can be seen that the low nickel content (3% single layer) remains sacrificial throughout the test. The 14% nickel single layer coating, however, becomes non-sacrificial after about 500 hours immersion. The dual layer coatings also all become non-sacrificial with immersion, with the lowest nickel content dual layers becoming non-sacrificial after a longer time than the higher nickel content dual layers. The 10/14% nickel dual layer has the shortest time to non-sacrificial behaviour being about 220 hours immersion.

The way in which the coatings electroplated onto 2014-T6 aluminium corrode is very similar up to the point of non-sacrificial behaviour. This can be seen by comparing the slopes of the curves in Figure 6-26. Initially the corrosion rate (rate of increase in charge) increases. The rate then decreases as the surface of the coating becomes more passive. This passivity is accompanied by de-zincification of the active areas of coating, leading to a rise in potential of the surface, eventually causing the zinc-nickel to become non-sacrificial.

After the coatings becomes non-sacrificial the slope of the charge passed changes and the system becomes more active. This is caused by corrosion of the 2014-T6 aluminium part of the couple rather than the zinc-nickel. The formation of an oxide layer, changing the potential of the 2014-T6 part of the couple does not occur to the same extent as for the detached coatings. There is some evidence of oxide or corrosion product formation in Figure 6-25 where the corrosion current can be seen to fluctuate around zero for a period of time.
The difference in the behaviour of the 2014-T6 part of the couple after non-sacrificial behaviour is established is due to the presence of 2014-T6 aluminium under the zinc-nickel coating. This 2014-T6 electrode cannot passivate. The presence of porosity within the coating also increases the actual surface area of zinc-nickel coating exposed to the solution. This increases the cathodic rate determining reaction, hence preventing passivation of the 2014-T6 aluminium alloy part of the galvanic couple.

The increase in the corrosion of the 2014-T6 aluminium alloy after non-sacrificial behaviour is established is the reason for the formation of deep pits in neutral salt fog testing (see Section 6-2). The level of pitting will be reduced if sacrificial behaviour has been maintained for longer as in the case of the lower nickel content coatings. This was indeed found to be the case.

The corrosion behaviour of zinc-nickel dual layer coatings electroplated onto 2014-T6 aluminium and coupled to cadmium electroplate on steel is shown in Figures 6-27 and 6-28. The galvanic compatibility of zinc-nickel with cadmium electroplate was
investigated because the likelihood of zinc-nickel being coupled to cadmium in an airspace environment is high, especially if zinc-nickel is used as a replacement for cadmium on electrical connectors.

Firstly, from Figure 6-27 it can be seen that by coupling to cadmium electroplate the time to non-sacrificial behaviour has been significantly reduced in most cases. The initial corrosion rate of the zinc-nickel coatings can also be seen to be greater than when coupled to 2014-T6 aluminium. Also from Figures 6-26 and 6-28 it can be seen that the zinc-nickel coatings are not passivating prior to becoming non-sacrificial when coupled to cadmium. De-zincification of the zinc-nickel coatings is therefore continuing at a faster rate over the whole zinc-nickel surface (a larger surface available for active corrosion). This reduces the time to non-sacrificial behaviour.

After non-sacrificial behaviour has occurred there is a difference in the way in which the cadmium corrodes. Instead of the corrosion rate increasing after non-sacrificial behaviour is reached a reduction in the corrosion rate can be seen. This may be due to the passive nature of cadmium, or perhaps due to the low corrosion rate typically
Corrosion of zinc-nickel coatings - results and discussion

exhibited by cadmium electroplate. In some cases (mainly 5/14% Ni) the corrosion rate of the cadmium then increases, leading to an increasing straight line portion on the curve in Figure 6-28, corresponding to general constant corrosion of the cadmium electroplate.

There is no evidence that the porosity is increasing the corrosion after the coating becomes non-sacrificial suggesting that it is the way in which the cadmium electroplate corrodes which is governing the response observed. In fact, the increase in porosity of the 10/14% Ni dual layer may in fact be increasing the time to non-sacrificial behaviour by increasing the surface area of zinc-nickel exposed and hence reducing the impact of de-zincification.

![Graph showing total charge passed with time for dual layer zinc-nickel coatings, electroplated onto 2014-T6 aluminium, immersed in 3.5% sodium chloride solution and coupled to cadmium electroplated onto steel.]

The results of galvanic measurements undertaken on zinc-nickel coatings electroplated onto steel and coupled to 2014-T6 aluminium are shown in Figures 6-29 and 6-30. Commercial zinc-nickel electroplate on steel was also tested to give an indication of the difference between the experimental zinc-nickel coating produced in this work and what is commercially available.
From Figure 6-29 it can be seen that the presence of a steel substrate causes accelerated de-zincification of the coating leading to significantly shorter times to non-sacrificial behaviour. Even the commercial zinc-nickel coating suffers from this accelerated de-zincification. However, the time to non-sacrificial behaviour of the commercial coating is still longer than the time for the 9% nickel coating to become non-sacrificial. Although the time to non-sacrificial behaviour is considerably reduced there is no corresponding increase in initial current. This is because although the steel is influencing the rate of anodic reaction it is present on the anodic rather than the cathodic side of the couple, hence any increase in the cathodic current due to the presence of steel will offset the anodic reaction of zinc-nickel and not be seen in the measurement.

Figure 6-29 Current density measurements of zinc-nickel coatings, electroplated onto steel from solution 3, immersed in 3.5% sodium chloride and coupled to 2014-T6 aluminium alloy

From Figure 6-29 it can also be seen that the commercial zinc-nickel coating fluctuates around zero current for a while. This shows evidence of the 2014-T6
aluminium part of the couple fluctuating in potential in much the same way as the detached coating with 12% nickel did when coupled to 2014-T6 aluminium.

![Graph showing total charge passed with time for zinc-nickel coatings electroplated onto steel from solution 3, immersed in 3.5% sodium chloride solution and coupled to 2014-T6 aluminium alloy.](image)

Figure 6-30 Total charge passed with time for zinc-nickel coatings electroplated onto steel from solution 3, immersed in 3.5% sodium chloride solution and coupled to 2014-T6 aluminium alloy

From Figure 6-30 it can also be seen that the way in which the 2014-T6 aluminium corrodes after non-sacrificial behaviour is reached is very different from the coatings on 2014-T6 aluminium. Instead of the 2014-T6 staying passive, there is a small passive area in some cases followed by steady accelerated corrosion. The presence of steel must therefore be disrupting the oxide formed on the 2014-T6 surface. This may be due to some corrosion of the steel occurring prior to that part of the couple becoming non-sacrificial. This would lead to the presence of Fe ions in the solution, which will help to remove any oxide layer from the 2014-T6 aluminium surface as Fe is used to accelerate the oxide layer removal when used as part of a pre-treatment etch for aluminium alloys [203]. In fact after testing there were considerable signs of red rust on the zinc-nickel coatings suggesting that indeed the steel substrate had corroded.
The increase in the length of the passive region at the point of change from sacrificial to non-sacrificial behaviour of the commercial zinc-nickel coating helps support this. The commercial zinc-nickel is not as porous as the zinc-nickel produced using solution 3, hence not as many Fe ions will dissolve into solution, allowing the 2014-T6 to form a more stable incomplete oxide layer hence increasing the length of the less active region.

Results of galvanic couple experiments on dual layer zinc-nickel coatings electroplated onto steel and coupled to 2014-T6 aluminium are shown in Figures 6-31 and 6-32. Again, the accelerated de-zincification observed for the single layer coatings can be seen with times to non-sacrificial behaviour similar to the single layer coatings. The amount of nickel in the alloy again effects the time to non-sacrificial behaviour with the higher nickel content dual layer producing the shortest time to non-sacrificial behaviour.

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![Graph](image-url)

*Figure 6-31 Current density measurements for dual layer zinc-nickel coatings electroplated onto steel, immersed in 3.5% sodium chloride solution and coupled to 2014-T6 aluminium alloy*
From Figure 6-32 it can also be observed that the increased corrosion of the 2014-T6 portion of the couple seen for single layer coatings again occurs. There was also evidence of red rust on the zinc-nickel samples after testing. The current passed prior to reaching non-sacrificial behaviour is lowest for the dual layer coating, which becomes non-sacrificial first. This supports the theory outlined previously that the presence of the increased cathodic reaction on the steel part of the anodic couple is offsetting the anodic current leading to a lower measured current. The 5/14% nickel dual layer has significantly more porosity (see Section 4-7) than the 5/10% dual layer, again supporting this argument.

![Graph showing total charge passed with time for dual layer zinc-nickel coatings.](image)

**Figure 6-32** Total charge passed with time for dual layer zinc-nickel coatings, electroplated onto steel, immersed in 3.5% sodium chloride solution and coupled with 2014-T6 aluminium alloy

A short summary of the important points from this section is given in Table 6-4.
Corrosion of zinc-nickel coatings - results and discussion

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Coupled with</th>
<th>Observation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Detached</td>
<td>2014-T6 aluminium</td>
<td>Corrosion behaviour related to formation of passive layer, mainly staying sacrificial. Mechanisms proposed</td>
</tr>
<tr>
<td>2014-T6 aluminium</td>
<td></td>
<td>Time to non-sacrificial behaviour related to nickel content, 2014-T6 part of couple passivates after non-sacrificial behaviour reached, level of passivation related to porosity of zinc-nickel coating</td>
</tr>
<tr>
<td>Cd on steel</td>
<td></td>
<td>Shorter time to non-sacrificial behaviour, less effect of porosity on corrosion of Cd after non-sacrificial behaviour reached</td>
</tr>
<tr>
<td>Steel</td>
<td>2014-T6 aluminium</td>
<td>Even shorter times to non-sacrificial behaviour related to porosity of coating, destabilisation of oxide on 2014-T6 after non-sacrificial behaviour reached due to presence of Fe ions. Commercial Zn-Ni less porosity hence longer time to non-sacrificial behaviour</td>
</tr>
</tbody>
</table>

Table 6-4 Summary of galvanic compatibility results

6.6 Double polarisation

Double polarisation was undertaken in accordance with the method given in Section 3-6-7. The reason for carrying out double polarisation measurements was to give a more complete understanding of the way in which the zinc-nickel passivates, and to investigate the way in which the potential of the zinc-nickel changes with an applied potential.

Double polarisation measurements were undertaken on zinc-nickel coatings deposited onto steel and on detached zinc-nickel coatings. The results of carrying out double polarisation sweeps on zinc-nickel coatings are shown in Figure 6-33.

It can be seen that there is a larger difference in $E_{corr}$ values between the forward and reverse sweeps for the higher nickel content coating. This shows that the higher nickel content coating (14%) suffers from accelerated ennoblement and supports the finding of the potential monitoring with time.

For both coatings there is some indication of the formation of a more passive region. The formation of an area of passivity is shown as a change in slope of the region following the first $E_{corr}$. The size of the hysteresis loop on the return sweep is larger for the 14% nickel coating. This shows that the passivation is lost more quickly, i.e. is more unstable for the 14% nickel coating than for the 5% nickel coating. In both cases
the value of $I_{\text{corr}}$ for the reverse sweep is greater than for the forward sweep, showing considerable activation of the surface, with the 14% nickel coating showing a slightly higher level of activation.

Figure 6-33 Polarisation sweeps in 3.5% sodium chloride for zinc-nickel coatings electroplated onto steel using solution 3 and bath configuration 3

Figure 6-34 shows the results of carrying out double polarisation sweeps on detached coatings. Here it can be seen that there is no large difference in the $E_{\text{corr}}$ values for the forward and reverse sweeps for the higher nickel content coatings. This agrees well with the findings of the potential monitoring which showed the potential of the detached coatings to remain constant (or nearly constant) with time. This is illustrated in Figure 6-16.

Again, there is some indication of a change in activity of the surface after the first $E_{\text{corr}}$ has been passed. This is shown by the change of slope observed. The change of slope is not as pronounced for the 11% nickel detached coating. However, for the reverse scan, the passivity is not lost in the same way as for the coatings on steel, with the reverse sweep still more active but below rather than above the forward sweep
line. This is due to the lack of rapid ennoblement of the coatings on steel seen in Figure 6-33.

![Polarisation sweeps for detached coatings produced from solution 3 using bath configuration 2](image)

**Figure 6-34 Polarisation sweeps for detached coatings produced from solution 3 using bath configuration 2**

The size of the hysteresis loop on the reverse scan is largest in these cases for the lowest nickel content coating (5%). This shows that without the presence of the steel substrate the zinc-nickel corrosion rate is dependant on the nickel content and decreases with increase in nickel content. This supports the finding in neutral salt fog exposure tests obtained by other research [52]. The presence of the more passive regions help support the finding that the size and nature of the passive region is
important in the corrosion resistance mechanisms proposed in Figures 6-22, 6-23 and 6-24. Again in all case the value of $I_{\text{corr}}$ on the return sweep is greater than on the forward sweep indicating loss of passivity and activation of the surface.

The differences in the behaviour of the zinc-nickel coatings when detached and when electroplated onto steel show that the steel must have a significant role in the corrosion mechanism of the coating. This would only occur if there is through-thickness porosity present or if there were significant blind pores leading to weak areas in the coating, otherwise the steel substrate would not effect the results obtained. The presence of porosity has already been observed. The accelerated ennoblement of the higher nickel content coating has already been established and can account for the poor times to red rust in neutral salt fog exposure for these coatings.

A summary of the results obtained from this sub-section is given in Table 6-5.

