On the effect of boron on the mechanical properties of a new polycrystalline superalloy

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Abstract. Boron is used as a grain boundary strengthenener in the nickel-based superalloys, but the reasons for its effect and the optimum quantities which need to be added are not well understood. Recently, some of the authors have developed a new corrosion-resistant single crystal superalloy for power generation applications which has a good balance of mechanical properties and resistance to environmental degradation. Here, this same alloy system is studied but in the polycrystalline state with additions of boron and carbon. The influence of boron on creep behaviour has been quantified and rationalised, with an emphasis on the grain boundary phase transformations which occur. NanoSIMS is utilised to investigate the segregation of boron at grain boundaries, with SEM used to characterise the effect of boron on the precipitation of Cr23C6 type carbides at grain boundaries. When the boron content increases, the agglomeration of M23C6 carbides at grain boundaries is inhibited. Uniformly distributed discrete M23C6 carbides are observed at higher boron content, whereas a deleterious film of M23C6 along the grain boundaries arises as the boron concentration is reduced. Boron promotes also the formation of γ’ layers at the grain boundaries.

1. Introduction

Nickel-based superalloys play a pivotal role in the performance of industrial gas turbines (IGTs). Over the last few decades, many improvements have been made to their microstructure and as a consequence in many instances conventional casting has been replaced by directional casting and in many cases by single crystal superalloys. However, polycrystalline superalloys are still utilized effectively as components on hot sections of IGTs, such as guide vanes, where single crystal alloys cannot be cast due to their complicated geometries. Therefore, grain-boundary strengthening is often needed in these materials.

Boron, along with carbon, is known to promote grain boundary strengthening, and it is the focus of this paper. However, the mechanism through which boron improves the grain boundary strengthening of conventional cast superalloys remains highly controversial. Various strengthening mechanisms were proposed; among them the most popular include the increase of boundary interfacial energy [1,2] and the improvement of the grain boundary cohesive strength. Moreover, it has been suggested that the segregation of boron at grain boundaries may fill vacancies residing there, thereby the grain boundary diffusivity can decrease. As a consequence, as the diffusivity at the grain boundaries decreases, the rate of void formation decreases. Simultaneously the occurrence of γ’ denuded zones is retarded, so that the creep properties are improved [1].

Besides these mechanisms, it was proposed that minor additions of boron are advantageous on creep life and ductility by decreasing the agglomeration of M23C6 carbides at the grain boundaries during protracted service exposures or heat treatment processes [1,3–6]. It is well known that a continuous layer of M23C6 along the grain boundaries serves as a crack initiation site, since stresses concentrate there. Thereby, strain on the slip planes is impeded by this layer to move from one grain to the vicinal grain and accordingly, stress-relief cannot be achieved [7].

This article is concerned with the relationship between the grain boundary character and mechanical properties, particularly in creep, of a new polycrystalline nickel-based superalloy. The effect of boron on the precipitation of M23C6 carbides at grain boundaries and its influence on creep resistance was studied.

2. Experimental procedures

The prototype nickel-based polycrystalline superalloy STAL-15CC investigated in this study has composition Ni-5Co-15Cr-1Mo-3.5W-4.5Al-8Ta-0.1Hf-0.1C (wt-%). In order to investigate the effect of boron on the mechanical properties, test-bars were cast containing various amounts of boron. In particular, test-bars with no boron (boron free-BF), low boron (LB – 0.006 wt-%) and relatively higher boron (HB – 0.016 wt-%) content were produced.

Castings in the form of tapered rods (Fig. 1) were prepared at Doncasters Precision Castings Ltd., using casting stock melted by Ross & Catherall (Sheffield, United Kingdom). Ceramic moulds were used, which had been prepared from alumina, silica and zircon in the usual way. In addition,
cobalt aluminate was utilized in the primary slurry as nucleation catalyst, in order to achieve a desirable grain size.

2.1. Heat treatment

After conventional casting (CC) the test-bars were hot isostatically pressed (HIP) at 1195 °C for 5 hours under 175MPa pressure. Thermodynamic calculations using Thermocalc coupled with the TTN17 database indicated a γ' solvus temperature of 1148 °C and a solidus temperature of 1233 °C. The process of HIP was followed by a stage of primary ageing at 1120 °C for 4 hours and a subsequent second stage of ageing at 845 °C for 24 hours. Careful examination of the final heat treated microstructures revealed that the precipitated carbides at the grain boundaries exhibit different morphologies depending on the boron level.

In particular, both the BF and LB alloys exhibit a more or less continuous layer of M₂₃C₆ type along the grain boundaries, resulting from the degeneration of the MC type carbides. Moreover, the breakdown of MC carbide results in larger, irregular γ' particles at the grain boundaries, as illustrated in Figs. 2 and 3. It was found that the size of the γ' particles at the grain boundaries differs between the BF and the LB alloy. It was observed that in the LB alloy the γ' particles exhibit a relatively larger size than that of the boron free one.

As boron increases, the precipitation of smaller blocky M₂₃C₆ carbides at the grain boundaries is promoted (HB specimen); these carbides are enveloped within a continuous γ' layer at the grain boundaries. It is believed that this complex structure at the grain boundaries can improve the mechanical properties. The hard grain boundary carbides enveloped within the ductile γ' layers retard the crack initiation and thereby improve the rupture life and creep ductility at high temperatures [8]. Morphologies of the MC carbide, after its decomposition, and the precipitated M₂₃C₆ carbides enveloped within a γ' layer are illustrated in Fig. 4.

3. Experimental results

3.1. Segregation of carbon and boron

NanoSIMS analysis was carried out on fully heat treated samples with a CAMECA NanoSIMS 50. The samples were polished to attain flat surfaces. A 16keV Cs⁺ primary ion beam was used to sputter ions from each surface analysed. Prior to each measurement, the surface was cleaned with a high-energy primary ion beam.

