Secondary Reaction Zone Formations in coated Ni-base Single Crystal Superalloys

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Abstract. Ruthenium (Ru) has been added to the latest 4th Generation Ni-base superalloys to improve phase stability and modify creep life. Various coatings are routinely applied to these advanced alloys to protect the turbine blade at elevated temperature, however, this creates several problems such as the precipitation of brittle Topologically Close-Packed (TCP) phases and the formation of Secondary Reaction Zones (SRZ). The SRZ forms under the plat-aluminized coating of turbine blades and consists of γ, γ’ and TCP phases growing into substrate by the migration of high-angle grain boundaries. Surface residual stress and chemical super-saturation of alloying elements are associated to SRZ formation. In the thin sections of high-pressure turbine blades this is critical in determining blade performance and longevity. It is essential to know how Ru additions affect coating and SRZ morphologies during exposure. In this study, we focus on the effects of three variables on the SRZ formation: Ru concentration, alloy composition in Ru-containing alloys and surface finish. A series of Platinum-Aluminised superalloys containing 2-5wt% Ru and having various surface finishes was studied after isothermal exposure at 1100°C for up to 500h. The alloys were classified into two groups by their distinctive SRZ morphology. At the lowest Ru levels sporadic formation of SRZ was observed, whilst a continuous SRZ was formed in the higher Ru alloys. EBSD analysis revealed that the latter group have a higher nucleation rate of individual SRZ grains and also showed more rapid SRZ growth. The precipitation of TCPs in the substrate also inhibited the growth of the SRZ towards the end of the exposure further reducing the penetration of the SRZ into the substrate. It is concluded that Ru-additions to Ni-base superalloys are effective in impeding TCP phase formation in the substrate, but increase both the extent and the rate of SRZ formation beneath coating.

1. Introduction
Ni-base superalloys are used as single crystal castings to make high-pressure turbine blades which operate at up to 80% of their absolute melting temperature whilst retaining excellent mechanical properties and oxidation resistance. The latest 4th generation Ni-base superalloys, contain 2-5% Ruthenium (Ru), and this is very effective in improving the mechanical properties in part by suppressing the formation of deleterious intermetallic phases[1,2].
The improved mechanical properties come at the cost of the oxidation resistance and coatings, such as Platinum Aluminide coatings (PtAl) and MCrAlY, are necessary to protect the turbine blades from oxidation and corrosion during service, details of these coatings are given elsewhere [3-9].

Several major problems are associated with coated Ni-base superalloys leading to the loss of the coating, these include the precipitation of topologically close-packed (TCP) phases, the formation of the secondary reaction zone (SRZ) and the ‘rumpling’ of the coating caused by thermal cycling. These problems degrade the properties of coated Ni-base superalloys, and are potentially life-limiting to the turbine blades. In particular, TCP phase precipitation and Secondary Reaction Zone (SRZ) formation are regarded as the most serious problems in both coated and uncoated Ni-base superalloys.

Topologically Close-Packed (TCP) phases is a collective designation for several intermetallic compounds rich in the elements W, Mo, Re and Cr precipitated in Ni-base superalloys [10]. TCP phases form during service at elevated temperature in Ni-base superalloys that have high concentrations of these elements added to promote strength the loss of these elements from the matrix impairs the mechanical properties of the blade. Precipitation of the TCP phases deteriorates the ductility and creep resistance of Ni-base superalloys. Further details of TCP phases are given in references [11-13].

The Secondary Reaction Zone (SRZ) is an intermediate layer formed between an aluminized or Plat Aluminized coating and the substrate by a discontinuous precipitate reaction similar to recrystallization. Figure 1 shows a schematic image of the SRZ which is formed beneath the inter diffusion zone (IDZ) of the aluminide coating with the substrate. It transforms the metastable aluminium-enriched substrate microstructure into an equilibrium mix of $\gamma$, $\gamma'$ and TCPs. The TCPs align perpendicular to the growth direction facilitated by the rapid diffusion path of the high angle boundary. Therefore, the SRZ is associated with a boundary having both high mobility and diffusivity.

Among several potential risk factors for SRZ formation [14,15], nucleation appears to be associated with surface damage prior to coating as the SRZ was not observed when the surface was electropolished [15]. The driving force is the difference in free energy associated with the phase changes plus any loss of dislocation density and the reduction in the interface area brought about the coarsening of the precipitates. Also, an alloy containing more than 4-5wt% Re is found to have a high probability of forming SRZ [14,15].

As well as the precipitation of TCP phases, SRZ formation results in coarsening the $\gamma/\gamma'$ structure and causes the mechanical properties of the alloy to deteriorate. Also, SRZ formation beneath the coating is said to reduce the load bearing section of the blade [16]. The formation of SRZ indicates the inter-diffusion between coating and the substrate, so that phase instability is accompanied in the alloy [14].