<table>
<thead>
<tr>
<th>On steel</th>
<th>Accelerated ennoblement of high nickel content coating. Larger hysterisis of high nickel content coating. Size of $I_{\text{corr}}$ increases indicating a loss of passivity. The substrate effects the polarisation sweeps give an indication of porosity being present</th>
</tr>
</thead>
<tbody>
<tr>
<td>Detached</td>
<td>No accelerated ennoblement of coatings. Nature of hysterisis different. Larger hysterisis for low nickel contents, agrees with corrosion results obtained by others</td>
</tr>
</tbody>
</table>

Table 6-5 Summary of results of double polarisation measurements

### 6.7 Micro-hardness

Micro-hardness testing was undertaken in accordance with Section 3-7-2. This was carried out to give an idea of the hardness of the coatings, which may give an indication of the possible tensile strength and wear resistance of the coatings, which would affect their usage. Micro-hardness testing was only carried out on the zinc-nickel coatings electroplated onto 2014-T6 aluminium alloy coupons.

The results of the micro-hardness tests are given in Table 6-6. Five measurements were taken per sample and the average micro-hardness calculated. As can be seen both the single layer Zn-Ni coatings and the dual layer coatings produced similar values of micro-hardness. However, the micro-hardness was not as great as commercial Zn-Ni (10-12%) electroplated onto steel but was greater than both zinc
and cadmium electroplate. This difference may be due to the different substrate used. However, if this was the case the zinc and cadmium electroplate on steel would also show a higher hardness. This is not the case. Therefore, the increase in hardness of the commercial zinc-nickel must be due to a difference in morphology, due to the presence of different brighteners and levellers in the commercial electroplate solution.

Cadmium electroplated steel had the lowest micro-hardness, showing this property is not a suitable means of determining if a coating will resist the mating and un-mating required for electrical connectors. Although cadmium is soft in comparison to zinc-nickel its wear properties are good due to its inherent lubricity. Micro-hardness testing does not measure the friction and wear properties of the coating. A better test perhaps to determine the suitability of these coatings for electrical connector shells may therefore have been a friction or wear test.

<table>
<thead>
<tr>
<th>Coating</th>
<th>Average Hardness /Hv₀₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>5% Ni single layer on 2014-T6</td>
<td>201</td>
</tr>
<tr>
<td>7.5% Ni single layer on 2014-T6</td>
<td>192</td>
</tr>
<tr>
<td>10% Ni single layer on 2014-T6</td>
<td>150</td>
</tr>
<tr>
<td>14% Ni single layer on 2014-T6</td>
<td>213</td>
</tr>
<tr>
<td>Dual layer 5%/10% Ni on 2014-T6</td>
<td>159</td>
</tr>
<tr>
<td>Dual layer 7.5%/10% Ni on 2014-T6</td>
<td>179</td>
</tr>
<tr>
<td>Dual layer 5%/14% Ni on 2014-T6</td>
<td>200</td>
</tr>
<tr>
<td>Dual layer 7.5%/14% Ni on 2014-T6</td>
<td>197</td>
</tr>
<tr>
<td>Dual layer 10%/14% Ni on 2014-T6</td>
<td>193</td>
</tr>
<tr>
<td>Zinc on steel</td>
<td>95</td>
</tr>
<tr>
<td>Zn-Ni (10-12%) commercial on steel</td>
<td>450</td>
</tr>
<tr>
<td>Cadmium on steel</td>
<td>79</td>
</tr>
</tbody>
</table>

*Table 6-6 Hardness of electroplated coatings*

### 6.8 Electrical conductivity

Electrical conductivity measurements were carried out in accordance with the method described in Section 3-7-3 using the circuit layout illustrated in Figure 3-7. The aim of undertaking electrical conductivity tests was to ascertain whether the zinc-nickel coatings produced would be suitable for use on electrical connector shells. Electrical conductivity measurements were only undertaken on the zinc-nickel dual layers electroplated onto 2014-T6 aluminium alloy. The electrical resistance measurements are given in Table 6-7 taken prior to corrosion testing. The standard for electrical connectors specifies a shell to shell resistance of no more than 2 mΩ cm⁻¹ [27,204].
The electrical resistance of the dual layer coatings on average met this specification. It was not possible to measure the electrical conductivity after corrosion testing due to the build up of corrosion products. However, no passivation was applied to the connectors. This would detrimentally affect the electrical properties of the dual layers after corrosion testing due to the build up of corrosion products.

<table>
<thead>
<tr>
<th>1st layer /%Ni</th>
<th>2nd layer /%Ni</th>
<th>Electrical resistance /mΩ cm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>10</td>
<td>1.61</td>
</tr>
<tr>
<td>7.5</td>
<td>10</td>
<td>2.36</td>
</tr>
<tr>
<td>5</td>
<td>14</td>
<td>1.91</td>
</tr>
<tr>
<td>7.5</td>
<td>14</td>
<td>2.05</td>
</tr>
<tr>
<td>10</td>
<td>14</td>
<td>1.48</td>
</tr>
</tbody>
</table>

*Table 6-7 Electrical resistance of dual layer coatings*

### 6.9 Coating adhesion

The results of the adhesion tests are shown in Figure 6-35. Adhesion tests were undertaken using cross-hatch adhesion tests in accordance with Section 3-7-4. Testing was undertaken in duplicate and the results averaged. A rating of 1 was very good adhesion, while a rating of 5 corresponded to poor adhesion. Again only zinc-nickel dual layers electroplated onto 2014-T6 aluminium alloy were tested as these were the most likely to suffer from any adhesion problems due to, firstly, the use of 2014-T6 aluminium as a substrate and, secondly, the use of dual layers causing interlayer adhesion problems. As can be seen the adhesion of the electroplate to the aluminium was in most cases good. However, one combination of dual layers produced poor adhesion (7.5/10 % Ni). These samples were slightly blistered in places suggesting an incompatibility between the dual layers probably due to the different effect of the brightener at the different applied plating current density needed to produce the separate layers giving a highly stressed coating. It is interesting to note that this incompatibility is not observed for the 5/10 % Ni combination or the 7.5 /14% Ni combination.
Corrosion of zinc-nickel coatings - results and discussion

Figure 6-35 Cross hatch adhesion results

Photographs showing the difference in adhesion between the 7.5/10 % Ni coatings and the 7.5/14% Ni coatings are given in Figure 6-36.

It is also worth noting that the dual layer combination 7.5/10% Ni also showed the most charge transferred when coupled to 2014-T6 aluminium alloy (see Section 6-5). This increase in charge i.e. driving force for the corrosion reaction could therefore be related to the larger surface area of Zn-Ni coating exposed due to poor adhesion between the layers. It could also account for the longer time to non-sacrificial behaviour observed for this couple due to possibly the de-zincification of the top layer with time being off-set by the availability of the bottom layer to compensate due to poor interlayer adhesion. However, this may not be the case as the single layer coatings also exhibited long times to non-sacrificial behaviour in galvanic couples but would not suffer from poor interlayer adhesion. But the single layer coatings had less charge transferred over the test period. This would suggest that the poor adhesion between the layers for this couple was affecting the galvanic corrosion results. The poor adhesion gave rise to a larger surface area, hence a higher cathodic current rate and hence a higher total charge transferred.
Corrosion of zinc-nickel coatings - results and discussion

7.5/10% Ni adhesion results  7.5/ 14% Ni adhesion results

Figure 6-36 Photographs indicating cross-hatch adhesion test results

6.10 Summary

A summary of the results from undertaking corrosion and other tests on the zinc-nickel coatings is given in Table 6-8.

As can be seen the zinc-nickel coatings produced all showed a significant increase in porosity, except when electroplated using bath configuration 3. This increase in porosity has been shown to detrimentally effect the corrosion resistance of the coating, causing ennoblement and non-sacrificial behaviour on immersion. The porosity may also be leading to a reduction in micro-hardness. However, the micro-hardness of zinc and cadmium were both significantly less, showing that the level of micro-hardness may not be related to the possible wear characteristics of the coatings. The electrical conductivity was sufficiently high to meet the requirements for use as a coating for electrical connectors.
### Table 6-8 Summary of Zn-Ni corrosion and other test results from Section 6

<table>
<thead>
<tr>
<th>Test</th>
<th>Result</th>
<th>Significance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neutral salt fog exposure</td>
<td>Short time to red rust (100 hours), decreases with increase in nickel content due to density reduction as nickel content increases. Amount of white rust decreases as nickel content increases. Level of pitting increases as nickel content increases. Shape of pits different from bare 2014-T6 aluminium alloy. Dual layers slightly less pits</td>
<td>More hydrogen is being incorporated into the coatings as the nickel content increases, this is causing a reduction in density and hence a reduction in time to red rust. This and the shape of pits suggest that the coating is becoming non-sacrificial to both substrates on exposure</td>
</tr>
<tr>
<td>Potential monitoring with time</td>
<td>Rate of ennoblement increases as nickel content increases, except for detached coatings. Initial $E_{corr}$ related to nickel content. Rate of ennoblement dependent on the thickness of coating</td>
<td>Ennoblement dependent on presence of substrate, therefore due to porosity in coating. As the nickel content increases the porosity increases, hence rate of ennoblement increases. Sufficient ennoblement to suggest coatings are becoming non-sacrificial with immersion</td>
</tr>
<tr>
<td>Linear polarisation resistance</td>
<td>$E_{corr}$ increases as nickel content increases. Dependant on morphology. $I_{corr}$ also increases as nickel content increases, again dependant on morphology</td>
<td>Increase in $I_{corr}$ as nickel content increases due to presence of porosity within coating. Level of change of porosity less for bath configuration 3, hence this does not follow same trend</td>
</tr>
<tr>
<td>Galvanic compatibility</td>
<td>Detached coating stays sacrificial compared to 2014-T6 aluminium. Coatings on 2014-T6 and steel all become non-sacrificial with time, dependant on substrate and on coupling material. Commercial zinc-nickel longer times to non-sacrificial behaviour</td>
<td>Level of porosity and driving force between the different couples dictating time to non-sacrificial behaviour. A more active coupling material leads to shorter times to non-sacrificial behaviour and higher overall corrosion rates</td>
</tr>
<tr>
<td>Double polarisation</td>
<td>Different behaviour on steel and when detached. On steel there is a loss of passivity and an increase in activity, along with ennoblement</td>
<td>Due to porosity. Ennoblement suggest that coatings are becoming non-sacrificial to substrate, not due to presence of nickel in coating but due to porosity</td>
</tr>
<tr>
<td>Micro-hardness</td>
<td>Greater than zinc and cadmium, not as high as commercial zinc-nickel</td>
<td>Commercial zinc-nickel greater due to reduced level of porosity</td>
</tr>
<tr>
<td>Electrical conductivity</td>
<td>Approximately less than 2 m$\Omega$ cm$^{-1}$</td>
<td>Meets the requirements for electrical connectors</td>
</tr>
</tbody>
</table>
7 Corrosion of zinc-nickel-manganese coatings- results and discussion

7.1 Introduction

The results obtained within this section were produced using the experimental techniques detailed in Section 3. A summary of Section 3 is given in Table 3-7.

In order to present the results of corrosion and other testing undertaken on zinc-nickel-manganese coatings this section will be divided into a number of sub-sections. Firstly the results obtained from neural salt fog testing will be given and compared with those obtained in section 6 on zinc-nickel coatings. Then the alternate immersion tests results will be given followed by marine exposure results. The electrochemical testing carried out on the zinc-nickel-manganese coatings, including potential monitoring, double polarisation and galvanic tests, will then be presented. Other tests performed such as porosity, micro-hardness and electrical conductivity will then be presented. A brief summary finally completes the section.

Two different zinc-nickel-manganese electroplating solutions were investigated, one based on the complexant sodium citrate and the other on TRIS, were assessed. Several different pre-treatments were undertaken on the steel substrate prior to electroplating, these are detailed in Section 3. In addition, two different electroplating techniques were briefly examined, DC and pulse electroplating. Corrosion results within this section were compared to the results obtained for zinc-nickel in section 6.

7.2 Neutral salt fog exposure

Neutral salt fog testing was undertaken in accordance with Section 3-6-5. Time to 5% red rust and the amount of white rust obtained were determined. The aim of carrying out neutral salt fog testing was to give an indication of the corrosion performance of the alloy. The way in which the corrosion performance in neutral salt fog varied with alloy composition was investigated. The results were also compared to those obtained for zinc-nickel electroplate onto steel.
The effect of density and thickness of electroplate on time to red rust was also investigated. In this way an understanding of the corrosion properties of zinc-nickel-manganese coatings could be begun to be investigated.

The results of investigating the way in which the alloy content affected the performance in neutral salt fog exposure are shown in Figure 7-1. As can be seen for both solutions there is no correlation between alloy composition and time to red rust in neutral salt fog.

Figure 7-1 Variation of time to 5% red rust in neutral salt fog exposure with alloy content of zinc-nickel-manganese electroplated from solution 6 and solution 7 onto steel
On comparing the results obtained for zinc-nickel-manganese coatings in Figure 7-1 with those obtained for zinc-nickel on steel (Figure 6-1) it can be seen that there is a reduction in the time to red rust for the zinc-nickel-manganese coatings. There is also no correlation between composition and corrosion performance (composition is related to applied electroplating current density). This suggests that some other factor rather than composition is effecting the time to red rust for zinc-nickel-manganese coatings in neutral salt fog. For zinc-nickel coatings in Figure 6-2 it was found that the density of electroplate had a significant effect on the corrosion performance of zinc-nickel. Hence the effect of density of electroplate was investigated.

