### A NEW TYPE OF MICROSTRUCTURAL INSTABILITY IN SUPERALLOYS - SRZ

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#### Abstract

A new type of instability in superalloys has been observed in advanced alloys containing high levels of refractory elements. One instability occurs under the diffusion zone of coatings and has been called secondary reaction zone or SRZ. Similar instabilities, in the form of cellular colonies, have been observed along grain boundaries and in dendrite cores. These microstructural instabilities are characterized and interpreted in terms of a nucleation and growth transformation. The similarities and differences between a similar phenomenon, cellular recrystallization, are outlined. The degradation of properties due to the SRZ and cellular colonies is described. Methods are shown that have successfully reduced or eliminated these instabilities. Finally, the implications of these new types of instabilities on superalloys in general are discussed.

# Introduction

Recent advances in the creep rupture strength of single crystal superalloys have been accomplished by the addition of higher levels of refractory elements. These additions result in microstructural stability being even more important during alloy development. Precipitation of Topologically Close-Packed (TCP) phases in superalloys is well known and is a function of many variables, including temperature and alloy composition. Second and third generation single crystal superalloys all precipitate TCP phases under some conditions, however, in general, the quantity that precipitates does not significantly degrade properties. Thus, the occurrence of a moderate amount of TCP phases is not cause for general concern.

Most superalloy turbine airfoil components are put into service with an environmental coating. These coatings are typically either a diffusion aluminide or a MCrAlY. The interdiffusion of these coatings with advanced superalloy substrates causes phase instability at the surface. For many alloys, it is typical to observe TCP phases in the interdiffusion zone after high temperature exposures. Again, the occurrence of a moderate amount of TCP phases below the coating is not considered a problem.

A new type of instability in superalloys has been observed in alloys containing high levels of refractory elements. The new instability differs significantly from past TCP phases in morphology and effect on mechanical properties. This instability was first observed beneath the diffusion zone of an aluminide coating and was termed SRZ (secondary reaction zone). The occurrence of the SRZ-type of instability, however, is not limited to coating interdiffusion zones. In cases where the SRZ-type instability is observed along low angle grain boundaries and in dendrite cores away from the coating, it will be referred to as cellular colonies. This paper discusses the conditions under which the instability occurs, the effect on properties and methods of prevention.

#### **Experimental Procedures**

Many alloys have been evaluated for their propensity to form SRZ, however one particular alloy has been evaluated in-depth and is reported in this paper. This alloy is an experimental third generation single crystal superalloy with the composition given in Table 1.<sup>[1]</sup> In order to achieve the necessary creep rupture strength, this alloy contains a high amount of refractory elements compared to previous generation superalloys. Small additions of Hf, C and B were made to improve the strength of low angle grain boundaries, when present in the casting.<sup>[2]</sup>

Single crystal slabs measuring 1.3 x 5 x 10 cm were directionally solidified at commercial suppliers. The castings were solution heat treated at 1315°C for 2 hours followed by an aging heat treatment of 1120°C for 4 hours. Following heat treatment, the microstructure consisted of a  $\gamma$  matrix and 65 vol.% cuboidal  $\gamma$ ' precipitates with an edge length of about 0.5  $\mu$ m. A small number of MC carbides were also present in the interdendritic regions. Following specimen preparation, various diffusion aluminide coatings were applied. Final coating thicknesses were typically 50-75  $\mu$ m thick. A diffusion heat treatment at 1080°C was performed, followed by the final alloy aging cycle at 870°C. Elevated temperature exposures were then conducted from 980-1150°C for times up to 400 hours to promote SRZ formation.

In an attempt to eliminate SRZ beneath coatings, specimens were coated with various elements prior to aluminization. Elements examined were Ni, Ta, Hf, B and C. The Ni and Ta were applied with a DC magnetron

sputtering device using 6" diameter targets. The Hf, B and C were deposited in a small chemical vapor deposition (CVD) reactor with a 6" x 12" hot zone. After element application, pack aluminization was performed using the Codep process. SRZ exposures were performed to assess the effectiveness of each element.

