Influence of Ru Addition on Microstructure, Creep and Rupture Properties of Nickel based DS Superalloy

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Abstract

The effect of Ru addition on the microstructure, creep and rupture properties of the directionally solidified (DS) Ni based superalloy, DMD4 has been evaluated. The microstructural characterization of the alloys has been carried out using scanning electron microscopy and electron microprobe analysis. The morphology of $\gamma'$ precipitates was more cuboidal in the Ru-bearing superalloy as compared to the Ru-free superalloy. Further, Ru addition was found to increase the volume fraction of $\gamma'$ precipitates from 51% to 54% and decrease the width of the $\gamma$ channels from 90nm to 76nm. Creep and rupture properties, evaluated at stress/temperature combinations ranging between 90-500 MPa / 850-1100°C, showed significant improvement in rupture life of the Ru containing superalloy over that of the Ru free alloy, at all combinations of stress and temperature. Such enhancement in the rupture life can be attributed to the formation of a well elongated rafted structure and the inherent higher volume fraction $\gamma'$ precipitates in the Ru-containing alloy. Larson-Miller plots derived from the creep tests suggest that addition of Ru enhanced the temperature capability of the alloy by about 11°C for 100hrs life at 140MPa.

Keywords: Nickel base superalloy; directionally solidified; ruthenium; creep properties; rafting

1. Introduction

Directionally Solidified (DS) Nickel based columnar grained and single crystal super alloys are used in turbine blades and vanes at elevated temperature. The strength possessed by superalloy at elevated temperature is primarily attributed to (i) solid solution strengthening by high concentration of solute elements such as cobalt, chromium, and refractory solute elements such as molybdenum, tungsten, rhenium, tantalum, ruthenium etc. as well as (ii ) precipitation strengthening imparted by dispersion of ordered (L1$_2$) intermetallic particles of Ni$_3$(Al, Ta, Ti) ($\gamma'$) in the Ni based alloy matrix ($\gamma$) [1]. The continuing demand for developing increased temperature capability and improved creep resistance in Ni based superalloys has led to alloys with increasing amount of refractory alloying additions. The total refractory elements contents have increased from 14% in 1st generation to more than 20% in third generation alloy [2]. If the concentration of refractory elements is too

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large topologically close pack (TCP) phases can form during long term exposures to elevated temperature [3]. The TCP phases along with casting defects are known to be the potential sites for damage initiation during creep [4]. Moreover formation of TCP phases cause considerable degradation of solution strengthening effect because of the depletion of the solid solution strengthening elements such as Mo, Re, Cr, W etc [4] in the matrix. During last few years the addition of Platinum group metal such as Ruthenium (Ru) has been reported to (i) increase the micro structural stability during thermal exposure and suppress the formation of TCP phases [3, 5], (ii) Improve the creep strength [5], (iii) improve the liquidus temperature [6] and (iv) high temperature corrosion resistance [7].

However the effect of Ru on the partitioning behavior of different alloying elements in Ni based superalloys is still controversial. In the present investigation a third generation DS superalloy DMD4, developed at the Defence Metallurgical Research Laboratory [8] has been selected to study the influence of Ru addition on microstructures, creep and rupture behavior of this alloy. The high temperature creep properties of DS superalloys are influenced by factors such as volume fraction and morphology of $\gamma'$ [9-10], rafting behavior of $\gamma'$ precipitates [10], formation of TCP precipitates [5] etc. Detailed studies on some of these aspects were carried out to establish the role of Ru during high temperature application of DMD4.

2. Materials and experimental procedures

The alloys used in the present work were prepared in the form of 5 kg ingot, and subsequently, DS rods of 12mm diameter and 160mm length were processed in a vacuum induction melting cum directional solidification furnace using a withdrawal rate of 24cm/h under high thermal gradient. The chemical compositions of both the alloys are shown in Table 1. The as cast rods were subjected to solutionizing and aging heat treatments in a vacuum heat treatment furnace using the schedule shown in Table 2. For both the alloys creep experiments were carried at stress and temperature ranges of 90–500MPa and 850–1100°C, respectively. The microstructures of as-cast, heat treated and creep-ruptured samples were analyzed by optical microscope (OM), scanning electron microscope (SEM) and electron probe micro analyzer (EPMA). Samples for microstructure examination were prepared by standard metallographic procedures with an etchant of 10 ml HCl, 10 ml HNO₃, 0.3gm molybdic acid and 15 ml H₂O. The amount and the size of $\gamma'$ were measured using image analysis software.