The way in which the density of electroplate affects the time to red rust for zinc-nickel-manganese coatings electroplated onto steel is shown in Figure 7-2. The data points in Figure 7-2 represent the average time to red rust versus the average coating density of duplicate coatings with the same composition. Here it can clearly be seen that an increase in density of the electroplate leads to an increase in time to red rust, hence the density of electroplate has a larger effect on the neutral salt fog results than composition.

The amount of white rust produced during neutral salt testing is shown in Figure 7-3. There is again less scatter on this graph showing that the amount of white rust is more dependant on the composition of the coating than the time to red rust. In all cases there is a decrease in the amount of white rust with increasing nickel and manganese content within the alloy. The level of white rust is smaller than that obtained for zinc-nickel coatings after neutral salt fog (see Figure 6-3), where the amount of white rust was between 20 and 60% for a nickel content of 12 atomic % nickel. When zinc-nickel-manganese is subjected to neutral salt fog the amount of white rust was about 10 % for an alloy containing 12 atomic % nickel and some manganese. The presence of manganese within the ternary alloy has therefore reduced the amount of white rust.
The effect of increasing the manganese content of the alloy by increasing the molarity of sodium citrate within solution 6 on the time to red rust and amount of white rust is shown in Figure 7-4 (the nickel content also varied but by only 1-3 atomic % nickel and has hence, been omitted for clarity). Again, there can be seen to be a reduction in the amount of white rust as the manganese content of the alloy is increased. It can also be seen that there is no change in the time to red rust as the manganese content is increased. This shows the time to red rust to be independent of the manganese content within the alloy and supports the finding of Figure 7-1.
Figure 7-3 Variation of amount of white rust after neutral salt fog testing with alloy content for ternary zinc-nickel-manganese electroplated onto steel
The effect of thickness on time to red rust for zinc-nickel-manganese coatings electroplated from solution 6 using bath configuration 5 is shown in Figure 7-5. As can be seen there is an increase in time to red rust as the thickness of electroplate is increased. This is a similar trend to that observed for zinc-nickel coatings produced from solution 3 in Figure 6-4. However, the effect of changing the composition of zinc-nickel-manganese is much less than that observed for changing the composition in Figure 6-4. Also, the slope of time to red rust with thickness is different. The zinc-nickel coating produced about the same times to red rust at 5 μm thickness and significantly improved times of about 160-180 hours to red rust when the coating thickness was increased to 20 μm. With zinc-nickel-manganese and a coating of 8-10 μm the time to red rust is about 50-60 hours whereas for the zinc-nickel coatings in Figure 6-4 a similar thickness gave a time to red rust of about 70-80 hours.
This reduction in slope of the time to red rust against thickness of electroplate suggests that the zinc-nickel-manganese coating is not sacrificially corroding in the same way as the zinc-nickel coatings on steel. The increase in the dependency of the density of coating on the time to red rust also suggests that porosity or density of electroplate is playing a more significant role in the corrosion mechanism for zinc-nickel-manganese than for zinc-nickel (see Figure 7-2).

![Figure 7-5 Effect of changing the thickness of electroplate on the time to red rust in neutral salt fog exposure for zinc-nickel-manganese coatings produced from solution 6 using bath configuration 5 onto steel](image)

The swirly nature of the morphology of the zinc-nickel-manganese coating produced from solution 6 is also not having a significant effect on the corrosion mechanism. This can be seen in Figure 7-2 where the times to red rust of the coatings produced from the different solutions can be seen to be about the same, at similar values of density. Other morphological observations about the different electroplate are also not affecting the corrosion performance of the zinc-nickel-manganese coatings, with the larger grained more compact coatings produced from using a longer pulse period from solution 6 not producing a change in time to red rust. This lack of influence of morphology in the corrosion resistance suggests that possibly the coating is acting as
a barrier, hence only its level of porosity and not its morphology control the corrosion properties.

The lack of effect of the composition, and the reduction in the dependency of the corrosion rate on the thickness, suggest that perhaps the presence of manganese in even small quantities is causing the coating to not act sacrificially to the substrate. The increase in dependency of the corrosion performance on the density of electroplate would also suggest this. There is still some dependency on the thickness of electroplate. However, as the electroplate becomes thicker there is likely to be a reduction in through thickness porosity even if there is no increase in density. This would cause an increase in time to red rust as the coating got thicker. The use of a thin nickel barrier layer has a slight effect on the time to red rust at lower densities of electroplate (see Figure 7-2). However, this effect is not present as the density of electroplate is increased. The nickel layer is therefore not acting as a true barrier layer between the coating and substrate, probably due to the thin nature of the layer (about 0.5 μm) and is causing some improvement due to a limited amount of decrease in through thickness porosity at low values of electroplate density. As the electroplate density is increased this improvement is lost as it is related to the area of substrate seen and hence is not as significant at higher values of electroplate density.

Further investigation will be undertaken in the sub-sections on electrochemical corrosion measurements to analyse the possibility of the coating not being sacrificial to the substrate. A short summary of the results obtained from neutral salt fog testing of the zinc-nickel-manganese coating is given in Table 7-1.
Corrosion of zinc-nickel-manganese coatings - results and discussion

<table>
<thead>
<tr>
<th>Effect</th>
<th>Result</th>
<th>Conclusion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Composition</td>
<td>No effect on time to red rust for either an increase in nickel or manganese content. Reduction in amount of white rust as nickel and manganese content increased, less white rust than zinc-nickel</td>
<td>Corrosion rate not related to composition, but presence of manganese reducing the amount of white rust</td>
</tr>
<tr>
<td>Density</td>
<td>Increase in time to red rust as density increases</td>
<td>Corrosion resistance dependent on density (possibly through thickness porosity)</td>
</tr>
<tr>
<td>Thickness</td>
<td>Increase in time to red rust as thickness increased. Less dependent on thickness than zinc-nickel</td>
<td>Possibly zinc-nickel-manganese not acting sacrificially to substrate. Improvement in time to red rust due to reduction in through thickness porosity</td>
</tr>
<tr>
<td>Nickel underlayer</td>
<td>Some increase in time to red rust at low values of density. No change as density increased</td>
<td>Nickel underlayer too thin to effect through thickness porosity except at very low values of density</td>
</tr>
<tr>
<td>Morphology</td>
<td>No significant effect, but through thickness porosity not evaluated</td>
<td>Zinc-nickel-manganese is acting as a barrier rather than a sacrificial coating</td>
</tr>
</tbody>
</table>

Table 7-1 Summary of neutral salt fog exposure results and their possible significance

7.3 Alternate immersion testing

Alternate immersion tests were undertaken on a selection of coatings according to the method described in Section 3-6-4. The aim of conducting alternate immersion tests was to ascertain whether the test type used previously, namely neutral salt fog exposure, was affecting the results obtained. Unpassivated zinc alloy based coatings normally perform poorly in neutral salt fog testing [28]. Alternate immersion tests would give a better understanding of how the zinc-nickel-manganese coatings performed in alternate wet and dry conditions, and may give a better indication of their likely performance in non-accelerated corrosion testing.

The results of carrying out alternate immersion tests on a selection of coatings are given in Figure 7-6. As can be seen overall there is a decrease in the amount of white rust present when compared to testing using neutral salt fog. There is also a correlation between the amount of red rust present and the composition of the coating. This correlation was not observed for neutral salt fog testing. As the nickel and manganese content of the coating increased the amount of red rust tended to increase.
especially if the results after 500 hours testing are compared. This increase in red rust with nickel content would agree well with non-accelerated outdoor tests undertaken on zinc-nickel coatings [65]. There was some scatter, suggesting that the correlation is weak, with the 6% nickel, 4% manganese coating producing significantly more red rust after 1000 hours exposure than expected. However, it showed no red rust after 500 hours where as the higher nickel, manganese content coating did.

The commercial zinc-nickel coatings tested showed more white rust than the corresponding zinc-nickel-manganese coatings with the same nickel content. The amount of white rust decreased as the nickel content increased. This increase in amount of white rust for zinc-nickel coatings is consistent with results obtained when neutral salt fog testing was undertaken. The decrease in white rust for the zinc-nickel-manganese coatings seems to e related more to the manganese content of the coating with even 1% manganese giving an improvement in the amount of white rust compared to 1% nickel 0% manganese (still a very small amount of manganese present but less than 1%).

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Figure 7-6 Results of alternate immersion tests on zinc-nickel-manganese coatings and commercial zinc-nickel coatings electroplated onto steel

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Unlike neutral salt fog testing, alternate immersion testing was able to distinguish between the different compositions of zinc-nickel-manganese coatings, not just in terms of white rust but also when the amount of red rust was considered. Non-accelerated corrosion testing of the coatings may help to confirm this trend, and show the increased sensitivity of the alternate immersion test. Alternate immersion testing, like neutral salt fog, still showed commercial zinc-nickel to have longer times to red rust than the zinc-nickel-manganese coatings.

7.4 Marine exposure trials

To further clarify the corrosion process, marine exposure trials were undertaken. The procedure used is given in Section 3-6-3. Previous work [65], has shown a better correlation between real time exposure testing and alternate immersion trials than with neutral salt fog exposure tests. Therefore, it was hoped that the marine exposure trials would show correlation between the composition and amount of red and white rust.

The results after 12 months exposure for selected zinc-nickel-manganese coatings, commercial zinc, zinc-nickel, and cadmium coatings on steel are given in Table 7-2. The cadmium electroplate showed the smallest amount of corrosion damage after 12 months exposure, with no spots of red or white rust. Commercial zinc electroplate showed more extensive corrosion damage, with specs of white rust over the surface. There was no red rust present after 12 months exposure. The commercial zinc-nickel coatings also showed evidence of corrosion, with the higher nickel content coating showing clear evidence of red rust after 12 months.

The zinc-nickel-manganese coatings showed no red rust if the composition of both nickel and manganese was below 9% Ni, 5% Mn. However, there were spots of white rust present. When the nickel and manganese content was raised, the amount of white rust was reduced. However, the amount of red rust was increased, especially for the highest nickel content coating. Photographs of the zinc-nickel-manganese coatings after marine exposure for either 12 or 18 months are given in Figures 7-7 and 7-8.
Corrosion of zinc-nickel-manganese coatings - results and discussion

<table>
<thead>
<tr>
<th>Coating</th>
<th>Appearance after 12 months exposure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cadmium</td>
<td>Small amount of light grey staining</td>
</tr>
<tr>
<td>Zinc</td>
<td>Background dark brown, large spots of dark grey/black staining, speckling effect from white rust, no red rust</td>
</tr>
<tr>
<td>Zinc-nickel (5-7%) commercial</td>
<td>Dark grey staining and speckling of white rust, no red rust</td>
</tr>
<tr>
<td>Zinc-nickel (10-12%) commercial</td>
<td>Very dark grey surface, some white staining and spots of red rust</td>
</tr>
<tr>
<td>99% Zn, 1% Ni, &lt;1% Mn</td>
<td>Very dark grey, black surface, speckling of white rust, no red rust</td>
</tr>
<tr>
<td>98% Zn, 1% Ni, 1% Mn</td>
<td>Very dark grey, black surface, speckling of white rust, no red rust</td>
</tr>
<tr>
<td>95% Zn, 3% Ni, 2% Mn</td>
<td>Slightly lighter surface, more white corrosion spots, no red rust</td>
</tr>
<tr>
<td>90% Zn, 6% Ni, 4% Mn</td>
<td>Dark grey surface, less white rust spots, no red rust</td>
</tr>
<tr>
<td>86% Zn, 9% Ni, 5% Mn</td>
<td>Dark grey surface, no white rust spots, small spots of red rust</td>
</tr>
<tr>
<td>84% Zn, 10% Ni, 6% Mn</td>
<td>Dark grey, black surface, no white rust, numerous small spots of red rust</td>
</tr>
<tr>
<td>84% Zn, 13% Ni, 3% Mn</td>
<td>Dark grey, black surface, no white rust, numerous spots of red rust</td>
</tr>
</tbody>
</table>

Table 7-2 Marine exposure results after 12 months exposure, all coatings approximately 8μm thick

From these figures it can clearly be seen that there is a correlation between the amount of white and red rust and the composition of the coating. This supports the alternate immersion test findings. The amount of white rust reduces as the nickel and manganese contents increase, the amount of red rust increases. However, the 10-12% nickel commercial zinc-nickel coating showed evidence of red rust after 12 months testing. This is in contrast to the alternate immersion tests, which showed the commercial zinc-nickel coatings to have significantly longer times to red rust than the zinc-nickel-manganese coatings.
The poorest coating in terms of red rust was zinc-nickel-manganese with a high nickel content and low manganese content. This can clearly be seen in Figure 7-8. This suggests that it is the nickel rather than the manganese content in the alloy, which is the cause of any accelerated de-zincification leading to a non-sacrificial coating and red rust. Potential monitoring, under immersion conditions, would give an indication of any acceleration of de-zincification, and will be examined within the next subsection.
Corrosion of zinc-nickel-manganese coatings - results and discussion

Figure 7-8 Appearance of zinc-nickel-manganese coatings after exposure to a marine environment for either 12 or 18 months.

Marine exposure gave, on the whole, a better indication of the possible corrosion performance of the zinc-nickel-manganese coatings. It showed, like alternate immersion, a correlation between composition and amount of both white and red rust. It also showed certain zinc-nickel-manganese coatings to have comparable corrosion performance to commercial zinc-nickel and zinc coatings. This was in contrast to both the neutral salt fog and the alternate immersion tests and showed the benefit of allowing the manganese to passivate properly. Alternate immersion was more sensitive to the changes in manganese and nickel contents than neutral salt fog as it allowed a limited passivation of the manganese component of the ternary alloy. Marine exposure allowed further passivation to occur, giving the zinc-nickel-manganese comparable corrosion performance to commercial zinc-nickel coatings.
Corrosion of zinc-nickel-manganese coatings - results and discussion

The nature of the passivity of manganese will be investigated further in the following sections on electrochemical testing.