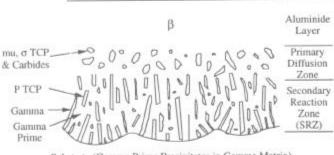
Table 1. Major Elements in Alloy 5A, weight %.

Alloy	Ni	Co	Cr	Al	Ta	Re	W
Alloy 5A	Bal	12.50	4.50	6.25	7.00	6.25	5.75

## Results

#### SRZ Structure

The SRZ beneath coatings and the cellular colonies observed elsewhere in the microstructure have the same structural features and similar compositions. Figure 1 shows a schematic of SRZ beneath a coating with the individual phases labeled. The SRZ structure consists of a  $\gamma'$  matrix containing  $\gamma$  and P phase (TCP) needles. The  $\gamma$  and P phase needles tend to be aligned perpendicular to the growth interface. Figures 2 and 3 show the interface between the advancing SRZ and the  $\gamma'$  microstructure. The matrix transforms from  $\gamma$  (superalloy) to  $\gamma'$  (SRZ) once the incoherent boundary passes. The P phase in the SRZ is continuous with the  $\gamma$  phase at the interface. Nucleation of the P phase on the  $\gamma$  phase is shown in Figure 4.



Substrate (Gamma Prime Precipitates in Gamma Matrix)

Figure 1. A schematic showing the secondary reaction zone under an aluminide coating.

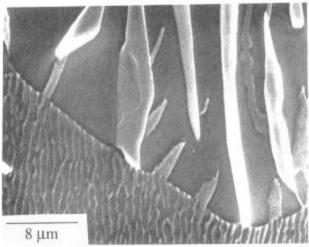


Table 2 shows the compositions of the phases ahead of the SRZ interface and within the SRZ. The phase compositions within the SRZ were determined by electron microprobe, and the phase compositions in the bulk alloy were determined by phase extraction. [3] The P phase is composed of nearly 50% Re with high levels of W, Cr and Co. P phase is similar in composition and structure to the sigma TCP phase with the major difference being a larger period on one axis. As a result of the high levels of Re and W in the P phase, the  $\gamma$  phase within the SRZ is depleted of these elements compared to the  $\gamma$  phase in the bulk alloy. The  $\gamma'$  phase within the SRZ is enriched with Al and Ta compared to the  $\gamma'$  phase in the bulk alloy, which may explain the stabilization of the  $\gamma'$  matrix. Other than these changes, the  $\gamma$  and  $\gamma'$  phases within the SRZ constituent have very similar compositions to the  $\gamma$  and  $\gamma'$  phases in the bulk alloy.



Figure 2. TEM micrograph showing the SRZ/alloy interface. The SRZ has a  $\gamma$  (gray) matrix, while the alloy has a  $\gamma$  (black) matrix.

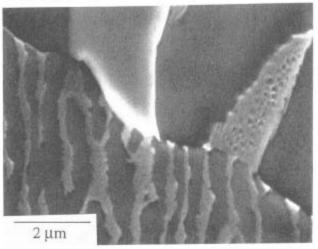


Figure 3. BSE SEM micrograph showing the SRZ/alloy interface. Note the relationship between the P phase (white) and the γ phase (gray).

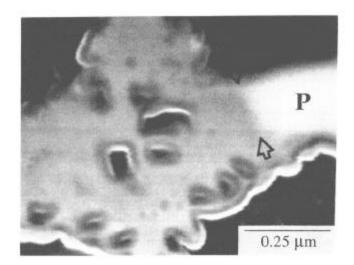


Figure 4. High magnification SEM micrograph showing the P phase nucleation from the γ phase (between the arrows).

Table 2. Composition of Phases Within and Adjacent to SRZ.

