Microstructural characterisation of creep tested 9CR welds for MarBN steel

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MICROSTRUCTURAL CHARACTERISATION OF CREEP TESTED 9CR WELDS FOR MARBN STEEL

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ABSTRACT
Creep properties of 9Cr heat resistant steels can be improved by the addition of boron and nitrogen to produce martensitic boron-nitrogen strengthened steels (MarBN). The joining of this material is a crucial consideration in the material design since welds can introduce relatively weak points in the structural material. In the present study, creep tests of a number of MarBN weld filler metals have been carried out to determine the effect of chemistry on the creep life of weld metal. The creep life of the weld metals was analysed, and the evolution of creep damage was investigated. Significant differences in the rupture life during creep have been observed as a function of boron, nitrogen and molybdenum concentrations in the weld consumable composition. Although the creep lives differed, the particle size and number in the failed creep tested specimens were similar, which indicates that there is a possible critical point for MarBN weld filler metal creep failure.

INTRODUCTION
In order to achieve higher efficiency in thermal power plant, there is a drive for higher temperature and higher pressure operation. This increase in material demand requires that materials are developed which can withstand these aggressive environments. Martensitic steels strengthened with boron and nitrogen (MarBN, 9Cr-3W-3Co-VNbBN), have the potential to operate at these demanding conditions because the addition of boron and nitrogen enhances the creep strength of steel to satisfy the high temperature and pressure operational requirements [1]. Understanding the joining of MarBN steels is crucial for the future successful application of these materials as welds can introduce relatively vulnerable areas within the structures [2], for example, welded joints of martensitic 9-12%Cr steels are especially prone to premature cracking during service [3]. A lot of research in this area focuses on the mechanism of heat affected zone (HAZ) failure during long term service [3,4,5,6]. Currently there is no commercial weld consumable specifically for MarBN steels therefore, in the present study, the properties and microstructures of weld metals design for joining MarBN have been examined.

In order to identify the most suitable filler material, it is necessary to increase the understanding of the relationship between the creep properties of MarBN weld filler metal and its corresponding microstructural changes during creep tests and exposure to high temperatures. The distribution and quantity of M23C6 carbides and fine MX-type carbonitrides in the martensitic matrix are very effective in the stabilisation of a variety of boundaries during creep exposure [7,8], whilst the formation of intermetallic Fe5(Mo,W) Laves phase during creep exposure is generally considered detrimental to the creep properties [9]. The formation of boron nitride (BN) particles removes B and N from solution and reduces the strengthening effect of both B and N simultaneously [10]. Therefore, the formation of BN can also be detrimental to the mechanical properties of weld metal.

In this paper, the microstructural evolution of the weld metals has been examined as a function of time at temperature. The purpose of this research is to optimise the chemical composition of weld
filler material for joining MarBN steel both from a creep performance point of view and on the microstructural level. From the results obtained, the linkage between the creep properties of MarBN weld metal and its corresponding microstructural changes during creep exposure is discussed.

EXPERIMENTAL

In the present study, there are five MarBN-based weld consumable compositions with minor differences in boron, nitrogen, nickel and molybdenum which were examined to clarify the effects of these elements on the properties and microstructure of the weld metal. The descriptions of these five weld consumables are shown in Table 1. Two core wires, a P92 commercial wire and a bespoke alloy wire, were used to give different weld metal compositions. The bespoke alloy wire is a MarBN based composition. The P92 weld wire is high in nickel and molybdenum compared with the bespoke wire. The base plates used were CMn steel but the joints were buttered with the relevant electrodes to reduce dilution from the base metal.

Two comparisons can be made among these weld consumables. One comparison was made between V1, V3 and V4b to clarify the effects of boron and nitrogen in the weld consumable on the creep properties of the weld metal. The other comparison was made between V4a and V4b to determine the functions of nickel and molybdenum on the creep properties of weld metal.

Table 1: The descriptions of MarBN weld consumable composition

<table>
<thead>
<tr>
<th>Weld consumable No.</th>
<th>Core wire</th>
<th>Descriptions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Variant 1 (V1)</td>
<td>Bespoke alloy wire</td>
<td>V1</td>
</tr>
<tr>
<td>Variant 2 (V2)</td>
<td>P92</td>
<td>V1 - high Ni, Mo, N, low B</td>
</tr>
<tr>
<td>Variant 3 (V3)</td>
<td>Bespoke alloy wire</td>
<td>V1 - nil B</td>
</tr>
<tr>
<td>Variant 4a (V4a)</td>
<td>P92</td>
<td>V1 - high Ni, Mo, N</td>
</tr>
<tr>
<td>Variant 4b (V4b)</td>
<td>Bespoke alloy wire</td>
<td>V1 - high N</td>
</tr>
</tbody>
</table>

Two, differently stressed creep tests were carried out on these weld metals. Before testing, the weld metals received a post-weld heat treatment (PWHT) at 760°C for 2 hours prior to the creep test bars being prepared longitudinally from the weld metals only, as the schematic diagram shown in Fig. 1 and images shown in Fig. 2 illustrate. The creep test conditions of these weld metals are shown in Table 2.