7.5 Potential monitoring with immersion

Potential monitoring with time was undertaken on the zinc-nickel-manganese coatings. The procedure used is described in Section 3-6-1. Potential monitoring was carried out to investigate the de-zincification of the alloy with immersion. Any de-zincification would lead to an increase in potential, the rate of increase gives an indication of the speed of de-zincification. Marine exposure trials suggested that the rate of de-zincification may be more dependant on the nickel rather than the manganese content of the coating. This will be examined further within this subsection.

The results of undertaking potential monitoring with immersion time for various coatings and substrates are given in Figure 7-9. Here it can be seen that for commercial zinc electroplated onto steel the potential remains fairly constant with exposure, rising slightly with time. Zinc electroplate remains sacrificial to steel until a point where most of the zinc has reacted and the substrate is exposed. This occurs after about 370 hours immersion.

Cadmium electroplate on steel shows a potential very similar to steel and more noble than zinc. It again becomes slightly more noble than steel after about 300 hours immersion. The very small difference in potential between cadmium and steel suggest that there is only a very small potential driving force for corrosion to occur, so cadmium is likely to corrode at a slower rate than zinc. Galvanic measurements would be needed to confirm this, although results of non-electrochemical corrosion testing all suggest that cadmium has a lower corrosion rate than zinc with less corrosion products.

Commercial (10-12%) zinc-nickel on steel shows clear evidence of de-zincification with immersion, starting at a negative potential of about -0.85 V versus SCE and rising rapidly to a steady potential of about -0.58 V versus SCE after about 120 hours immersion. Commercial zinc-nickel becomes non-sacrificial to steel after about 50 hours continuous immersion. This shows that the red rust spots shown on zinc-nickel
(10-12%) on undertaking marine exposure are likely to be caused by de-zincification of the alloy leading to the coating becoming non-sacrificial with exposure. The rate of ennoblement is unlikely to be the same as under immersed conditions due to more complete passivation occurring in the atmosphere, but potential monitoring can still give an indication of the possibility of de-zincification occurring. This is because although incomplete passivation occurs under immersion conditions some passivation is possible due to the presence of oxygen leading to a shift to more positive potentials with immersion time. Commercial zinc-nickel even becomes non-sacrificial with exposure to 2014-T6 aluminium alloy, whereas neither zinc or cadmium electroplate do.

![Graph](image)

**Figure 7-9** Results of undertaking potential monitoring with immersion in 3.5% NaCl with immersion time for various coatings and substrates

A detached coating of zinc-nickel-manganese was used to investigate the potential rise with time to remove any effects of the substrate. The results for undertaking potential time monitoring in 3.5% sodium chloride are also shown in Figure 7-9. Here it can be seen that initially the zinc-nickel-manganese has a potential more negative than zinc-nickel and zinc. The potential then rises rapidly with immersion, showing clear evidence of de-zincification with time, becoming more noble than steel after
about 60 hours. The potential continues to rise, even becoming more noble than 2014-T6 aluminium alloy after about 100 hours. The rise in potential for zinc-nickel-manganese is faster than for zinc-nickel, even although there is less nickel and only a very small amount of manganese present within the coating. The zinc-nickel-manganese coating also reaches a steady potential value greater than the commercial zinc-nickel coating with a larger nickel content. This suggests that the presence of manganese even in very small amounts is causing an increase in the ennoblement of the coating.

The results of undertaking potential monitoring with immersion in 3.5% sodium chloride for various zinc-nickel-manganese coatings electroplated onto steel are shown in Figure 7-10. Again there can be seen to be clear evidence of de-zincification with immersion time, with all the coatings reaching a steady more noble potential after less than 200 hours immersion.

![Figure 7-10 Time dependency of the potential of various zinc-nickel-manganese coatings in 3.5% NaCl solution](image)

The high nickel content coatings all show a very rapid ennoblement, with the lower nickel content coatings showing a slight reduction in the rate of ennoblement. However, the rate of ennoblement with nickel content is hard to quantify, with a lower
Corrosion of zinc-nickel-manganese coatings - results and discussion

Nickel content coating (1%) producing a more rapid ennoblement than a higher nickel content coating (3%). This coating contained more manganese. Other coatings with high manganese contents did not show a reduction in rate of ennoblement. There are therefore some competing mechanisms occurring with the overall rate of ennoblement having a complex relationship to the alloy composition. Further investigation into the sacrificial behaviour of the ternary zinc-nickel-manganese coating would be needed to quantify the relationship. Certainly the observation that the nickel content is influencing the amount of red rust in marine trials is reinforced by these results, with the higher nickel content coatings all showing more rapid ennoblement.

In conclusion, the zinc-nickel manganese coatings all show signs of rapid ennoblement with immersion. The rate of ennoblement seems to be dependant on the nickel and manganese content although the exact nature of the relationship is not known. This rapid ennoblement leads to the coatings becoming non-sacrificial with immersion, helping to explain the short times to red rust in neural salt fog and alternate immersion testing. The presence of red rust following marine exposure for both the zinc-nickel (10-12% nickel) and zinc-nickel-manganese coatings can also be explained by this ennoblement. The lack of red rust for commercial zinc-nickel in alternate immersion shows, however, that continuous immersion in high chloride solution gives an indication of the likelihood of a coating becoming non-sacrificial but cannot allow for passive film stabilisation during the drying cycle, and hence cannot be used to give a total indication of the rate of ennoblement in other environments.

7.6 Double polarisation sweeps

In order to gain a better understanding of the way in which manganese passivates and the nature of the corrosion reaction occurring on zinc-nickel-manganese coatings double polarisation sweeps in 3.5% sodium chloride solution were undertaken. The procedure used is described in Section 3-6-7. The coatings were only polarised for 250 mV anodically to prevent extensive damage to the coating on the anodic sweep, which would invalidate the results obtained from the second cycle. It was felt that 250 mV was sufficient to give some indication of passivation without significantly damaging the coating.
Initially the polarisation behaviour of a detached zinc-nickel-manganese coating was investigated. The resulting sweep is shown in Figure 7-11. Also shown is a double polarisation sweep for electrodeposited manganese on steel. This was undertaken to assess the role of manganese within the passivation behaviour of the alloy. Here it can be seen that there is no change in the value of $E_{\text{corr}}$ on the reverse or second sweep for detached zinc-nickel-manganese. This result agrees well with the line obtained for the detached coatings of zinc-nickel in Figure 6-34. There is no large change in the slope of the curve following the first $E_{\text{corr}}$ showing there to be no large change in the activity of the coating. The value of the second $I_{\text{corr}}$ is slightly greater than that of the first indicating that the surface is becoming more active with exposure to 3.5% sodium chloride solution. The size of the hysteresis loop is small. This indicates that the level of change in activity is also small and the corrosion rate of the coating ought to be low.

Figure 7-11 Double polarisation sweeps for a detached coating of 98% Zn, 1% Ni, 1% Mn and for electrodeposited manganese on steel in 3.5% sodium chloride solution
Corrosion of zinc-nickel-manganese coatings - results and discussion

The lack of change in \(E_{\text{corr}}\) contradicts the results obtained on undertaking potential monitoring of detached zinc-nickel-manganese coatings in Figure 7-9. However, the potential monitoring of the detached zinc-nickel-manganese coating was undertaken on a coating containing more nickel. This change in nickel content could account for the discrepancy in these results, with the higher nickel content used for potential monitoring leading to rapid ennoblement of the coating, while the low nickel content coating used for the polarisation sweeps not leading to as rapid an ennoblement, or any ennoblement within the test duration. This is quite possible as the rate of ennoblement is known in some way to be affected by the nickel content within the alloy (see Figure 7-10).

The double polarisation sweep on manganese electroplated steel gives an initial \(E_{\text{corr}}\) of \(-1272\) mV verses SCE. After the first sweep there is a shift in \(E_{\text{corr}}\) to a more noble value. This shows evidence of the passivation of the manganese surface. The corrosion current density \((I_{\text{cor}})\) is also reduced on the return sweep. This again shows that the surface is becoming more passive and is in contrast to the detached zinc-nickel-manganese coating. This would be expected for manganese electroplate due to the formation of gamma-Mn_2O_3 [70]. The surface is not, however, completely passivated as there is still a corrosion current. On removal of the test sample, red brown Mn_2O_3 was clearly visible on the test area, again giving further evidence of passivation. The initial value of \(E_{\text{corr}}\) for the first sweep for manganese electroplated onto steel is more negative than that obtained for zinc-nickel-manganese or for zinc-nickel. This is expected as manganese is known to exhibit a considerably more negative \(E_{\text{corr}}\) than either zinc-nickel or zinc [28].

Polarisation sweeps of two different zinc-nickel-manganese coatings electroplated onto steel are given in Figure 7-12. The coating with 1 atomic % Ni and no manganese in Figure 7-12 was electroplated from the ternary bath so may contain a very small amount of manganese. Again, there was a significant increase in \(E_{\text{corr}}\) value on the return sweep. However, unlike the pure manganese coating there was no corresponding decrease in the corrosion current. In fact, there was an increase in corrosion current for both coatings. This would affect the corrosion rate adversely and could hence indicate the possibility of a high corrosion rate for this alloy. This would support the neutral salt fog data obtained previously and is similar to the results
obtained for zinc-nickel coatings in Figure 6-33. An increase in both the value of $E_{\text{corr}}$ and $I_{\text{corr}}$ would result in the coating becoming possibly both non-sacrificial to the substrate with time (i.e. if further sweeps were undertaken on the same area) and also more active. This would lead to significant corrosion and possibly accelerated corrosion of the substrate at the site of any pores.

Figure 7-12 Double polarisation sweeps of 99% Zn, 1% Ni, <1% Mn and 90% Zn, 4% Ni, 6% Mn coatings electroplated onto steel using solution 6

The result obtained for the low nickel, manganese coating in Figure 7-12 on steel is in contrast to the result obtained for the detached coating in Figure 7-11 with similar composition, which showed no change in $E_{\text{corr}}$ value. The size of the return hysteresis loop is also considerably different being much greater. This shows a considerable change in the activity of the surface and again supports the observation that the coating is becoming more active and that corrosion is accelerated in the presence of the steel substrate.
The coating with the low nickel content in Figure 7-12 started with a lower value of $E_{\text{corr}}$ than the coating with 4% Ni and 6% Mn. This can be expected as the value of $E_{\text{corr}}$ is dependent on the percentage of nickel in the alloy. The corresponding second or return $E_{\text{corr}}$ value was less noble for the lower percentage nickel coating. The values of $E_{\text{corr}}$ were in all cases greater than for pure manganese.

The size of the return hysteresis loop for the 90% Zn, 4% Ni, 6% Mn coating is about the same as that observed for the lower nickel and manganese content coating in Figure 7-12, however, the $I_{\text{corr}}$ value is slightly greater on the return sweep and there is a larger change in slope after the first $E_{\text{corr}}$. This change in slope indicates that part of the coating is passivating. The rest of the coating is in contrast becoming more active, this is indicated by the increase in $I_{\text{corr}}$ on the return sweep. This increasing contrast in the activity of different regions on the same coating could be leading to the formation of areas of higher corrosion rate on the surface, leading to dissolution of the more active areas and hence patchy or non-uniform corrosion. The results of the neutral salt fog testing confirms this with patches of red rust being formed, while other areas of coating remain intact. The patchy nature of the corrosion in neutral salt fog of zinc-nickel-manganese is illustrated in Figure 7-13.

![Image of corrosion results](image)

Figure 7-13 Appearance of zinc-nickel-manganese coatings after neutral salt fog testing. All coatings produced from solution 6
From Figure 7-13 it can be seen that when the nickel content is high, more patchy red rust is formed (there is also a small change in the manganese content as the nickel content increases). It can also be seen that there is a reduction in the amount of white rust present as the manganese and nickel content in the coating is increased. This has already been observed (see Figure 7-3).

Double polarisation sweeps for zinc-nickel-manganese coatings containing a higher nickel and manganese content are given in Figure 7-14. Like the lower nickel and manganese content coatings illustrated in Figure 7-12 for the 88% Zn, 8% Ni, 4% Mn coating there is a positive shift in E<sub>corr</sub> on the return sweep. This change in potential is slightly larger due to the increase in nickel and manganese content within the coating. A change in slope indicating passivity is again present after passing through the first E<sub>corr</sub>. The size of the hysteresis loop is similar to that observed in Figure 7-12. The effect of slightly increasing both the nickel and manganese content of the coating is therefore small, with the only major difference being a slight increase in the difference between the two E<sub>corr</sub> values.

![Figure 7-14 Double polarisation sweeps of 88% Zn, 8% Ni, 4% Mn and 77% Zn, 11% Ni, 12% Mn electroplated onto steel using solution 6](image)
However, as both the nickel and manganese content of the coating are increased further there is a larger difference in the double polarisation sweep obtained. This is also illustrated in Figure 7-14 (77% Zn, 11% Ni, 12% Mn). Here it can be seen that the first value of $E_{corr}$ is significantly more noble than obtained previously. There is still a difference in the $E_{corr}$ values between the forward and return scans. The difference is, however, not as great, mainly due to the more noble first $E_{corr}$. The second $E_{corr}$ value is more positive than seen previously, probably due to the increase in nickel content within the coating. The size of the hysteresis loop is also much smaller, and the change of slope indicating passivity was not so pronounced.