There are many studies examining the effect of Ru on the structure and stability of 4th generation superalloys [17], however the effect of Ru coated alloy has not been fully clarified. This is the subject of this paper.

2. Experimental

Nominal compositions of the Ni-base single crystal superalloys use in this paper are listed in Table 1. All alloys were supplied in the fully heat treated condition. The alloys contain Ru in the range of 2-5wt%, replacing Ni all other elements remaining constant. The coatings were applied to surfaces cut normal to the bar axis, nominally [001]. Specimens are polished up to 600 SiC paper prior to Pt coating, and
Table 1. Alloy composition (wt%).

|        | Co | Cr | Mo | W  | Re | Ru | Al | Ta | Hf | Ni |
|--------|----|----|----|----|----|----|----|----|----|----|
| UCSX-2+2Ru | 8.0 | 3.0 | 1.0 | 8.0 | 6.5 | 2.0 | 5.4 | 8.0 | 0.1 | 58.0 |
| UCSX-2+3Ru | 8.0 | 3.0 | 1.0 | 8.0 | 6.5 | 3.0 | 5.4 | 8.0 | 0.1 | 57.0 |
| UCSX-2+5Ru | 8.0 | 3.0 | 1.0 | 8.0 | 6.5 | 5.0 | 5.4 | 8.0 | 0.1 | 55.0 |

Figure 2. Summary of microstructures of UCSX alloys (a) as coated and (b) after 500h exposure.

vapour aluminised after Pt coating. Isothermal exposure tests were conducted at 1100°C to investigate the microstructure by means of SEM and EBSD (Electron Back-Scattered Diffraction).

The thickness of the SRZ was measured to determine the growth of the SRZ. For each specimen an average of 10 points was measured, depending the area fraction of SRZ. Further details of specimen preparations and SRZ thickness measurement should be referred elsewhere [18].

3. Results

3.1. Effect of Ru content on SRZ formation

Figure 2 (a) shows a montage of the microstructures of the as Pt-Aluminized specimens. All the specimens consist of $\beta$ (Pt,Ni)Al surface layer, an Inter Diffusion Zone (IDZ), and the substrate in that order. The specimens had developed Secondary Reaction Zones (SRZ) during the 1 h heat treatment at 1100°C after aluminizing. Depending on the alloy composition the alloys showed a much greater effect. All the UCSX-2+2Ru samples showed sporadic SRZ formation, whereas the UCSX-2+3Ru and UCSX-2+5Ru specimens showed more continuous SRZ formation. This suggests that a higher amount of Ru in the substrate encourages SRZ nucleation at an early stage.

Figure 2(b) shows the microstructures after 500 h exposure. All the specimens have now developed a full SRZ layer and show profuse TCP precipitation in the SDZ. UCSX-2+2Ru in particular, showed the highest proportion of TCP phases in SDZ. Some of these TCP plates in the substrate are aligned with rows of incoherent precipitates in the SRZ indicating that the SRZ continues to grow after the TCPs form in the substrate. In other instances, TCP phases, precipitated in SDZ, prevent further growth of the SRZ. This seems to be the case where the TCP plate lies parallel to the boundary plane [18].

The higher Ru alloys, UCSX-2+3Ru and UCSX-2+5Ru, showed more SRZ growth than UCSX-2+2Ru. At the same time, these two alloys showed less TCP precipitation in the SDZ than UCSX-2+2Ru.
2+2Ru. There is hence a negative correlation between TCP precipitation in the substrate and SRZ formation.

3.2. Microstructural Evolution of the SRZ and the SDZ

Figure 3 shows the growth kinetics of the SRZ in each specimen during the first 500 h exposure. Quantifying the SRZ thickness reveals a number of interesting trends. In the alloy UCSX-2+2Ru the SRZ ceases to grow after about 50 h exposure for the vapor aluminized specimens, whereas the SRZ in alloys UCSX-2+3Ru and UCSX-2+5Ru continues to grow substantially after 50 h.

Figure 4 shows EBSD mappings and the corresponding pole figures for typical SRZ areas between the IDZ and the substrate. The normal to the coated surface for all alloys lies within 20° of the [001] direction, but the sections were cut at various angles giving a variety of substrate orientations perpendicular to [001] in Figure 4. Hence the [001] pole figures have in all cases been rotated to locate the substrate [001] orientation normal to the page and the [100] and [010] orientations along the x and y axes. The black areas correspond to the TCP phases which were generally not recognized by the software under the conditions used for mapping.

The number of SRZ grains nucleated during the early stages of growth varies greatly with alloy content. This has been quantified by counting the number of grains at the root of the SRZ adjacent to the coating and at the end of the SRZ adjacent to the substrate. A straight line was drawn at each location and all orientations where two or more adjacent points were indexed were included; the results are given in Table 2.