Phase	Ni	Co	Cr	Al	Ta	Re	W	Hf
P in SRZ	10.5	9.7	9.2	0.1	1.6	49.5	20.0	0.0
γ' in SRZ	64.1	11.2	2.7	8.7	8.2	1.1	4.4	0.1
y in SRZ	50.6	18.8	9.7	4.5	2.6	8.3	5.3	0,0
γ' in Alloy	69.1	8.8	1.9	4.8	6.5	1.1	4.8	0.2
γ in Alloy	45.6	18.7	9.3	6.6	1.2	16.0	6.6	0.0

## SRZ Under Coatings

Interdiffusion between the coating and the substrate alloy and mismatch strains in the alloy create an unstable situation in which  $\gamma$  and  $\gamma'$  are no longer the equilibrium phases beneath the coating. In many alloys, the diffusion zone consists of  $\beta'$  and TCP phases. However, in alloy 5A, SRZ occurs beneath the diffusion zone of simple aluminide, platinum aluminide and overlay coatings. In other, more stable alloys, SRZ may only occur under the diffusion aluminide coatings. Figure 5 shows a typical example of SRZ beneath a platinum aluminide coating in alloy 5A. Depending upon the coating characteristics and surface preparation, the SRZ can be continuous or occur in isolated cells. It is believed that the Al activity of the coating and the residual stress state of the surface play key roles in determining the propensity of a specimen to form SRZ.

# Cellular Colonies at Grain Boundaries

A similar microstructure to the SRZ was observed along low and high angle grain boundaries in alloy 5A. Figure 6 shows that the morphology of the cellular colonies along grain boundaries is similar to the SRZ under coatings. Both constituents consist of a  $\gamma'$  matrix with needles of  $\gamma$  and P phase. Compositional analysis of the cellular colonies show phase compositions to be similar to those of the SRZ shown in Table 2. It was typical to observe the cellular colonies to form only on one side of a grain boundary. However, along the same grain boundary, the cellular colonies may form on either side of the boundary but never on both sides at the same time. It was also observed that the formation of the cellular

colonies was more favorable on higher angle boundaries. In alloy 5A, grain boundaries with relative misorientations as low as 10° formed cellular colonies. However, in other more stable alloys, higher misorientations were required to form cellular colonies. In a thorough study on a similar alloy, Pollock and Nystrom found that the cellular colonies appeared to nucleate on P phase grain boundary precipitates. [4]

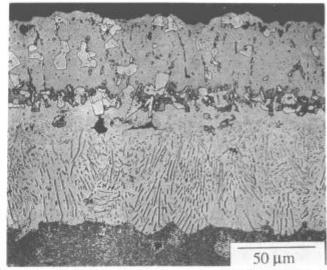


Figure 5. SRZ under a PtAl coating in alloy 5A following a 1093°F/400 hour exposure.

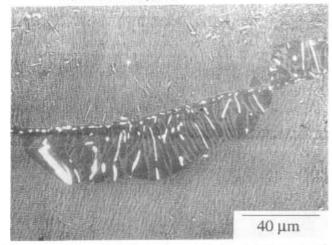
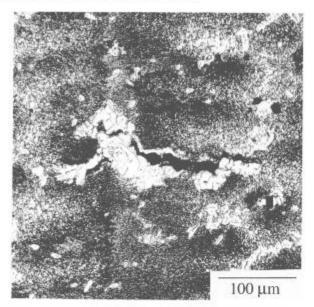


Figure 6. Cellular colonies along a grain boundary (-14° misorientation) in alloy 5A.

### Cellular Colonies in Dendrites

Cellular colonies have been observed in dendrite cores with the same microstructure as those found along grain boundaries and the SRZ under coatings. The occurrence of the cellular colonies in the dendrite cores occurred to a much lesser extent than the other two reactions. The cellular colonies were primarily observed in either unstressed, as-cast specimens or in creep rupture specimens tested at temperatures near 1100°C. Figure 7 shows a longitudinal section of a failed creep rupture specimen showing cracking along one of the cellular colonies. Unlike the other two reactions, the cellular colonies in the dendrites were isolated occurrences without the presence of a boundary. A higher

magnification view of one of these colonies is shown in Figure 8. It was common to observe a cracked interface along the cellular colonies in dendrite cores in creep rupture specimens. The effect of these cracked colonies on properties will be discussed later.



 Cellular colony formed in a dendrite in a failed creep rupture specimen tested at 1093°C.

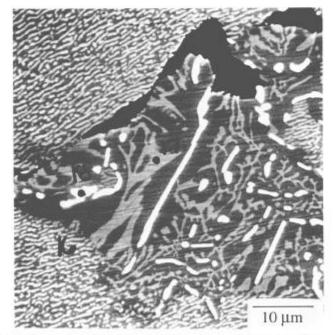


Figure 8. Crack running along the interface of a cellular colony in a failed creep rupture specimen tested at 1093°C.