The much smaller hysteresis loop and the lack of passivity would indicate that the corrosion rate for this coating ought to be less. In neutral salt fog testing, alternate immersion and marine trials the amount of white rust has been shown to be reduced as the nickel and manganese content of the coating increases. This reduction in white rust suggests that the corrosion products and hence the corrosion rate is slower, supporting this observation. The amount of red rust was, however, found to be greater. The amount of red rust present will be determined by the time required for the coating to become non-sacrificial to the substrate. The more positive value of $E_{corr}$ obtained in Figure 7-14 tends to suggest that this coating would become non-sacrificial sooner, leading to more red rust in a shorter time although the corrosion rate of the actual zinc-nickel-manganese coating is less. Further investigation into the galvanic behaviour of this coating would be needed to confirm this.

Whether the increase in the manganese or the increase in the nickel content is causing the change in $E_{corr}$ and activity of the coating was investigated further by undertaking a polarisation sweep on coatings containing less manganese and about the same nickel content. The result is illustrated in Figure 7-15 (82% Zn, 15% Ni, 3% Mn coating).
Again, there can be seen to be a significant increase in the value of the first $E_{corr}$. This shows that the nickel content rather than the manganese content is the cause of the change in initial potential. The second $E_{corr}$ is also slightly more positive, again reflecting the increase in nickel content when compared to Figure 7-14 (77% Zn, 11% Ni, 12% Mn coating). The size of the hysteresis loop is greater. This indicates that the corrosion rate may be higher although the nickel content is greater. The presence of the manganese is therefore the likely cause of the decrease in corrosion rate observed for the 77% Zn, 11% Ni, 12% Mn coating. The change of slope indicating a less active region is larger than for the higher manganese content coating in Figure 7-14. The value of $I_{corr}$ for the second sweep is, like all the other zinc-nickel-manganese coatings on steel, greater than for the first sweep. This again shows some areas of the coating to be becoming more active while other areas are becoming less, again giving an indication that non-uniform patchy corrosion may result. This increase in difference between activity of different areas of coating seems to have increased as the manganese content decreases.
The fact that the passivation of the coating has become more pronounced as the manganese content of the coating has decreased shows that the nickel rich areas of the coating are also become more passive. The increased activity is therefore likely to be occurring on the zinc rich areas of coating. The level of difference in passive and active areas of coating could hence be related to the morphology of the coating (it is unlikely to be related to compositional variation across the sample, due to current density changes as all polarisation sweeps were undertaken in the centre of the coated area). This was investigated further by comparing sweeps undertaken on coatings produced from solution 7, which had a very different morphology to coatings produced from solution 6. The result of undertaking double polarisation sweeps on a high nickel and manganese coating with similar composition to that of Figure 7-14 is also shown in Figure 7-15 (76% Zn, 13% Ni, 11% Mn coating).

As can be seen from Figure 7-15, there is a slight reduction in the level of passivity for the higher manganese content coating when compared to the 82% Zn, 15% Ni, 3% Mn coating in Figure 7-15, however, there is an increase when compared to the similar composition coating in Figure 7-14. This indicates that the morphology of the coating is slightly influencing the level of passivation occurring and may be hence influencing the corrosion driving force between active and passive regions of coating.

The second $E_{corr}$ value obtained in Figure 7-15 is very similar to that obtained in Figure 7-14 for the similar composition coatings (76% Zn, 13% Ni, 11% Mn versus 77% Zn, 11% Ni, 12% Mn) and shows the $E_{corr}$ values not to be influenced by morphology in the same way. The value of the first $E_{corr}$ is, however, slightly reduced. It is therefore possible that the manganese in the coating in Figure 7-15 is initially more active than that in Figure 7-14 and is hence reducing the first $E_{corr}$ value obtained. If this was the case the more active manganese regions would passivate more, leading to an increase in the change of slope observed and hence account for the difference between Figures 7-14 and 7-15 for the similar composition coatings. This change in initial activity of the manganese, perhaps due to morphological differences, could account for the differences in ennoblement observed in potential time monitoring. Hence, the rate of ennoblement is dependant not only on the nickel and manganese contents but also on the activity of the manganese component, which is influenced by morphological differences in the coating.
A summary of the findings from this sub-section on double polarisation is given in Table 7-3.

<table>
<thead>
<tr>
<th>Coating and substrate</th>
<th>Observation</th>
<th>Significance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Detached Zn-Ni-Mn</td>
<td>No change in $E_{\text{corr}}$</td>
<td>No ennoblement of coating when detached</td>
</tr>
<tr>
<td>Manganese on steel</td>
<td>Increase in $E_{\text{corr}}$, reduction in $I_{\text{corr}}$, change in slope indicating passivation</td>
<td>Ennoblement of coating due to passivation, formation of red brown $\text{Mn}_2\text{O}_3$ (see page 237)</td>
</tr>
<tr>
<td>Zn-Ni-Mn on steel</td>
<td>$E_{\text{corr}}$ increases, increase in $I_{\text{corr}}$</td>
<td>Ennoblement with increase in activity, due to presence of steel</td>
</tr>
<tr>
<td></td>
<td>Final $E_{\text{corr}}$ dependant on nickel content</td>
<td>More de-zincification as nickel content increased</td>
</tr>
<tr>
<td></td>
<td>Increased difference in activity of different regions of electroplate</td>
<td>Leading to non-uniform patchy corrosion</td>
</tr>
<tr>
<td></td>
<td>Change in starting $E_{\text{corr}}$ and level of passivation with morphology</td>
<td>Starting $E_{\text{corr}}$ and level of passivation dependent on initial activity of the manganese component, which is dependant on morphology</td>
</tr>
</tbody>
</table>

Table 7-3 Summary of double polarisation results

### 7.7 Galvanic compatibility trials

Galvanic compatibility tests were undertaken as described in Section 3-6-2. The cell configuration used is given in Figure 3-6. The reasons for carrying out galvanic tests were to find out if the coatings were becoming non-sacrificial with respect to the substrates with time during their immersion, and to get an indication of the magnitude of the current involved. By getting this information, the role that the zinc, nickel and manganese play in the corrosion mechanism can be further investigated, as well as the role of the substrate.

The results obtained for cadmium, zinc and manganese electroplated coatings coupled to 2014-T6 aluminium alloy are given in Figures 7-16 and 7-17. Figure 7-16 shows the actual current measurements and shows whether the coating is becoming non-sacrificial (any negative current readings show non-sacrificial behaviour). Figure 7-17 shows the calculated total charge passed with time. This gives an indication of the magnitude of the corrosion reaction.
From Figure 7-16 it can be seen that the cadmium electroplate on steel shows a low overall current with the coating staying sacrificial throughout the duration of the test indicating a low corrosion rate when coupled to 2014-T6 aluminium. The zinc electroplated steel shows a higher current, with the coating again staying sacrificial throughout the test. This indicates a higher corrosion current than cadmium and hence a higher corrosion rate for zinc when coupled to 2014-T6 aluminium alloy. The fact that both coatings stay sacrificial throughout the test supports the potential monitoring results shown in Figure 7-9.

The manganese electroplate in contrast shows an initial higher current, this decreases with time as the manganese coating passivates. This passivation of the manganese leads to a shift in $E_{corr}$ value causing the coating to become non-sacrificial to 2014-T6 aluminium after about 180 hours. Corrosion of the 2014-T6 side of the couple then occurs. This increase in $E_{corr}$ value with increasing passivation of the manganese coating has already been observed in Figure 7-11.
Corrosion of zinc-nickel-manganese coatings - results and discussion

The total charge passed with time in Figure 7-17 gives an indication of the way in which the corrosion rate changes with time for the different coatings. Cadmium shows a steady slightly decreasing slope with time indicating slow passivation of the surface due to corrosion product building up. The total charge passed is low indicating a low corrosion rate.

Zinc shows a larger total charge indicating a higher corrosion rate. Again the rate decreases with immersion time as corrosion products and areas of passivation build up on the surface.

![Graph showing total charge passed with time for zinc, cadmium, and manganese coatings.](image)

*Figure 7-17 Total charge passed with time for electroplated manganese, zinc and cadmium coatings, immersed in 3.5% sodium chloride solution and coupled to 2014-T6 aluminium alloy*

The manganese electroplate also shows a comparable value of total charge indicating an initial corrosion rate similar to zinc. This rate then decreases as the manganese surface passivates. The slope of the graph then increases sharply as non-sacrificial behaviour is initiated and the 2014-T6 part of the couple starts to corrode. The presence of the manganese within the solution seems to be inhibiting the formation of an oxide layer on the 2014-T6 aluminium leading to steady corrosion of the 2014-T6 part of the couple.
The results of undertaking galvanic measurements of zinc-nickel-manganese coatings coupled to 2014-T6 aluminium alloy are given in Figure 7-18 for the current measurements and in Figure 7-19 for the total charge passed with time. All the zinc-nickel-manganese coatings can be seen to initially have about the same corrosion current of about 10 μA cm⁻², which is about the same as for zinc in Figure 7-16. All zinc-nickel-manganese coatings then become rapidly non-sacrificial to the 2014-T6 aluminium alloy.

![Figure 7-18 Current density measurements of zinc-nickel-manganese coatings electroplated onto steel, immersed in 3.5% sodium chloride solution and coupled to 2014-T6 aluminium alloy](image)

The time taken for the current to become negative (non-sacrificial behaviour) is dependant on the manganese rather than nickel content of the coating with the higher manganese content coatings giving a much shorter time to non-sacrificial behaviour. On comparing the times to non-sacrificial behaviour with those obtained for zinc-nickel coatings on steel in Figure 6-29, it can be seen that there is considerable acceleration of the time to non-sacrificial behaviour in the presence of manganese.
Corrosion of zinc-nickel-manganese coatings - results and discussion

Figure 7-19 Total charge passed with time for zinc-nickel-manganese coatings electroplated onto steel, immersed in 3.5% sodium chloride solution and coupled to 2014-T6 aluminium alloy

Figure 7-19 shows the total charge passed with time for zinc-nickel-manganese coatings coupled to 2014-T6 aluminium alloy. Here, it can be seen that the initial corrosion rate of the zinc-nickel-manganese is low up to the point of initiation of non-sacrificial behaviour. The 2014-T6 part of the couple then starts to corrode. The rate of corrosion of the 2014-T6 is steady and does not change with time. It is, however, dependant on the amount of nickel in the zinc-nickel-manganese coating with the lower nickel content coatings giving a lower overall total charge, corresponding to a lower corrosion rate of the 2014-T6 aluminium alloy.

The galvanic behaviour of cadmium, zinc and manganese electroplate when coupled to steel rather than 2014-T6 aluminium is shown in Figures 7-20 and 7-21. The size of the corrosion current is, in all cases, larger than when coupled to 2014-T6 aluminium alloy (see Figures 7-16 and 7-17). The increase in corrosion current is due to the more active nature of the steel part of the couple, which leads to a higher rate determining cathodic current and hence a higher overall corrosion current. The corrosion current for cadmium electroplate is the lowest overall and does not vary much with time. Zinc shows a higher steady corrosion current.
Manganese electroplate again shows a difference in galvanic behaviour, with an initial large corrosion current, which drops as the manganese passivates. The manganese electroplate then becomes non-sacrificial to the steel causing the measured current to become negative. Unlike when coupled to 2014-T6 aluminium the measured corrosion current then fluctuates around zero, becoming both positive and negative. The time taken for the manganese coating to become initially non-sacrificial is shorter than when coupled to 2014-T6 aluminium alloy, being about 90 hours. This decrease in the time is probably a result of the increased initial corrosion current causing the active areas of manganese electroplate to corrode faster, leading to an increased rate of passivation of the manganese and hence an increased rate of ennoblement of the manganese coating. The reason for the fluctuation around zero after non-sacrificial behaviour has been reached is the presence of the steel substrate beneath the manganese being exposed. This will influence the value of \( E_{\text{corr}} \) causing fluctuation as the exposed steel under the manganese becomes first sacrificial to the other steel component of the couple then non-sacrificial.
From Figure 7-21, showing the way in which the total charge varies with immersion time, it can be seen that cadmium has a steady corrosion rate with time. Contrary to when it is coupled to 2014-T6 aluminium, the cadmium does not passivate with time. This is also true for the zinc electroplate which shows a steady higher total charge with time. Manganese electroplate on the other hand is shown to passivate even in the presence of steel. The lack of passivation of the cadmium and zinc electroplate in the presence of steel indicates that when electroplated onto a steel substrate they will both continue to corrode at the same rate. The presence of the steel part of the couple is therefore somehow inhibiting the formation of a passive layer on the zinc and cadmium surface.

![Graph](image)

*Figure 7-21 Total charge passed with time for electroplated manganese, zinc and cadmium coatings, immersed in 3.5% sodium chloride solution and coupled to steel*

The way in which the measured current changes for zinc-nickel-manganese coatings when coupled to steel is shown in Figure 7-22. The related total charge passed with time curves are given in Figure 7-23. From Figure 7-22 it can be seen that the time to non-sacrificial behaviour is again related to the composition of the zinc-nickel-manganese coating, with the low nickel content coating remaining sacrificial over the test duration. This agrees with the double polarisation measurements on detached low
nickel, zinc-nickel-manganese coatings. The size of the corrosion current for the coatings are again greater when coupled to steel rather than 2014-T6 aluminium. However, the level of corrosion current for the low nickel and manganese, zinc-nickel-manganese coating is lower than that of zinc electroplate when coupled to steel in Figure 7-20. This shows correlation with the reduction in corrosion rate observed for zinc-nickel coatings reported elsewhere [52], in neutral salt fog testing and suggests that the corrosion behaviour of the 98% Zn, 1% Ni, 1% Mn coating may be similar to zinc-nickel under immersed conditions.