The detectors were aligned to detect the ion species $^{12}$C−, $^{11}$B$^{12}$C−, $^{11}$B$^{16}$O$_2$− and $^{52}$Cr$^{16}$O$_2$−. The $^{11}$B$^{16}$O$_2$− signal was chosen in preference to the $^{11}$B− and
NanoSIMS images showing segregation of B and C at grain boundaries in a fully heat treated HB specimen, prior to creep test.

Figure 5.

SEM image showing the analysed area by NanoSIMS of the HB specimen.

Figure 6.

NanoSIMS images showing segregation of B and C at grain boundaries in a fully heat treated LB specimen, prior to creep test.

Figure 7.

SEM image showing part of the analysed area by NanoSIMS of the LB specimen, see the labelled area in Fig. 8.

Figure 8.

are the most abundant in nickel-based superalloys with high chromium content and form from the decomposition of MC carbides, either during heat treatment processes or prolonged service exposures. The dominant carbide reaction is 

\[ \text{MC} + \gamma \rightarrow \text{M}_{23}C_6 + \gamma', \]

where the MC carbides serve as source of carbon and chromium is depleted from the matrix to form the Cr_{23}C_6. In addition, it was observed that B can substitute for C in M_{23}C_6 resulting in Cr_{23}(B,C)_6 carbides at grain boundaries, which is consistent with previous work [4,10].

3.2. Creep behaviour

The creep curves measured for the three distinct chemical compositions are given in Fig. 10, it is seen that the minor additions of boron dramatically improve the creep resistance of STAL15-CC. In particular, both low and high boron content specimens performed similarly, in terms of rupture time. Consistent with the creep strengthening implied by the
data in Fig. 10, transverse grain boundaries act as crack initiation sites with evidence of grain boundary oxidation being prevalent at and close to the specimen surfaces.

4. Discussion & rationalisation of results

4.1. The formation of $\gamma'$ layers

During the design of new polycrystalline superalloys, it becomes apparent the necessity of having a thorough understanding of the relationship between grain boundary character and mechanical properties. In particular, the contribution of grain boundary elements, such as boron, to the carbide reactions taking place at the grain boundaries can play a pivotal role on the performance of conventional casting superalloys.

The occurrence of B-rich carbides at the grain boundaries can be rationalised by the higher mobility of boron in the $\gamma$ matrix than that of carbon. As a consequence, higher amounts of boron diffuse from the $\gamma$ matrix towards the growing M$_{23}$C$_6$ carbide [11]. Yan [12] has suggested that the segregation of boron to the grain boundaries can facilitate the formation of continuous $\gamma'$ layers along the grain boundaries. This is consistent with microstructural observations in this study. Relatively larger $\gamma'$ precipitates were found at the grain boundaries of the LB specimen (Fig. 3), compared to those observed in the boron-free specimen (Fig. 2). Further increase of the amount of boron results in continuous $\gamma'$ layers along the grain boundaries (HB specimen – Fig. 4).

The precipitation of $\gamma'$ layers exerts a beneficial effect on the grain boundary character of STAL15-CC. The occurrence of these layers at the grain boundaries can suppress the diffusion of chromium from the matrix towards the grain boundary. Thereby, undesirable continuous films of M$_{23}$C$_6$ are avoided at the grain boundaries. At the same time, the occurrence of secondary $\gamma'$ denuded zones in the vicinity of grain boundaries is minimized. It is known that areas depleted of chromium can be created close to grain boundaries due to the diffusion of chromium from the matrix towards the grain boundaries in order for Cr-rich carbides to form there. Thereby, the solubility for nickel and aluminium increases locally causing $\gamma'$ to disappear.

4.2. The effect of $\gamma'$ layers on the creep resistance

An interesting observation lies on the relatively lower strain rate of the high boron specimen. The above observation can be ascribed to the presence of $\gamma'$ layers in the microstructure, prior to the creep test. It is well known that carbides can serve as crack initiation sites at the grain boundaries. However, the complex microstructure of brittle carbides enveloped within the ductile $\gamma'$ envelopes can accommodate controlled slip at elevated temperatures, resulting in lower strain rates.

Moreover, it was observed that the presence of $\gamma'$ layers at grain boundaries can enhance the fracture resistance of the alloy. In particular, microstructural
Figure 12. γ’ layers impede crack propagation at grain boundaries.

Figure 13. γ’ layers precipitate at the grain boundaries of the low boron specimen after the creep test.

Figure 14. Primary M23C6 serving as crack initiation sites at grain boundaries in the low boron specimen.

5. Conclusions

Creep tests at 850 °C-235MPa were performed on a prototype nickel-based polycrystalline superalloy containing various amounts of boron. The following conclusions can be drawn from this work:

- The absence of boron in the microstructure results in continuous films of M23C6 type carbides at grain boundaries of fully heat treated specimens. As boron content increases, small discrete M23C6 carbides precipitate along the grain boundaries.
- It is shown that NanoSIMS can be used to distinguish between grain boundary phases in this system, i.e. between M23(B,C)6 and MC. There is a significant substitution of B for C in M23(B,C)6.
- It is suggested that γ’ layers form around B-rich M23C6 during heat treatment processes and prolonged exposures at high temperatures.
- The presence of the ductile γ’ layers at the grain boundaries can improve the creep ductility, by surrounding the brittle MC and M23C6 carbides which can serve as crack initiation sites.
- It is demonstrated that γ’ envelopes at grain boundaries serve as obstacles to crack propagation, thus improving the fracture resistance at high temperatures.

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References