<table>
<thead>
<tr>
<th>Compositions</th>
<th>Chemical Analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>DMD4</td>
<td>Cr 3.02 Co 7.65 Ru - W 5.75 Re 6.10 Nb 0.35 Ta 6.78 Hf 1.12 Al 5.4 B 0.016 C 0.1 Ni Bal O &lt;10ppm N &lt;10ppm</td>
</tr>
<tr>
<td>DMD4R4</td>
<td>Cr 3.00 Co 7.62 Ru 3.2 W 5.74 Re 6.08 Nb 0.34 Ta 6.45 Hf 1.11 Al 5.5 B 0.015 C 0.1 Ni Bal O &lt;10ppm N &lt;10ppm</td>
</tr>
</tbody>
</table>

Table 2. Heat treatment schedule.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Solution heat treatment</th>
<th>First ageing heat treatment</th>
<th>Second ageing heat treatment</th>
<th>Third ageing heat treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td>DMD4</td>
<td>1290°C/15min → 3.5°C/h to</td>
<td>1150°C/6h/GFQ</td>
<td>870°C/20h/GFQ</td>
<td>760°C/30h/GFQ</td>
</tr>
<tr>
<td>DMD4R4</td>
<td>1310°C→1310°C/1.5h/GFQ</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

GFQ stands for gas fan quenching

3. Results and discussion

3.1. Microstructures of as cast and heat treated alloys

Typical optical micrographs depicting microstructures observed on transverse sections of as cast DMD4 (Ru free alloy) and DMD4R4 (with 3.2%Ru) alloys, are shown in Fig.1 (a) and (b), respectively. It is possible to see
severely cored or segregated dendrite morphology in both the alloys with formation of γ/γ’ eutectic regions at the inter-dendritic portions. The chemical composition of dendrite core (DC), secondary dendrite arm (SDA) and interdendritic regions (IDR) was obtained by quantitative microanalysis with the help of WDS on EPMA. Results obtained from EPMA analysis have been analyzed by calculating the partition coefficient (PC), which is defined as \( \approx \frac{[\text{wt}\%\text{DC} + \text{wt}\%\text{SDA}]}{2(\text{wt}\%\text{IDR})} \) \[11-12\] and its value for each alloying element are shown using bar charts in Fig. 2. It can be seen from the Fig. 2 that the element segregation existed during the solidification process of the alloys. In addition Fig. 2 also suggests: (i) segregation of alloying element such as W and Re at DC and depletion those element in IDR (PC>1), (ii) Enrichment of both Al and Ta at IDR (PC<1) and their depletion in other locations and (iii) very weak partitioning of Cr, Co and Ru (in DMD4R4) in DC region (PC<1). Figure 2 also indicates that Ru does not have strong effect on segregation behaviour of other alloying elements in superalloy during directional solidification. These observations are in reasonable agreement with the result reported earlier for Ru bearing and Ru free superalloys [2, 13].

![Fig.1. As cast optical micrograph of transverse section: (a) DMD4 and (b) DMD4R4.](image)

![Fig.2. Partitioning coefficient of as cast alloy measured using EPMA.](image)