The other zinc-nickel-manganese coatings all became non-sacrificial to the steel component of the couple in a very short time, with the highest nickel and manganese content coating having a time to non-sacrificial behaviour of only about 20 hours.

![Graph showing current density measurements for zinc-nickel-manganese coatings](image)

*Figure 7-22 Current density measurements for zinc-nickel-manganese coatings electroplated onto steel, immersed in 3.5% sodium chloride solution and coupled to steel*

After the coatings become non-sacrificial to steel both the lower manganese coatings (82% Zn, 9% Ni, 9% Mn and 82% Zn, 15% Ni, 3% Mn) cause the steel part of the couple to corrode in the same way, with a steady low corrosion rate. The other zinc-nickel-manganese coating, with more manganese, shows an increase in the corrosion
Corrosion of zinc-nickel-manganese coatings - results and discussion

rate of the steel after the steel has been sacrificial for about 100 hours. This similarity in corrosion behaviour after the coatings have become non-sacrificial seems to be related to the zinc content of the coating, with the same zinc content giving the same corrosion behaviour of the steel. This can be seen very clearly in Figure 7-23. During the initial corrosion of the zinc-nickel-manganese coatings, zinc will be lost from the coating matrix until the coating becomes non-sacrificial. The solution will then contain zinc ions, which could precipitate onto the surface of the steel (as the steel may be cathodic due to oxygen reduction generating a higher pH), this would lead to accelerated corrosion of the steel. This dependency on the zinc content of the coating is not observed when coupled to 2014-T6 rather than steel.

![Graph showing total charge passed with time for zinc-nickel-manganese coatings electroplated onto steel, immersed in 3.5% sodium chloride solution and coupled to steel.]

Figure 7-23 Total charge passed with time for zinc-nickel-manganese coatings electroplated onto steel, immersed in 3.5% sodium chloride solution and coupled to steel

A summary of the results obtained from undertaking galvanic corrosion testing is given in Table 7-4.
Corrosion of zinc-nickel-manganese coatings - results and discussion

<table>
<thead>
<tr>
<th>Coating</th>
<th>Coupled to 2014-T6</th>
<th>Coupled to steel</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cadmium</td>
<td>Very low current decreasing with immersion time, always sacrificial</td>
<td>Higher current but still lowest of coatings tested, not decreasing with immersion time, always sacrificial</td>
</tr>
<tr>
<td>Zinc</td>
<td>Higher steady current, decreasing with immersion time, always sacrificial</td>
<td>Higher than when coupled to 2014-T6, not decreasing with time, always sacrificial</td>
</tr>
<tr>
<td>Manganese</td>
<td>High initial current dropping with immersion time, becoming non-sacrificial after 180 hours</td>
<td>High initial current dropping as manganese passivates, becoming non-sacrificial after 90 hours. Non-sacrificial behaviour fluctuates due to presence of steel on both sides of the couple</td>
</tr>
<tr>
<td>Zn-Ni-Mn</td>
<td>Accelerated time to non-sacrificial compared to zinc-nickel, dependant on manganese content. Initial corrosion rate same as zinc. Corrosion of 2014-T6 after coating becomes non-sacrificial related to nickel content of alloy.</td>
<td>Lowest nickel manganese content coating always sacrificial with a lower current than zinc. Other coatings accelerated time to non-sacrificial behaviour, even faster than when coupled to 2014-T6. Corrosion of steel after non-sacrificial behaviour initiated related to the zinc content of the coating</td>
</tr>
</tbody>
</table>

Table 7-4 Summary of galvanic compatibility test results

7.8 Porosity

A qualitative assessment of the porosity of the zinc-nickel-manganese coatings was undertaken in accordance with the method described in Section 3-7-1. This was to obtain an indication of the level of porosity present within the zinc-nickel-manganese coatings and to assess whether it varied with composition.

The results of the evaluation on various zinc-nickel-manganese coatings are shown in Figure 7-24. As can be seen there is significant porosity present on all coatings. The smallest amount of porosity is shown by the 99% Zn, 1% Ni coating electroplated from solution 6 (containing <1% Mn). Even on this coating there are still significant very small areas of blue (ferrous cyanide complex caused by the presence of the steel substrate), representing porosity. The 98% Zn, 1% Ni, 1% Mn shows even more porosity especially in the central area. This high level of porosity is also seen in the centre of the 96% Zn, 2% Ni, 2% Mn coating. The 90% Zn, 6% Ni, 4% Mn coating does not show as much porosity in the central region, but has increased porosity at the edges.
Corrosion of zinc-nickel-manganese coatings - results and discussion

The last photograph shows the same composition coating, but in this case the coating was applied over a thin nickel barrier layer, which was supposed to reduce the through coating porosity. However, it can clearly be seen that there are, in this case, still very high levels of porosity. This may be due to poor adhesion between the barrier nickel layer and the ternary alloy coating, leading to loss of coating on neutral salt fog testing and hence a significant increase in porosity. More testing of post neutral salt fog tested samples would be required to confirm this.

It can also be seen that not all the red corrosion product seen on the corroded sample is iron-based. This suggests that some Mn₂O₃ is present, having similar colouration [70].

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**Figure 7-24 Porosity evaluation of Zn-Ni-Mn coatings on steel**

The level of porosity exhibited by the zinc-nickel-manganese coatings is so significant to cause the poor corrosion results obtained, if the coating is becoming non-sacrificial with time. The rest of this section has shown the coating does become
non-sacrificial rapidly on immersion in 3.5% NaCl except at very low nickel and manganese contents, which showed reduced porosity. It is therefore reasonable to suppose that the ternary coating would also become non-sacrificial with exposure to neutral salt fog. Hence, the level of porosity would become significant in causing the poor corrosion resistance.

The high level of porosity may be related to the low current efficiency of the electroplating process. This would lead to excessive hydrogen evolution and hence an increase in porosity with hydrogen being trapped on and within the coating. A high level of porosity can also explain the reduction in density of the electroplate with increasing applied electroplating current density. This was also observed for the zinc-nickel coatings in Figure 4-27.

7.9 Micro-hardness

Micro-hardness testing of the coatings was carried out according to the procedure given in Section 3-7-2. In addition to the zinc-nickel-manganese coatings, manganese, nickel and zinc electroplates on steel were tested. The results of undertaking micro-hardness testing are shown in Figure 7-25.

The micro-hardness of the coatings all increased as the nickel and manganese content of the coatings increased, as the zinc content in the alloy decreased. This is expected as both nickel and manganese have a higher hardness value than zinc. On comparing the results obtained for the zinc-nickel-manganese with those obtained for zinc-nickel in Table 6-6 it can be seen that the micro-hardness of the zinc-nickel-manganese coatings were on the whole higher than that obtained for zinc-nickel coatings electroplated from solution 3. However, the value of micro-hardness for commercial zinc-nickel was about 450 Hv0.2, which is comparable with the highest hardness zinc-nickel-manganese coatings in Figure 7-25. From Figure 7-25 it can be seen that there is some difference in micro-hardness between coatings produced from the two different solutions, with coatings produced from solution 7 exhibiting a lower micro-hardness for the same zinc content. This reduction could be related to the microstructure, with the swirly distinct morphology of the coatings produced from solution 6 giving rise to a higher micro-hardness.
7.10 Electrical conductivity

Electrical conductivity measurements were undertaken as in Section 3-7-3 using the circuit described in Figure 3-7. The electrical resistance of the zinc-nickel-manganese coatings was found to be on average 2.56 mΩ cm⁻¹, which is just above the requirements for electrical connector shells of 2 mΩ cm⁻¹ [27,204]. The results of the electrical conductivity tests are shown in Figure 7-26. As the zinc content of the coating increases the electrical resistance decreases to a value around 2 mΩ cm⁻¹ at a zinc content of about 90%. Coatings with high nickel and manganese contents exhibit higher electrical resistance, outside of the requirements for electrical connector shells. There is only a small difference in electrical resistance results for coating produced from the two different solutions indicating that the nature of the morphology does not influence the electrical resistance to as large an extent as it influences the micro-hardness. Comparing the results for electrical resistance with those obtained for zinc-nickel coatings in Table 6-7 it can be seen that zinc-nickel-manganese coatings have similar perhaps slightly higher values of electrical resistance to zinc-nickel coatings.
Corrosion of zinc-nickel-manganese coatings - results and discussion

Figure 7-26 Surface electrical resistance of zinc-nickel-manganese coatings produced from solutions 6 and 7

7.11 Summary

A summary of the results obtained from undertaking corrosion and other tests on zinc-nickel-manganese coatings is given in Table 7-5. As can be seen, the nature of the corrosion test strongly influences the result obtained, with marine exposure trials giving the most accurate and highest corrosion performance for zinc-nickel-manganese. This is related to the passivation ability of zinc-nickel-manganese. Under immersed conditions the zinc-nickel-manganese shows rapid ennoblement and non-sacrificial behaviour, accounting for the poor times to red rust in neutral salt fog testing.

The coatings produced all showed significant levels of porosity due to hydrogen evolution. This level of porosity had a detrimental effect on the rate of ennoblement and the corrosion results obtained in accelerated testing. Electrical measurements showed the coatings to be about as conductive as zinc-nickel, even though the morphology (see Section 5) was significantly different.
## Corrosion of zinc-nickel-manganese coatings: results and discussion

<table>
<thead>
<tr>
<th>Test</th>
<th>Result</th>
<th>Significance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neutral salt fog exposure</td>
<td>Short times to red rust. Reduction in white rust compared to zinc-nickel, decreasing amount with increase in nickel and manganese in alloy. Time to red rust related to density of coating.</td>
<td>Time to red rust related to porosity of coating, suggesting coating is becoming non-sacrificial with exposure. Less white rust due to passivation of manganese component of alloy.</td>
</tr>
<tr>
<td>Alternate immersion tests</td>
<td>More red rust than commercial zinc-nickel but less white rust. Amount of red rust related to nickel and manganese content of alloy</td>
<td>Alternate immersion more sensitive to alloy content than neutral salt fog as neutral salt fog does not allow the manganese component to passivate fully.</td>
</tr>
<tr>
<td>Marine exposure trials</td>
<td>Zinc-nickel-manganese coatings comparable to commercial zinc-nickel, with less white rust, nearly as good as cadmium electroplate</td>
<td>Marine exposure allows for complete passivation of the manganese component, leading to longer times to red rust than expected from accelerated tests and less white rust.</td>
</tr>
<tr>
<td>Potential monitoring with immersion time</td>
<td>Shows rapid ennoblement with immersion. Rate dependent on nickel and manganese content in alloy. Detached coating still showed ennoblement.</td>
<td>Ennoblement due to presence of manganese as well as presence of porosity. Explains the level of red rust obtained in neutral salt fog and alternate immersion tests.</td>
</tr>
<tr>
<td>Galvanic compatibility</td>
<td>Both cadmium and zinc electroplate stay sacrificial, but manganese does not. Zinc-nickel-manganese shows very short times to non-sacrificial behaviour</td>
<td>The presence of manganese and the substrate is causing accelerated ennoblement and loss of sacrificial behaviour, accounting for poor times to red rust on accelerated testing.</td>
</tr>
<tr>
<td>Double polarisation</td>
<td>Manganese passivates but zinc-nickel-manganese becomes more active. $E_{corr}$ increases but not for detached coating</td>
<td>There is an increased difference in activity between passive and active regions, causing patchy non-uniform corrosion.</td>
</tr>
<tr>
<td>Porosity</td>
<td>Significant porosity present</td>
<td>May be related to excess hydrogen evolution.</td>
</tr>
<tr>
<td>Micro-hardness</td>
<td>Higher than zinc-nickel, related to zinc content</td>
<td>Zinc has lower micro-hardness than nickel and manganese, this is reducing the hardness of zinc-nickel-manganese.</td>
</tr>
<tr>
<td>Electrical conductivity</td>
<td>Similar to zinc-nickel, less than 2 mΩ cm$^{-2}$ if the zinc content is greater than about 90% zinc</td>
<td>Zinc-nickel-manganese would be suitable as a coating for electrical connectors.</td>
</tr>
</tbody>
</table>

*Table 7-5 Summary of results obtained from Section 7*
8 Overall Summary

The aim of this Section is to compare and discuss the results obtained for zinc-nickel and zinc-nickel-manganese coatings. Specific details and differences will not be examined, as these are already covered in the proceeding sections. However, the overall achievements, problems, conclusions and recommendations will be addressed. In this manner it is hoped to get an indication of the possibility of using either multi-layer coating or ternary alloy coatings as replacements for cadmium on electrical connectors and fasteners for use on aircraft. Firstly, the work on zinc-nickel will be reviewed, followed by zinc-nickel-manganese. The overall problem of replacing cadmium will then be discussed.

8.1 Zinc-nickel

The overall aim of this area of work was to assess the suitability of using multi-layer coatings, to improve the corrosion resistance of zinc-nickel and hence make it a more suitable replacement for cadmium. By concentrating on the use of multi-layered coatings, inherent problems with the use of zinc-nickel as a replacement for cadmium such as lubricity were not addressed. Even if multi-layer coatings of zinc-nickel were found to significantly improve the corrosion performance of the alloy, its use as a replacement for cadmium is unlikely due to this lack of lubricity unless lubricious particles were also added to produce a composite Zn-Ni coating.