There is a clear effect of the higher Ru content resulting in a much higher nucleation rate, for example the number of grains increases by nearly 70% from the 2% Ru alloy to the 5% Ru alloy. The number of grains converges on a similar number as the SRZ grows with the 2% Ru alloy nucleating further grains and the 5% Ru alloy losing some orientations.

4. Discussion

The effect of Ru on the formation of SRZ is an issue of importance to the alloy developer. In this study the concentration of Ru was varied over the range found necessary to effectively suppress the formation of TCP phases in the substrate [15,19] whilst keeping the cost of the...
alloy within reasonable bounds and avoiding the formation of the delta phase [20].

The formation of the SRZ involves the nucleation of grains of a distinct orientation and their subsequent migration into the substrate by the passage of a high angle grain boundary. The boundary provides a fast diffusion path enabling the rationalization of the fine γ/γ’ microstructure of the substrate to a lower-energy, coarser morphology and at the same time the precipitation of the TCP phases at approximately equilibrium volume fractions for the local composition. This is, of course, modified by the diffusion of the Al into the substrate which varies throughout the exposure. SRZ formation is thus a discontinuous precipitation process.

Ru increases the thickness of the SRZ for the specimens in Figure 3. In the first 50 hours SRZ grows in all three alloys at about the same rate but after that time growth continues in the 3% and the 5% alloy but not the 2% alloy. The continuous growth of the SRZ facilitates the diffusion of Al into the substrate thus reducing the Al levels in the SRZ and increasing the proportion of γ.

There is a significant increase in the nucleation rate as the Ru content increases as shown by the very large numbers of grains at the root of the SRZ in UCSX-2+3Ru and UCSX-2+5Ru. The lowest Ru alloy UCSX-2+2Ru was the only sample to show evidence of retained substrate between the coating and the SRZ, in all other cases the SRZ nucleated directly below the NiAl coating. It is not clear why this occurs but may reflect an increased driving force for the formation of the SRZ with Ru content.

It was expected that the number of grains in the SRZ would decrease as growth competition between the grains selected those with the boundary misorientation which had the greatest mobility. This does not appear to be the case as no preferred orientation for the grains of the SRZ was observed. The number of grains increased or decreased with growth towards a constant value. At the outer edge of the SRZ the average width of a grain is about 6 μm, very similar to the spacing of the TCPs.

Growth of the TCPs is analogous to eutectoid precipitation with the TCPs lying approximately parallel to the growth direction, and it can be seen that the TCP phases frequently lie at the boundaries between the grains. It appears that the width of a grain is ultimately determined by the spacing of the TCP precipitates. This, in turn, should be a compromise between the diffusion distance along the moving boundary and the minimization of the interphase boundary energy between the γ and the TCPs. As the volume fractions of the TCPs for the Polished specimens are all approximately 15% after 20 h it is understandable why the spacing of the grains adjusts to a similar value in all the specimens.

All the boundaries between the SRZ and the substrate were high angle boundaries with misorientation between 20°-60°, consistent with the report by Lavigne [21]. Hence some selectivity in either nucleation or growth in the very early stages of the SRZ formation has occurred to eliminate the less mobile lower angle boundaries.

We observe a clear increase in the number of grains nucleated as the Ru content increases. However this is associated with a lower growth rate of the SRZ in all alloys particularly in the first 50 h exposure. The same effect is seen with respect to the surface damage [18]. It is not clear that the grain size is necessarily the cause of the lower growth rate, merely that lower growth rate is associated with a smaller grain size resulting either from high surface damage or high Ru content. Further investigations are required to differentiate these effects.

The mechanism by which the number of grains reduces is clear: some orientations simply become occluded by others, particularly where these are separated by a TCP plate. But the mechanism by which the number of grains increases is less obvious; one possibility is simply the nucleation of new orientations by the formation of twins which form 20% of boundaries between SRZ grains in Table 3.

| Table 2. Number of grains in SRZ. |  | Table 3. Percentage of twin boundaries in SRZ. |
|---|---|---|
| Alloy | 2Ru | 3Ru | 5Ru | Alloy | 2Ru | 3Ru | 5Ru |
| Number at root | 31 | 47 | 52 | % of Twin boundaries | 16.5 | 18.9 | 19.7 |
The percentage of twins increased with Ru content in substrate. Twin boundaries forms with lower energy than normal grain boundary. Thus, more formations of twin boundaries might be associated with deeper SRZ penetration in higher Ru alloys.

5. Conclusions
Secondary Reaction Zones in Pt-Al coated 4th generation Ni-base blade alloys were investigated, and following sequences are obtained.

- Ru is effective in inhibiting TCP formation in substrate, but promotes greater SRZ formation.
- TCP precipitation in the substrate inhibits SRZ growth.
- Higher Ru resulted in an increased nucleation rate of the SRZ.

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