![Figure 1: Schematic diagram showing the origin of creep test specimens](image-url)
Table 2: The creep test conditions of MarBN weld metals

<table>
<thead>
<tr>
<th>Creep test (longitudinal)</th>
<th>Temperature(°C)</th>
<th>Stress (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Short test with relatively high-stress</td>
<td>675</td>
<td>142</td>
</tr>
<tr>
<td>Long term test with relatively low-stress</td>
<td>675</td>
<td>127</td>
</tr>
</tbody>
</table>

In addition to creep testing, samples of the weld filler material were also aged in a dry-air furnace at the same temperature as the creep test, 675°C, for up to 5000 hrs, to investigate the microstructural changes with an absence of strain.

In order to examine the microstructure of both the creep tested samples and the laboratory isothermally aged weld material, samples were cut using a precision cutting saw, mounted in electrically conducting Bakelite, ground and polished to a 1 µm surface finish followed by polished with colloidal silica. Samples were then examined using a range of analytical tools including Scanning Electron Microscopy (SEM), Focused Ion Beam (FIB) and Transmission Electron Microscopy (TEM) to reveal the significant changes in the material under strain/applied stress.

RESULTS AND DISCUSSION

Creep test results

The creep test results for all weld metal compositions are shown in Fig.3. V4b gives the best creep strength, especially at the relatively low stress of 127 MPa, being the best candidate amongst all five weld consumable compositions. The creep rupture life of V4b was almost 10 times and 5 times longer than V2 under 127 MPa and 142 MPa applied stresses, respectively.
Significant differences in the creep life can be observed as a function of chemistry additions in the weld consumable. In order to determine the reasons behind this difference, the microstructures of the creep tested welds were examined.

**Microstructure recovery during creep tests**

EBSD image quality maps taken from both the gauge length and the head portions of the creep-tested samples show the microstructural changes caused by strain applied during creep.

A recovered deformed structure (i.e. an equiaxed structure) with a grain size of less than 5 μm can be seen in the region very close to the point of fracture (Fig.4(a)) whereas, a recovered
deformed structure which has experienced some grain growth can be observed in the region 2 mm away from the fracture surface (Fig.4(b)). In the un-stressed head of the test specimen a lath-like martensitic structure was found (Fig.4(c)).

The boundary length in each area (563.2 µm²) has been quantified, as shown in Fig.5, where a low angle boundary is defined as an orientation difference of 2° to 15°, which indicates the presence of a sub-grain boundary, and a high angle boundary measuring 15° to 180° representing lath boundaries, block boundaries and prior-austenite grain boundaries. The macro images of failure interfaces for these three creep tested variants are also shown in Fig.5. Both the low and high angle boundary length per area decrease from the head portion to the fracture surface due to the applied creep strains promoting recrystallisation and matrix recovery in the gauge length. In the 127 MPa creep tested V1 and V3, the low angle boundary density near to the fracture surface is high since the plastic deformation is significant in this region, as indicated by the macro image which shows a relatively ductile failure.

Precipitation behaviour during creep testing

Four types of precipitates were investigated as part of this study: M₂₃C₆ carbide, Laves phase, fine MX particles and boron nitride (BN). The presence of certain types of these precipitates can strengthen the materials by means of dispersion strengthening (e.g. MX) and microstructure stabilisation whereas some of these precipitates are reported to be detrimental to the mechanical properties (e.g. Laves) [7,8,9]. The effect of precipitation strengthening is approximately inversely proportional to the particle size[11]. This investigation considered possible links between the creep property of MarBN weld metal with the particle precipitation behaviours.
**M₂₃C₆ carbide precipitation behaviour**

A quantitative analysis of M₂₃C₆ carbides and Laves phase precipitate behaviours from the near-fracture region to the head portion was carried out and the results are plotted in Fig.6(a) and (b).