# Nucleation and Growth

The factors that affect the nucleation of the SRZ and cellular colonies have been studied in alloy 5A. These constituents have been observed after exposures at temperatures from 980 to 1150°C. Typical exposures were for 400 hours, however exposures as short as one hr at 1120°C.

have produced SRZ. One of the difficult aspects in studying the nucleation of these constituents is that there appears to be a large nucleation barrier to their formation. Thus, predicting nuclei formation as a function of time and temperature is difficult, and observing the earliest stages of nucleation is almost impossible.

The observation that isolated occurrences can occur under coatings, along boundaries or in dendrite cores is consistent with a high nucleation barrier. Otherwise, it would be more common to observe continuous cellular colonies along grain boundaries and cellular colonies in most dendrite cores. Contributions to the nucleation of the SRZ and cellular colonies can be described by the following equation for homogeneous nucleation: [5]

$$\Delta G = n(\Delta G_{\Omega/\Omega'} + \Delta G_F) + \eta \gamma n^{2/3}$$
(1)

where  $\Delta G$  is the free energy of formation for an SRZ nuclei,  $\Delta G_{\alpha I \alpha'}$  is the free energy difference between parent and product phases per unit volume (supersaturation),  $\Delta G_{\epsilon}$  is a strain energy term,  $\eta$  is a shape factor,  $\gamma$  is the surface free energy between the phases and  $\eta$  is a volume term. Nucleation is controlled by a number of factors, including supersaturation, surface energy, strain energy and the number of heterogeneous sites. Supersaturation can occur either by external (coating) or internal (segregation) chemistry imbalances. Strain energy can be introduced by surface preparation prior to coating or misfit strains along grain boundaries or between  $\gamma$  and  $\gamma'$ .

The growth of SRZ has been measured under a variety of coatings at  $1093^{\circ}$ C. Figure 9 shows the data for alloy 5A plotted as a function of the square root of time. The linear dependence shows that diffusion is controlling the rate of growth. The interdiffusion coefficient calculated from the SRZ layer thickness is  $6.73 \times 10^{-11} \text{ cm}^2/\text{sec}$ . Janssen and Rieck have measured the diffusivity of Ni and Al in Ni-Al compounds and found the diffusivity at  $1093^{\circ}$ C of Ni to be  $2.5 \times 10^{-11} \text{ cm}^2/\text{sec}$  in  $\gamma$ ;  $4.0 \times 10^{-11} \text{ cm}^2/\text{sec}$  in  $\gamma$ ; and  $5.0 \times 10^{-11} \text{ cm}^2/\text{sec}$  in  $\beta$ . The diffusion rate calculated from the SRZ growth is slightly higher than the volume diffusion rates for Ni and Al. This is likely due to enhanced diffusion in the SRZ along the growth interface.

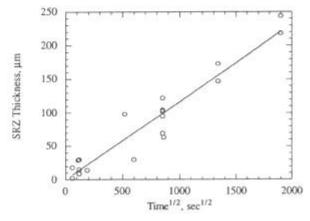


Figure 9. A straight line relationship between the thickness of the SRZ and the square root of time indicating a diffusion controlled process.

#### Effect of Composition

A large number of single crystal superalloys have been evaluated for their propensity to form SRZ and cellular colonies. Based on these evaluations, it is clear that composition plays a key role in the formation of these constituents. A systematic study of alloys similar to alloy 5A was conducted to determine the effect of various alloy additions on the formation of SRZ beneath a platinum aluminide (PtAI) coating. The same surface preparation and coating process was performed on each alloy since it was known that these factors could affect the amount of SRZ formation. Following PtAI coating the specimens were exposed at 1093°C for 400 hours. The total linear percent of SRZ around the periphery of the specimen was measured. A value of 100% meant that SRZ was continuous beneath the coating. The depth of the SRZ was not measured in this analysis. Statistical analysis of the results of these evaluations produced the following relationship for use in predicting the amount of SRZ which will form in an alloy:

$$[SRZ(\%)]^{1/2} = 13.88 (\%Re) + 4.10(\%W) - 7.07(\%Cr)$$
(2)  
- 2.94(\%Mo) - 0.33(\%Co) + 12.13

The elements in this equation are in atomic percent, and this equation is valide for third generation single crystal superalloys. It is clear that Re is the most potent element for determining an alloy's propensity to form SRZ. Minor variations in the Al content of the alloy did not influence the formation of SRZ beneath the coating. However, significant Al enrichment occurs beneath the coating, and this plays a large role in the formation of SRZ.