The solutionizing heat treatment (as per Table 2) was performed to dissolve coarse, primary as well as eutectic γ’ and to reduce the degree of chemical segregation caused by partitioning of some of the elements to DC, SDA and IDR. Solutionized samples are subjected to ageing heat treatment in order to get best combination of volume fraction, size, morphology and distribution of γ’ precipitate phase since all these parameters are crucial for the high temperature creep properties of the alloys[9-10]. Typical microstructures of two investigated alloys after being aged at 1150°C for 6hrs are shown in Fig. 3 and Fig. 4. The morphology of γ’ precipitates has been found to be more cuboidal (Fig. 4) in Ru bearing alloy as compare to Ru free alloy (Fig. 3). It has been reported that Ru partitioned preferentially to the matrix [14], resulting in more negative lattice misfit \( \delta = (a_{\gamma’} - a_{\gamma})/a_{\gamma}, \) which is responsible for better cuboidal precipitates after ageing [15]. Furthermore the volume fraction of γ’ precipitates is increased while the γ channel width is decreased under the influence of Ru addition. The average γ’ volume fraction in DMD4 is 51% and it has increased to 54% in DMD4R4. In addition the average width of γ channel in the Ru containing alloy is 76nm which is about 84% (90nm) of that of Ru free alloy.
3.2. Effect of long term thermal exposure

Typical microstructures in the dendritic core of DMD4 and DMD4R4 after being exposed at 1100°C for 1200hrs are shown in Fig. 5 and Fig. 6 respectively. Figure 5 reveals the presence of needle-like TCP precipitates in DMD4 (marked by arrows); EDS microanalysis in combination of SEM examination have shown that needle precipitates are enriched in Re and W. In addition to that a limited amount of TCP precipitates were found to form in DMD4 alloy even after 400hrs of exposure at 1100°C. The microstructures of alloy DMD4R4 have not shown any evidence of needle like phases (Fig. 6). The result suggested that addition of Ru suppress the TCP phase formation in the investigated superalloys. This observation agrees with the result of earlier reports in literature [3, 5]. It has been shown in course of earlier studies that formation of TCP precipitates is detrimental to mechanical properties as its formation is associated with depletion of substitutional solute atoms, disruption of rafted structure of $\gamma'$ precipitates, and high stress concentration at TCP-$\gamma'$ interfaces [16]. Hence better long term high temperature performance is expected from Ru containing alloy DMD4R4 than that of the Ru free alloy. Furthermore comparison of microstructures, shown in Fig. 5 and Fig. 6 clearly indicates that the coarsening behavior of $\gamma'$ varies with addition of Ru. Without application of any stress a significant amount of rafts have been observed in Ru containing superalloy on thermal exposure at 1100°C for 1200hrs (Fig. 6). This observation suggests that rafting tendency of DMD4R4 has been increased due to addition of Ru.

3.3. Creep and stress rupture behaviour

The results obtained from the accelerated creep tests carried on the DMD4 and DMD4R4 alloys are shown in Table 3. A detailed examination of creep data leads to following inferences: (i) at all combinations of stress and temperature the alloy DMD4R4 shows significantly higher stress rupture life as compare to DMD4, (ii) minimum creep rates, which are lower by an order magnitude for DMD4R4 than DMD4 at all investigated
creep conditions. As the load increases from 138MPa to 170MPa at 1038°C, the minimum creep rate increases for both the alloys. However the difference in minimum creep rates between DMD4R4 and DMD4 is maintained, (iii) furthermore the addition of Ru has improved the 1% creep life of DMD4R4 as compare to DMD4.

A plot depicting the variation of stress with Larson-Miller parameter (LMP) for the investigated DMD4 and DMD4R4 alloys is shown in Fig. 7 along with results obtained for two other commercial DS Ni based superalloys including CM247LC and CM186LC [17] which are known to be comparable rupture strength. Comparison of these plots indicates that addition of Ru enhanced the temperature capability of the alloy by about 11°C for 100hrs life at 140MPa as compared to Ru free alloy.

Typical microstructures from gauge sections (parallel to stress axis) of DMD4 and DMD4R4 tested at 1100°C/90MPa, are shown in Fig. 8 and Fig. 9 respectively. For both the alloys microstructures reveal the evidence of coarsening of precipitates in a direction transverse to the applied stress (applied stress direction marked on the figures), as expected for the N-type rafts [18]. The formation of such rafts is known to occur by growth of precipitates perpendicular to the direction of stress followed by coalescence [18].