As shown in Fig.6(a), the number of M₂₃C₆ carbides in an area of 563.2 μm² changes from 340 in the near-fracture region to 1090 in the head portion, while the average size of the M₂₃C₆ carbides has 100 nm difference varying from 255 nm in the near-fracture region to 155 nm in the head portion. A continuously decreasing population of M₂₃C₆ particles and increasing M₂₃C₆ size can be seen from the head to the fracture surface. This means that there are fewer M₂₃C₆ carbides overall and they have larger size in the gauge length, which results in a reduction of their pinning effect on the stabilisation of a variety of boundaries which will eventually lead to creep failure. The differences in M₂₃C₆ carbide precipitation behaviour along the gauge length also indicates that the applied creep strains promote the coarsening of M₂₃C₆.

Comparisons of M₂₃C₆ carbide precipitation behaviour in the 8 creep tested specimens can be made to reveal the linkage between M₂₃C₆ precipitation behaviour and the material’s creep properties.

**Figure 6:** Quantitative analysis of (a) M₂₃C₆ carbides and (b) Laves phases along the gauge length and head portion in 127 MPa creep tested V3
Figure 7: Summaries of $M_{23}C_6$ carbide precipitation behaviour in all 8 creep tested specimens: (a) and (c) are for 142 MPa creep tested variants; (b) and (d) are for 127 MPa creep tested variants. The corresponding aged variants here means the closest-rupture-time aged variants.

Despite the vastly different creep rupture times for these weld metal variants (Fig.3), the size distribution of $M_{23}C_6$ carbides in the failed samples was seen to be similar between these variants in both the gauge and head portions, as shown in Fig.7. It also can be seen that the size of $M_{23}C_6$ carbides precipitated in the heads of the creep tested samples is similar to the sizes in the aged samples. Li [12], Hu et al. [13], Hasegawa et al. [14] and Yan et al. [15] reported that $M_{23}C_6$ carbides with 60-200 nm in size were found in sub-grain structures in varieties of 9-12 Cr steels during thermal or creep exposure. It was also reported in [16] that $M_{23}C_6$ carbides with a size of 65-200 nm can effectively pin the lath boundaries and then improve the stability of grains in high Cr ferritic steel. The size of $M_{23}C_6$ carbides in the gauge length for each of the creep tested samples reported here are all around 200 nm at the point of fracture which indicates that the $M_{23}C_6$ carbides may have lost their pinning effect under the applied creep strains. The numbers of $M_{23}C_6$ carbides in the gauge portions are all around 500 per area (563.2 $\mu$m$^2$). The similar population and size distribution of $M_{23}C_6$ carbides in the gauge lengths of the creep tested specimens suggests that there is a possible critical point of $M_{23}C_6$ carbide evolution for MarBN weld metal for creep failure. From the data presented here, this critical point may be ~500 $M_{23}C_6$ carbides per 563.2 $\mu$m$^2$ area with a size of ~200 nm. It has been widely reported [1,7,8,9,10,16] that the addition of boron can suppress the $M_{23}C_6$ coarsening rate and therefore improve creep properties. Therefore, one effective way to extend the creep rupture time is to slow the coarsening rate of $M_{23}C_6$ carbide which may include such measures as adding boron to weld consumable compositions.
**Laves phase precipitation behaviour**

The Laves phase precipitation behaviour from the fracture surface to the head portion was analysed and is presented in Fig.8 and Fig.6(b). In the 127 MPa creep tested V3, the population and size distribution of Laves phase within the gauge and head are similar. The size of Laves phase varies from 250 nm to 300 nm in the creep exposed weld metal. The presence of large Laves phase during creep exposure is harmful to the creep properties [17], since the formation of Laves phase could decrease the solid solution strengthening effect due to the consumption of dissolved W and Mo [18]. It was also reported in [18] that the formation of Laves phase is a function of the W and Mo concentrations. It was reported by Fujita [19] that the molybdenum equivalent ($\text{Mo}_{\text{equi}}$) given by $(\text{Mo} + 1/2\text{W})$ is required to be maintained at 1.2 to 1.5 wt.% to optimise the long term creep rupture strength and toughness, because too much Mo and W promote the formation of $\delta$-ferrite and Laves phase [20]. A comparison of Laves phase area fraction in the 8 creep tested specimens was made and is shown in Fig.8.

![Figure 8: A summary of Laves phase precipitation behaviours in creep tested specimens: (a) 142 MPa creep tested variants; and (b) 127 MPa creep tested variants](image)

There is more Laves phase in V4a than in the others as it was produced by using a P92 weld core wire, which is high in Mo concentration. The molybdenum equivalent value in V4a is 1.7 wt.%, outside of the optimised range suggested in [19]. In V1, V3 and V4b, there is a relatively low concentration of Mo. The molybdenum equivalent values in V1, V3 and V4b are 1.305 wt.%, 1.372 wt.% and 1.370 wt.% respectively which are all within the suggested optimum range. Comparing the molybdenum equivalent value to the Laves phase precipitation behaviour, it can be seen in Fig.8 that a higher Laves phase area fraction was found in V4a while there are fewer Laves phase precipitates in V1, V3 and V4b. As a conclusion, the high Mo concentration in the weld consumable promotes Laves phase precipitation during creep exposure which may lead to a reduction in creep performance of the weld metal which is in agreement with the creep test results.