While SRZ has been observed to some extent in many third generation single crystal superalloys, including René N6<sup>[9]</sup> and CMSX-10,<sup>[10]</sup> these alloys contain greater than 5 wt.% Re.<sup>[11,12]</sup> The overwhelming role of Re in SRZ formation in equation (1) suggests that it is not surprising that these alloys would form SRZ to some extent. However, even in alloys containing lower levels of refractory elements, including Re, SRZ has been observed. In rare cases, alloys with 3 wt.% Re have exhibited SRZ beneath aluminide coatings.<sup>[10]</sup> This surprising observation is most likely a result of extremes in alloy composition, surface preparation and coating parameters. Our experience suggests that alloys with less than 5 wt.% Re should rarely exhibit SRZ formation.

No quantitative expressions have been developed for the formation of cellular colonies along grain boundaries or in dendrite cores. However, it has been observed that it is easier to nucleate SRZ beneath the coating than it is to nucleate the cellular colonies along the grain boundaries or in dendrite cores. Thus, it is possible to screen alloys based on the above SRZ equation and obtain a qualitative indication of their propensity to form cellular colonies elsewhere.

### Property Degradation

The effect of SRZ and cellular colonies has been evaluated in a wide range of mechanical property tests on bare and coated specimens. These constituents can form after exposures from about 980 to 1150°C, with the most favorable temperature around 1100°C. SRZ beneath a coating can affect test specimens and turbine airfoils by reducing the load bearing cross section or by crack initiation along the cell interface. In alloy 5A, slight losses in rupture strength were found at temperatures

around 1100°C due to reduced cross section. Cracks emanating from SRZ were found in failed rupture specimens, however it was difficult to determine if these played a role in initiating premature failures. No decrease in fatigue properties has been attributed to SRZ, although it seems possible that SRZ could initiate cracks at early lives.

Cellular colonies along grain boundaries can reduce properties in a turbine airfoil. The magnitude of the reduction is a function of the grain boundary angle, the alloy's propensity to form the cellular colonies and the alloy's inherent grain boundary strength. In alloy 5A, stress rupture tests were conducted transverse to known low and high angle grain boundaries. It was found that above certain relative misorientations between grains, the presence of the cellular colonies reduced the rupture properties of the alloy.

The most detrimental form of these constituents are the cellular colonies in the dendrite cores. During rupture testing of alloy 5A at temperatures from 760-1150°C, a small number of tests at 1093°C had unusually low rupture lives. In many of the longer time tests at 1093°C, results were obtained that were as low as 30% of the expected rupture life, as shown in Figure 10. Cellular colonies formed in regions of high strain, cracked along the interface, and caused premature failure. Figure 11 compares a creep curve for a specimen with cellular colonies to a normal creep rupture curve. The unexpectedly low results only occurred in a small percentage of the rupture tests performed, however the effect of the cellular colonies was very dramatic when it did occur.

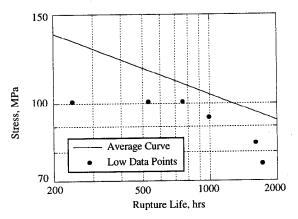


Figure 10. Rupture life of alloy 5A as a function of stress at 1093°C.

Cellular colonies near the fracture surface were found in the specimens exhibiting very low rupture lives.