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**Table 3. Results for creep tests and termination density calculation.**

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Temp. (°C)/ Stress (MPa)</th>
<th>Time for 1% creep (h)</th>
<th>Minimum creep rate (/h)</th>
<th>Rupture life (h)</th>
<th>Rupture strain (%)</th>
<th>Average termination density (No of termination X 10⁹/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DMD4</td>
<td>1100/90</td>
<td>185</td>
<td>2.19X10⁻⁴</td>
<td>354</td>
<td>8.1</td>
<td>540</td>
</tr>
<tr>
<td></td>
<td>1038/138</td>
<td>30</td>
<td>1.48X10⁻⁴</td>
<td>424</td>
<td>27.8</td>
<td>750</td>
</tr>
<tr>
<td></td>
<td>1038/170</td>
<td>5</td>
<td>1.8 X 10⁻³</td>
<td>72</td>
<td>26</td>
<td>950</td>
</tr>
<tr>
<td></td>
<td>982/240</td>
<td>17</td>
<td>1.36 X 10⁻³</td>
<td>130</td>
<td>28.7</td>
<td>1760</td>
</tr>
<tr>
<td></td>
<td>850/500</td>
<td>32</td>
<td>8.4X10⁻⁴</td>
<td>232</td>
<td>21.4</td>
<td>Not rafted</td>
</tr>
<tr>
<td>DMD4R4</td>
<td>1100/90</td>
<td>380</td>
<td>1.67X 10⁻⁵</td>
<td>655</td>
<td>13.4</td>
<td>205</td>
</tr>
<tr>
<td></td>
<td>1038/138</td>
<td>180</td>
<td>5.47 X 10⁻⁵</td>
<td>550</td>
<td>11.11</td>
<td>212</td>
</tr>
<tr>
<td></td>
<td>1038/170</td>
<td>20</td>
<td>1.8 X 10⁻⁴</td>
<td>219</td>
<td>14.1</td>
<td>350</td>
</tr>
<tr>
<td></td>
<td>982/240</td>
<td>50</td>
<td>2.3 X 10⁻⁴</td>
<td>266</td>
<td>8.62</td>
<td>720</td>
</tr>
<tr>
<td></td>
<td>850/500</td>
<td>73</td>
<td>1.3 X 10⁻⁴</td>
<td>517</td>
<td>11.98</td>
<td>Not rafted</td>
</tr>
</tbody>
</table>

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Fig.7. Plot showing variation of stress with LMP.
The directionally coarsened precipitates reduce the degree of continuity of the matrix in vertical direction; as a result dislocation climb is restricted around the $\gamma'$ precipitates, hence creep life of superalloy increases with degree of rafting behavior. The degree of rafting behavior of investigated alloys were quantified by calculating the average termination density, which represents physically the average number of terminations of the $\gamma'$ lamellae per unit area of micrograph, according to procedure established by Wall et al [19]. The termination densities of both the alloys are listed in Table 3 for four different creep conditions. It should be noted that for all the creep conditions the average termination densities decreased from DMD4 to DMD4R4 by more than 50 to 70%, and it is suggested that the degree of rafting behavior is increasing under the influence of Ru addition and hence at all combinations of stress and temperature the creep rupture life of Ru containing superalloy was significantly higher as compare to Ru free alloy. In addition to that higher volume fraction of $\gamma'$ in the alloy DMD4R4 as compared to alloy DMD4 is also responsible for better structural hardening induced by $\gamma'$ precipitates and hence better creep life of Ru containing alloy.

![Fig.8. Rafted microstructure in DMD4, 1100°C/90MPa.](image)

![Fig.9. Rafted microstructure in DMD4R4, 1100°C/90MPa.](image)

4. Conclusions

- Ru is a weak segregation element, and it has no effect on partitioning behavior of other alloying elements in superalloy during solidification.
- Ru addition improved the volume fraction of $\gamma'$ and reduced the $\gamma$ channel width along with addition Ru also improved the morphology of $\gamma'$.
- Additions of Ru improved microstructural stability at high temperatures by hindering the formation of needle-like TCP phases.
- 3.2wt. % Ru addition significantly improved the stress rupture properties of the alloy
- Ru addition makes the raft structures more complete and regular.

Acknowledgement

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