**Fine MX-type particle precipitation behaviour**

The chemistry distribution of $\text{M}_{23}\text{C}_6$ carbides and Laves phase in all creep tested variants showed consistency, however, this was not the case for the MX-type precipitates. The chemistry information from the MX-type precipitates in both the near-fracture and head portions is shown...
in Fig. 9. The ternary diagram in each area was created based on EDS analysis of more than 100 particles per sample.

<table>
<thead>
<tr>
<th>Near fracture surface</th>
<th>Head Portion</th>
</tr>
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<tbody>
<tr>
<td>127 MPa creep tested variant 1</td>
<td></td>
</tr>
<tr>
<td>127 MPa creep tested variant 3</td>
<td></td>
</tr>
<tr>
<td>127 MPa creep tested variant 4a</td>
<td></td>
</tr>
<tr>
<td>127 MPa creep tested variant 4b</td>
<td></td>
</tr>
</tbody>
</table>

**Figure 9:** A summary of chemistry distribution of MX-type precipitates in 127 MPa creep tested variants

More Nb-enriched MX precipitates are present in creep tested V1 and V3, while more V-enriched MX precipitates were observed in V4a and V4b, which agrees with the equilibrium prediction as shown in Fig. 10. The equilibrium prediction was produced by using Thermo-Calc 4.1 software with the database TCFE version 7.0. It can be seen in the equilibrium prediction that there is
virtually no Niobium Carbide (NbC-MX) predicted in V4a and V4b, and more Vanadium Nitride (VN-MX) than V1 and V3. The presence of more VN-MX type precipitates in V4a and V4b indicates that the higher nitrogen content in the weld consumable promotes the formation of fine VN-MX precipitates.

The mass percentage of MX (VN+NbC) in V2, V4a and V4b are all predicted to be around 0.3% which is higher than that in V1 and V3, 0.2%. The more MX carbonitrides precipitated in the weld metal can provide a pinning effect on dislocation motion in the martensitic laths during creep exposure [15] and result in lowering the dislocation density in martensitic lath and subgrains [15]. In addition to the MX prediction, the Laves phase prediction in these weld metals also shows agreement with experimental observation. More Laves phase is predicted in V2 and V4a because there is more Mo in their compositions.

**Figure 10:** Comparison of varies precipitates equilibrium prediction at 675ºC among all five weld filler metals

MarBN steel is strengthened by a combination of boron strengthening, nitrogen solid solution strengthening and precipitation strengthening by the finely dispersed nitrides [7,10,16]. The formation of boron nitride (BN) removes the strengthening effect of both the boron and nitrogen simultaneously and, therefore, the presence of BN in the weld metal could be harmful to its creep properties. The experimental observations suggest that there is no BN formation in all weld variants studied, since the heat treatments and creep testing carried out are below the temperature that it is stable [10]. A higher nitrogen concentration in the weld consumable composition shows some benefit to its creep life (perhaps through the increased number of MX particles or particle size control). However, an increase in nitrogen concentration introduces an increased possibility of BN formation, therefore attention needs to be paid to the presence of BN in the weld metal when optimising the nitrogen concentration in weld consumable.
CONCLUSIONS

The creep properties of MarBN-based weld metals have been discussed with respect to their microstructural evolution and chemistry in the present study. The microstructure, especially the precipitation behaviour of $\text{M}_2\text{C}_6$ particles, behaved in a similar manner amongst all creep tested weld variants in the gauge portion, with failure occurring when the $\text{M}_2\text{C}_6$ particles reached a size of $\sim 200$ nm and a count of $\sim 500$ per area ($563.2 \, \mu\text{m}^2$), which indicates there is a critical point of $\text{M}_2\text{C}_6$ precipitation for creep failure in MarBN. A higher Mo concentration in the weld consumable through the use of a P92 weld core wire strongly promotes Laves phase precipitation, which may cause a loss of creep strength. No BN has been observed in creep tested or furnace-aged weld metals. A higher nitrogen concentration in the weld metal contributes to the formation of V-rich MX precipitates which benefits the creep life of the weld metal. The applied creep strain promotes the formation of fine MX growth and $\text{M}_2\text{C}_6$ carbide coarsening in the weld metal, but it has little effect on the Laves phase precipitation.

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REFERENCES