# Prevention Methods

Clearly, the occurrence of SRZ and cellular colonies is undesirable, because of their effects on mechanical properties. The easiest method to reduce or eliminate the occurrence of these constituents is to change the alloy composition. Lowering the refractory content of the alloy, especially Re, will eventually eliminate the formation of these undesirable constituents. However, these alloys are designed for high creep rupture strength and reducing the refractory element content will have a direct negative effect on the strength of the alloy. A better understanding of the driving forces for SRZ and the effect of composition can lead to an alloy that balances strength and stability, as demonstrated by René N6. [9,11]

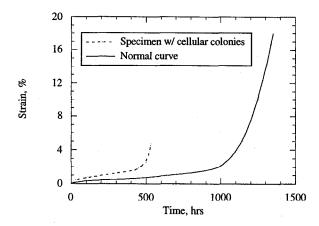


Figure 11. Comparison of a typical creep curve at 1093°C/103 MPa with a creep curve from a specimen containing cellular colonies.

Chemical supersaturation and surface residual stress are two important factors affecting the nucleation of SRZ beneath coatings. A set of experiments evaluated different surface preparations prior to coating ranging from electropolishing to shot peening. Following surface preparation, specimens were PtAl coated and exposed at 1093°C for 400 hours. The total linear percent of SRZ around the periphery of the specimen was measured. Figure 12 summarizes some of the data showing the effect of surface preparation on the amount of SRZ. It was found that electropolishing was effective at removing the surface stresses and subsequently eliminating the amount of SRZ beneath the coating after high temperature exposure. Low stress grinding, grit blasting or other moderate surface preparation techniques were sometimes effective at reducing the amount of SRZ compared to normal turbine airfoil production processing. However, these techniques produced significant scatter in the data, which is further evidence of the high nucleation barrier for SRZ. Shot peening and other aggressive surface preparation techniques resulted in complete coverage of SRZ due to a high contribution of strain energy to nucleation.

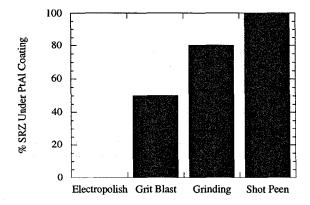


Figure 12. Effect of surface stress introduced by various methods on the occurrence of SRZ under a PtAl coating.

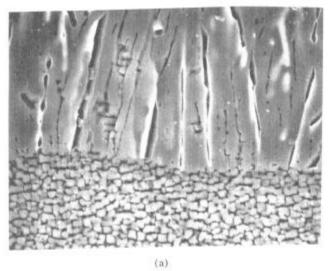
Another set of experiments were performed to modify the chemistry or microstructure of the surface of the superalloy prior to aluminide coating. Various elements were applied to the surface to stop the nucleation and growth of SRZ. Nickel was sputtered to reduce the concentration of refractories at the surface, while Ta was applied to decrease diffusivity. C and B were added by chemical vapor deposition (CVD) to form refractory boride and carbide precipitates that could reduce supersaturation and boundary mobility. Platinum was electroplated to determine if it exacerbated the formation of SRZ. Short anneals were given to the as-deposited specimens to determine if the addition of the new layer caused SRZ prior to aluminide coating. Additional specimens containing deposited surface elements were aluminized using the pack process. These specimens were evaluated for SRZ formation in the as-coated condition and following a 1120°C exposure for 50 hours, although little change in SRZ occurrence was observed with the 1120°C exposure.

Table 3 shows the qualitative results of this experiment. The Hf and Ta surface modifications resulted in SRZ formation under all conditions. These additions are  $\gamma$  stabilizers, which resulted in an unstable condition below the coating. The B treated specimens were extremely reactive to air and although the SRZ did not form, alloy 5A exhibited extensive boride formation and areas of local melting. The Pt plating by itself did not cause SRZ formation, however an abundant amount formed after aluminide coating. This is consistent with the observation that PtAl coatings promote SRZ formation more readily than simple aluminide coatings. It has been shown that Pt increases the amount of Al that assimilates into a coating.  $^{[13]}$  The Ni surface modification showed some improvement compared to specimens with no surface modifications. The thin layer of Ni appears to have helped to reduce the supersaturation in the coating diffusion zone.