By undertaking this research, however, some progress in the understanding of zinc-nickel electroplating and its corrosion has been achieved. It was found possible to produce zinc-nickel coatings with varying compositions from a single experimental bath. The use of dual layers was shown to be feasible, as was the use of a complexant in zinc-nickel electroplating. Normally the production of zinc-nickel does not require the use of complexants, however, in order to increase both the bath stability and the throwing power they can be used. By using a novel complexant a zinc-nickel electroplating solution which was robust towards variations in nickel solution content was produced. This enabled the production of zinc-nickel coatings from a single bath with known, predictable compositions and hence made the production of multilayers feasible. The throwing power of the electroplating bath was not as good as for cadmium electroplate, but it must be remembered that cadmium electroplate on
connectors is produced from cyanide containing baths. Hence, to achieve a coating from an experimental, non-optimised bath configuration with a thickness distribution near to cadmium was significant, and shows the advantage of using a complexant in zinc-nickel electroplating.

Although the corrosion resistance on 2014-T6 aluminium alloy with dual layer coatings showed some improvement in neutral salt fog testing, as well as some improvement in coating uniformity on connector shells, the improvement was slight and was not seen in all corrosion tests undertaken. The use of dual rather than single layer coatings cannot therefore, at present, increase the corrosion resistance significantly in order to compensate for the increased complexity of producing dual layers. Whether the use of multi-layer coatings (with more than two layers) would lead to further improvements in the corrosion performance of the zinc-nickel alloy would require more investigation.

The main problem with the experimental zinc-nickel coatings was found to be the increase in porosity as the nickel content was raised. This increase in porosity was found to significantly reduce the corrosion resistance of the higher nickel content alloys in all accelerated tests, leading to de-zincification and non-sacrificial behaviour. A significant reduction in porosity would be required, prior to making a true comparison between commercial zinc-nickel single layer coatings and the dual layer coatings produced in this programme. The level of porosity present was thought to be due to the increase in applied electroplating current density required to produce the higher nickel content coatings. Further investigation into changing the position of the anomalous co-deposition composition line to reduce the applied electroplating current density required for the high nickel content alloys would be needed. Means of changing the position of the composition line compared to the limiting current density, include the use of more bath agitation, higher nickel solution content, higher bath pH, and the use of pulse electroplating.

Once it has been proved possible to deposit, pore free zinc-nickel coatings with different nickel contents, then the use of multi-layers can be investigated. A means of producing the required nickel contents by the use of two separate commercial zinc-nickel baths to give high and low nickel contents may be justified in order to show
that multi-layers do give enough of an improvement in properties to make their use feasible, given the additional complexity of their production.

When evaluating the corrosion properties of zinc-nickel it would have been useful if real time, non-accelerated testing had been undertaken on the experimental as well as the commercial zinc-nickel coatings. None of the zinc-nickel coatings produced were micro-cracked. They therefore may not show any improvement in corrosion performance when compared to zinc in real time exposure tests. If zinc-nickel, without micro-cracks, does not show a significant real improvement in corrosion protection than zinc, the use of multi-layer zinc-nickel coatings would be unlikely to change this. This fundamental issue must be resolved, prior to any recommendation that zinc-nickel (let alone multi-layer zinc-nickel) should be used as a replacement for cadmium rather than zinc due to its improvement in corrosion resistance. It may in fact be found that the highly porous coatings produced in this programme offer better real corrosion protection than commercial zinc or zinc-nickel electroplate. If this is the case, further work on porosity reduction would not be necessary except to satisfy the industry’s reliance on neutral salt fog testing as a means of assessing the corrosion performance of coatings.

8.2 Zinc-nickel-manganese

The aim of alloying zinc-nickel with manganese was to attempt to increase the corrosion resistance of zinc-nickel and to reduce the amount of corrosion products. In this way it was hoped to produce a coating with properties which were more suitable for use on electrical connectors and fasteners as a replacement for cadmium.

Although this research has not managed to produce a suitable replacement for cadmium as yet, it has significantly increased the understanding of the properties of zinc-nickel-manganese coatings. Previous work has shown the feasibility of producing a ternary alloy of zinc-nickel-manganese from a sulphate bath [115]. However, the manganese content of the alloy was very small. This work has managed to produce higher manganese contents by the use of either citrate or TRIS as complexants and to then assess the corrosion performance and other important properties of the alloy.
The different complexants used were found to have a significant effect on the morphology of the coatings, with the citrate complexant producing a distinct swirly morphology. As real time exposure tests were not undertaken on the coatings produced from the TRIS solution, how the different morphology affects the true corrosion performance of the coating is not known. However, the use of TRIS seems to have a number of advantages, namely an increase in bath stability (additions of acid are not required to stabilise the precipitate), and an increase in bath operating pH. Coatings produced from the TRIS solution also showed more stability in terms of their nickel content over the electroplating current density range studied. Whether a stable nickel content, with a varying manganese content for the possible production of multi-layers would lead to a more corrosion resistance system is unknown. Certainly a more stable nickel content facilitates the understanding of the role of the two alloying elements on the properties of the coating.

As it was found possible to vary the manganese and nickel content of the coating achieved by variation of the applied electroplating current density, this makes the production of multi-layer coatings of zinc-nickel-manganese from a single solution feasible. The use of multi-layer coatings may improve the corrosion resistance of the coating system (see zinc-nickel, section 8-1). It would also help solve the main disadvantage of using manganese-containing coatings, namely the poor current efficiency of the process. By only having significant manganese present in the upper multi-layer the overall current efficiency of the process can be increased, reducing the amount of hydrogen produced, hence reducing the cost of the process and any through thickness porosity.

Like the zinc-nickel coatings produced, the zinc-nickel-manganese coatings contained significant porosity. This porosity coupled with the presence of manganese accelerated the ennoblement of the coating when compared to zinc-nickel, leading to a rapid time to non-sacrificial behaviour under immersion conditions. This coupled to the effect of the passivation of the manganese rich parts of the coating, lead to patchy corrosion of the substrate and short times to red rust in neutral salt fog and alternative immersion tests. The cause of the significant porosity is likely to be hydrogen incorporation in the coating during electroplating. The low level of current efficiency supports this. Before zinc-nickel-manganese can be used as a coating replacement for
Overall Summary

cadmium, this low current efficiency and high level of porosity need to be addressed. Even though the corrosion rate was significantly reduced on undertaking atmospheric marine exposure tests, and the corrosion resistance of the coating was found to be better than zinc-nickel, it was not quite as good as cadmium, with some red rust being produced on the high manganese content coatings. The presence of red rust suggests that the coatings are still becoming non-sacrificial to the substrate even under atmospheric conditions. Whether this is due to the high level of porosity of the coating, or a fundamental problem with zinc-nickel-manganese coatings would need to be assessed. Unlike zinc-nickel detached coatings, ennoblement of zinc-nickel-manganese detached coatings under immersed conditions was observed. This could mean that it is the presence of manganese rather than the through thickness porosity that is partly responsible for the ennoblement of zinc-nickel-manganese. This would require investigation before zinc-nickel-manganese could be recommended as a replacement for cadmium.

The level of corrosion products produced on the zinc-nickel-manganese, both in accelerated testing and in atmospheric testing, was reduced when compared to zinc-nickel, making zinc-nickel-manganese a more suitable coating replacement for cadmium than zinc-nickel. This is provided that it stays a sacrificial coating. However, it may be that the reduction in corrosion products required can only be achieved for zinc alloys if they become non-sacrificial to the substrate. The two requirements may in fact be mutually excludable.

Although the level of corrosion products was significantly reduced, manganese oxide is brown in colour, giving the appearance of rust although the substrate is still intact. This unattractive nature of the corrosion products may leave zinc-nickel-manganese with the same drawback as zinc-iron, namely unattractive corrosion products.

The zinc-nickel-manganese coatings produced were deposited quite evenly over the substrate. It would have been nice to compare the thickness distribution of the zinc-nickel-manganese coatings with zinc-manganese as one of the proposed advantages of using the former rather than the latter was the possibility of improving the throwing power of the coating process. It would also have been useful to assess the corrosion resistance of zinc-manganese to see if zinc-nickel-manganese could offer similar
corrosion protection for a significant reduction in manganese content. This would give zinc-nickel-manganese a distinct advantage, namely reduced production costs due to a higher electroplating current efficiency.

Other improvements to the solution to increase the current efficiency could also be carried out. By improving the current efficiency of the process it would also be hoped to reduce the level of porosity and hence increase the corrosion resistance. Methods to improve the current efficiency of the solution include the addition of selenium [31], the changing of the level of complexant, bath configuration design, the use of bath additives and increasing the level of agitation used as well as increasing the pH of the solution.

The fact that accelerated corrosion testing indicated that zinc-nickel-manganese offered a reduction in corrosion resistance when compared to zinc-nickel whereas atmospheric tests showed the opposite to be true shows the danger of relying on accelerated test methods when investigating novel coatings. This discrepancy between test methods seems to be increased when zinc-nickel-manganese is evaluated, due probably to the complex interactions between the passivating manganese and the active zinc components of the ternary alloy. The need to rely on real time exposure tests to give a true indication of the corrosion performance of zinc-nickel-manganese makes it a very difficult, slow process to optimise and investigate. This could preclude its use as a possible cadmium replacement as it may take years to develop a satisfactory coating.

8.3 Discontinuation of cadmium use

Although this research has gone some way towards finding a suitable replacement for cadmium, its replacement on electrical connectors and fasteners is still a long way off. Neither of the coatings investigated provide any inherent lubricity, which they would need if they were going to succeed as replacements for cadmium. They also do not, as yet, have comparable corrosion resistance and although their electrical resistance is satisfactory if the zinc content of the zinc-nickel-manganese coatings is greater than 90%, and their micro-hardness higher, wear and corrosion plus wear properties have not been determined. It may have been better in hindsight to concentrate on only one
method of improving the corrosion resistance and other properties of the available coatings so that a more complete investigation could have been undertaken.

As their electrical characteristics only just meet the requirement for electrical connectors at present, the future may be a problem with the possibility of the electrical resistance requirement getting even more stringent [27]. This would preclude their future use as replacements for cadmium on electrical connectors. It would also exclude the use of cadmium for connectors, forcing the redesigning of connectors to be undertaken. Without being able to use cadmium, or many of the proposed alternatives, there becomes a problem as to what to manufacture connector shells from. If the electrical resistance requirement or the galvanic compatibility requirement were removed it would enable a wider selection of component material to be investigated for use on electrical connector shells, including non-conducting and more noble coatings.
9 Conclusions

9.1 Zinc-nickel

1. It was found possible to electroplate zinc-nickel coatings from a single bath by variation in applied electroplating current density.

2. A novel zinc-nickel electroplating solution containing the complexant TRIS was investigated and found to give nickel contents in the range 3 to 20 atomic % nickel.

3. Electroplating was undertaken on mild steel and 2014-T6 aluminium alloys successfully.

4. Dual layer coatings were produced from a single bath.

5. Electroplating of actual aluminium alloy connector shells with varying compositions of zinc-nickel from a single bath was achieved.

6. The porosity of the coatings was found to increase as the nickel content increased. This porosity was thought to be due to hydrogen evolution and the proximity of the limiting current density during electroplating.

7. The presence of porosity caused accelerated ennoblement of zinc-nickel under immersion conditions leading to non-sacrificial coatings.

8. The presence of porosity also had a detrimental effect on the accelerated corrosion performance of the zinc-nickel coating in neutral salt fog testing.

9. Micro-hardness was found to be greater than for zinc or cadmium electroplate.

10. Electrical resistance measurements showed the zinc-nickel coatings to have a high enough electrical conductivity to meet the requirements for electrical connector shells.

11. Although some progress was made in the use of dual layers, no multilayer systems (with more than two layers) were produced so it was not possible to tell if the use of multilayers with more than two layers would increase the corrosion performance and other properties of the coating enough to justify the increased complexity of the multi-layer electroplating process.
9.2 Zinc-nickel-manganese

1. It was possible to electroplate zinc-nickel-manganese coatings from sulphate based solutions containing either the complexant sodium citrate or TRIS, with higher manganese contents than obtained by other researchers.

2. The nature of the complexant had an effect on the morphology of the coatings with all the zinc-nickel-manganese coatings produced from the citrate containing solutions having a distinct swirly morphology while those electroplated from a TRIS complexed solution did not.

3. The nickel and manganese content could be varied by changing the applied electroplating current density, this made the possible production of multilayers feasible.

4. The zinc-nickel-manganese coatings suffered from low current efficiency and high porosity. This, along with the presence of manganese, caused accelerated ennoblement and hence non-sacrificial behaviour. The low current efficiency was thought to be due to hydrogen evolution and could account for the high level of porosity.

5. The corrosion resistance in accelerated testing was poor due to the ennoblement of manganese and the porosity present.

6. Marine exposure tests, however, produced a higher level of corrosion resistance than zinc-nickel, nearly comparable with cadmium.

7. As the manganese content of the alloy was increased the level of corrosion products decreased. Overall, the level of corrosion products was lower than zinc-nickel in both accelerated and non-accelerated tests.

8. Electrical resistance values were comparable with zinc-nickel and just sufficient to meet the current requirements for electrical connectors provided the zinc content in the alloy was greater than 90%.


9.3 Overall as replacements for cadmium

1. Zinc-nickel-manganese offers potential as a replacement for cadmium, but not if only accelerated tests are used for corrosion resistance evaluation.

2. Significantly, more work is required to assess and optimise the coatings performance.
3. Although the use of dual layers was demonstrated, the use of multilayers with more than two layers was not, hence not excluding multilayer coatings as possible replacements for cadmium. However, they do not offer as much potential as cadmium replacements as the use of a third alloying element, combined possibly with the use of multilayers.

4. Perhaps in the long term, one of the more feasible ways to replace cadmium would be to redesign connector shells eliminating the need for either galvanic compatibility or low electrical resistance, making the use of noble coatings and non-conducting coatings a possibility.
10 Recommendations

1. The actual atmospheric corrosion performance of zinc-nickel coatings produced from the TRIS containing solution needs to be evaluated, along with standard zinc, zinc-nickel coatings and cadmium electroplate. This would ascertain whether there is any improvement in corrosion resistance of zinc-nickel when it is not micro-cracked. If the experimental porous zinc-nickel coatings give an increased corrosion resistance compared to commercial non-porous zinc-nickel then there is no need to undertake further solution development to reduce the porosity of the coating. If, however, this does not occur, further solution development would be required.

2. It is recommended that for both zinc-nickel and zinc-nickel-manganese that further solution development is undertaken in an attempt to reduce the level of porosity and hopefully therefore improve the corrosion resistance. There are a number of ways of reducing the porosity of the coatings, these include modification of the solution chemistry to change the position of the composition current density curve and hence reduce the applied current density required to produce a given composition. Another way of perhaps changing the level of porosity is the use of increased agitation, the increase of pH and the incorporation of surface modifying additives to the electroplating bath.

3. In the case of zinc-nickel the use of pulse electroplating from the TRIS complexant solution should be undertaken as this may reduce the porosity without having to change the solution composition.

4. For zinc-nickel-manganese an attempt should be made to increase the current efficiency of the process. This could be achieved by the use of a small quantity of selenic acid within the electroplating bath [31]. Not only would this help to reduce the porosity of the coating, but it may also reduce the production costs.

5. Both zinc-nickel and zinc-nickel-manganese coatings may show an increase in corrosion resistance if they are electroplated in multilayers. This should be investigated.

6. Wear testing in a corrosive environment ought to be undertaken to explore the relationship between the measured micro-hardness and the wear properties of the coatings.
Recommendations

7. Both coatings would make more suitable replacements for cadmium if they possessed some inherent lubricity. It may be possible to achieve this by the co-deposition of other materials to the alloy matrix, such as PTFE.
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Composition and Morphologies of Electrodeposited Zinc-nickel-manganese Coatings

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SUMMARY — A ternary alloy of Zn-Ni-Mn was electrodeposited onto mild steel from a sulphate-citrate bath containing boric and ascorbic acid using both pulse and direct current (DC). The relationships between current density, current efficiency and composition were investigated. Thickness measurements, current efficiency calculations, and compositional analysis using energy dispersive X-ray analysis (EDAX) and SEM characterization, were undertaken. It was possible to produce an alloy containing up to 10% Ni and 6% Mn. The nickel underwent anomalous co-deposition and the manganese regular co-deposition. Both DC and pulse electrodeposition showed an increase in the Mn and Ni percentage as the applied current density was increased. DC electrodeposition tended to produce higher nickel and manganese contents.

INTRODUCTION
Zinc plating is extensively used in the corrosion protection of steel for many structural and general engineering purposes. Coatings are commonly applied by hot dipping, metal spraying or electrodeposition processes. Zinc coatings are comparatively cheap to apply and provide a high level of corrosion protection particularly in marine and rural environments. Zinc is anodic with respect to steel and so provides sacrificial protection when employed as a coating.

Significant improvements to the corrosion performance of electrodeplated zinc have been made through alloying of coatings with additions of nickel1,3, cobalt1 and iron1,4. Electroplating solutions are available commercially and have found applications mainly in the automotive industry. Other alloy systems have been studied, including zinc-manganese4 but to date these have not been developed beyond the laboratory stage.

The zinc-nickel and zinc-cobalt alloy systems suffer from a number of problems, including the formation of white corrosion products1 and de-zincification3,8. The onset of white rust can be delayed by applying a chromate based passivation treatment to the surface of the coating. The loss of zinc from alloy coatings on exposure to a corrosive environment reduces their effectiveness as sacrificial coatings. Zinc-manganese coatings do not suffer from the above problems but are difficult to electrode plate due both to the low current efficiency of the plating solution and its lack of throwing power. Published data indicate that a manganese content of more than 50% is required if significant improvements in corrosion protection are to be achieved8.

Research published in 1985 indicated that the formation of a ternary alloy coating containing zinc, nickel and manganese was feasible1. By alloying zinc-nickel with manganese the problem of de-zincification with exposure time could be alleviated. The presence of manganese should help to counteract the embrittlement of the alloy. The addition of manganese should also help reduce the amount of white corrosion products as manganese forms a dense adherent corrosion product of γ-MnO2. This would be more suitable for aerospace fastener applications. Less manganese should be required to improve the corrosion performance due to the presence of nickel compared to zinc-manganese. This should also increase the efficiency of the process. In addition, the levelling ability should also be improved compared to zinc-manganese due to the presence of nickel1,3, which is well known for its levelling properties.

The aim of this research was to investigate the factors influencing the electrodeposition of a ternary zinc alloy of zinc-nickel-manganese onto steel. In particular the effects of current density and pulse plating on coating composition and morphology have been studied.

EXPERIMENTAL
Coating preparation
Electroplating was carried out using two methods, direct current (DC) electrodeposition and pulse electrodeposition. In this study coatings were electrodeposited onto mild steel coupons, which were first degreased in acetone and then etched in 10% v/v hydrochloric acid (SG 1.18). Immediately prior to plating, the coupons were weighed.

Details of the electroplating bath composition are given in Table I. The bath is primarily a mixture of zinc, nickel and manganese sulphates. Polyoxyethylene sorbitan monolaurate (Tween) was added to help reduce the porosity of the resultant coating and to increase the surface wetting. An antifoaming agent was employed to enable air agitation to be carried out during the plating process. The citrate ions were added to complex the manganese, and ascorbic and
boric acids were used to help stabilise the solution. In order to prevent the precipitation of manganese citrate during the life of the plating bath, additions of hydrochloric acid were made. The low bath pH precluded the use of a zinc anode and instead an inert lead anode was employed.

All electrodeposition was performed galvanostatically. DC electrodeposition was carried out at two current densities, 0.2 A cm\(^{-2}\) and 0.4 A cm\(^{-2}\). Trials conducted at higher current densities were found to produce burnt deposits. Pulse electrodeposition was conducted over a larger current density range of 0.2 A cm\(^{-2}\) to 1.0 A cm\(^{-2}\). A square pulse with an on-time of \(2 \times 10^{-3}\) s and an off-time of \(4 \times 10^{-3}\) s was used. A constant charge of 60 coulombs was applied in all cases to yield a coating thickness of approximately 8 \(\mu m\).

Coating characterisation
Following electroplating, all coupons were re-weighed to enable the weight of coating deposited to be determined. Thickness measurements were carried out using a magnetic current probe with 10 measurements being made per sample over the area of the coupon excluding the extreme edges. At least 9 samples were used for each experimental set. The average standard deviation of the thickness was used to give an indication of the levelling ability of the solution. The microstructures and compositions of selected coated panels were examined using a scanning electron microscope fitted with an X-ray energy dispersive analysis system.

**RESULTS AND DISCUSSION**

Coating appearance
Scanning electron microscope micrographs are shown in Figures 1 and 2 for the pulse plated and DC plated coatings respectively.

Both types of electroplating yield coatings which have a nodular structure. The nodules are irregular in shape and, for pulse electroplating, show a tendency towards a more featureless characteristic at the lower values of current density. For pulse electrodeposition the average nodule size is reduced from \(\sim 25 \mu m\) to less than 3 \(\mu m\) as the current density is increased from 0.2 A cm\(^{-2}\) to 1.0 A cm\(^{-2}\). The number of surface defects and porosity are correspondingly increased. These observations suggest that the deposition is inhibited as the current density is raised, either due to the increasing proximity to the limiting current density or due to the higher levels of both nickel and manganese in the deposit.

The microstructures of the two coatings prepared by DC electroplating are compared in Figure 2. In this case there appears to be only a slight change in average, nodule size with current density. However there is a large change in porosity as the applied current density approaches the limiting current density.

**Effect of current density on coating thickness**
The results of the thickness measurements are given in Figure 3. As can be seen the average thickness was between 6 and 9 \(\mu m\) for all values of current density. The average thickness of the samples pulse electrodeposited showed a decrease as the current density increased, this downward trend with increasing current density was not observed for the DC electroplated samples.

The DC electrodeposited samples showed little or no variation in thickness with current density. This can be attributed to a significant increase in porosity of the DC coatings, which can be observed in the micrographs in Figure 2. This does not occur to the same extent for the pulse electrodeposited coating, hence there is a downward trend in thickness as the current density is increased for the pulse coatings.

The corresponding graph for average standard deviation of the thickness measurements is shown in Figure 4.
For the pulse electrodeposited coatings the average standard deviation of the thickness was low and nearly constant over the entire current density range. The average standard deviation of the thickness measurements for the DC electrodeposited samples increased with increasing applied current density. The cause of this may be the greater porosity and higher level of surface defects present in the coating produced at 0.4 A cm⁻² DC. The rise in average standard deviation could in part be due to the increased proximity to the limiting current density causing some burning at the edges of the samples. The average standard deviation of the thickness measurements was, in all cases, low for a manganese containing alloy. The average standard deviation did not increase as the percentage manganese in the alloy increased (with increase in current density) for the coatings produced using a pulsed electrodeposition. This shows, to some extent, the advantage of adding nickel to the alloy i.e. the levelling is improved.

Influence of current density on electroplatting efficiency

The current efficiency of the electrodeposition process was calculated assuming that as with zinc and nickel, manganese was a two-electron deposition process, using equation 1:

$$CE(\%) = \frac{g_m}{g_t} \times 100 \quad (1)$$

where $CE$ is the current efficiency (%), $g_m$ the actual deposit weight, and $g_t$ the theoretical deposit weight.

The theoretical deposit weight was calculated from equation 2:

$$g_t = \frac{t \times W_e}{F} \quad (2)$$

where $i$ is the current in Amps, $t$ the time of electrodeposition, $F$ the Faraday constant, $W_e$ the chemical equivalent. For a ternary alloy $W_e$ is given by equation 3:

$$W_e = \frac{W_e \times W_e + F_1 \times W_1 + F_2 \times W_2}{F_1 + F_2 + F_3} \quad (3)$$

where $W_e, W_1$, and $W_2$ are equivalent weights of metals 1, 2 and 3 respectively and $F_1, F_2$, and $F_3$ are the fractions of metals 1, 2 and 3 in the alloy ($F_1 + F_2 + F_3 = 1$).

The change in current efficiency with current density is illustrated in Figure 5. For both DC and pulse electroplating the current efficiency decreased with an increase in applied current density. The calculation of current efficiency is probably a better indication of the efficiency of electrodeposition rather than thickness, as this latter is dependent on other coating characteristics such as density and porosity of the coating. The downward trend in current efficiency with increasing current density can be attributed to two factors, firstly the increasing proximity to the limiting current density and secondly the increasing percentage of manganese in the coating producing higher levels of hydrogen evolution. The current efficiencies were, in all cases, lower to the complex nature of the solution used (a complex bath tends to give better levelling than a simple ion bath).

Influence of electroplating current density on alloy composition

The variation of nickel content in the alloy with current density is shown in Figure 6. The maximum percentage nickel was 10%, which is significantly less than the metal ion percentage present within the solution (see Table 1). Clearly, therefore, nickel is exhibiting anomalous co-deposition over the whole current density region studied because this is normally the case when nickel is co-deposited with zinc. The addition of borax acid may also have made the deposition more anomalous with respect to nickel.

For pulse electrodeposition, the nickel content is low and consistent up to 0.4 A cm⁻². It then increases up to a value of 7% for pulse electrodeposition at 1.0 A cm⁻². Pulse electrodeposition was not undertaken at larger values of current density due to the limiting current density being reached. The corresponding plot for DC electrodeposition is very different. The values of nickel content within the alloy were higher for DC electrodeposition than for pulse electrodeposition at the same value of current density. The difference in the nickel content could be due to the different thickness of the diffusion layer and the different effects of the various additives within the electrodeposition solution when they are subjected to the different electrodeposition modes. There may also be localised differences in pH, which would effect the nickel content due to the
hydroxide suppression mechanism, which is thought to be responsible for the anomalous co-deposition of the nickel.

Like nickel the manganese content in the resultant alloy increased with increasing current density. This is illustrated in Figure 7. The electrodeposition however in this case was normal with the more noble zinc being deposited preferentially over all values of current density. Although the nature of the electrodeposition process was different DC electrodeposition still produced higher percentages of manganese than pulse at the same current density values. This suggests that the change in percentage is probably not due to local pH changes as this would only significantly affect the anomalous nickel deposition and not the normal manganese deposition.

CONCLUSIONS
It was possible to produce a zinc alloy coating of zinc-nickel-manganese from a complexed acid citrate bath using both DC and pulse electrodeposition containing up to 10% nickel and 6% manganese. The percentage of both nickel and manganese increased with increasing current density although the nature of the electrodeposition process was different for each of these metals.

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Appendix

CONCLUSIONS
It was possible to produce a zinc alloy coating of zinc-nickel-manganese from a complexed acid citrate bath using both DC and pulse electrodeposition containing up to 10% nickel and 6% manganese. The percentage of both nickel and manganese increased with increasing current density although the nature of the electrodeposition process was different for each of these metals.

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Appendix