The most promising surface modification for preventing SRZ formation was the deposition of carbon prior to coating. [14] Table 3 shows that no SRZ formed even after the high temperature exposure following aluminizing. The sub-micron W- and Ta-rich carbides penetrated to a depth below the diffusion zone of the subsequent coating. These carbides accomplished two objectives. First, they tied up the refractory elements in stable compounds reducing the chemical driving force for SRZ nucleation. Second, they precipitated in sufficient amounts to preclude movement or growth of the SRZ colony. Both of these effects served to eliminate the formation of SRZ.

Table 3. Amount of SRZ Formation Following Substrate Surface Modifications.

Surface Modification	As Deposited + 1080°C/1 hr Anneal	Aluminized + 1080°C/1 hr Anneal
CVD Hf	Abundant	Abundant
Sputtered Ta	Abundant	Abundant
CVD B	None	Melted
Electroplated Pt	None	Abundant
Sputtered Ni	None	Little
CVD C	None	None



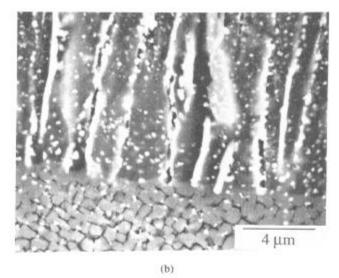


Figure 13. An aluminide coated turbine airfoil showing (a) SRZ and (b) the absence of SRZ following a carburizing treatment. Small white particles in the primary diffusion zone are carbides.

Figure 13 shows the successful use of carburization to eliminate SRZ on an engine component of alloy 5A. This figure shows two turbine airfoils following a 1120°C/50 hour exposure. One turbine airfoil sample was carburized prior to PtAl application and the other airfoil was only PtAl coated. Figure 13a shows the SRZ/alloy interface, while Figure 13b shows the fine carbides present through the normal diffusion zone which prevented the formation of SRZ. The key condition for carburization to succeed was for the carbide precipitation depth to be greater than the depth of the coating's primary diffusion zone. Carburized specimens were tested in a cyclic oxidation/hot corrosion burner rig test with no detrimental effect from carburization.

Surface prevention methods can lead to reduced SRZ under the coating, but they do not affect the formation of cellular colonies along grain boundaries or in dendrite cores. The formation of these cellular colonies is a direct result of the supersaturation of the γ matrix with P or γ forming elements. Short of changing alloy composition, heat treatment appears to be the only method to reduce the supersaturation. Solution heat treatment trials were performed on alloy 5A to reduce the segregation of Re and other refractory elements present in the dendrites. Rhenium is the most important element causing SRZ and the slowest diffusing element in superalloys. Thus, a parameter was developed to measure the segregation of Re in directionally solidified superalloys:

Electron microprobe analysis of specimens was conducted following a series of heat treatments from 1310-1330°C for times from 2-25 hours. Figure 14 shows a summary of these data. As expected from diffusion theory, there is an initial rapid decrease in Re segregation followed by a more gradual decrease. In as-cast specimens of alloy 5A, Re levels as high as 9.5 wt.% were found in the dendrite core compared to the bulk level of 6.25 wt.%. This high level of Re, along with other refractory elements, leads to an unstable condition in the dendrite cores. Extended solution heat treatments can lower the level of Re in the dendrite core

closer to the bulk alloy level so that the dendrite core is no longer unstable. For alloy 5A, it was found that a Re  $\Delta$  of approximately 30% was necessary to eliminate the occurrence of cellular colonies in the dendrite cores. The analysis used in Figure 14 is valid for other third generation single crystal superalloys, however the appropriate Re  $\Delta$  value to eliminate cellular colonies will vary for each alloy.

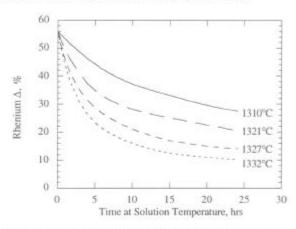


Figure 15. Effect of time at the maximum solution heat treatment temperature on the dendritic segregation of Rhenium.

# Discussion

## SRZ: Cellular Precipitation

The SRZ and cellular colony reactions that have been observed in alloy 5A and other superalloys containing high levels of Re are cellular precipitation reactions. This type of precipitation event has been observed in many alloys systems, including Pb-Sn, [15,16] Cu-In, [17] Ni-Al, [18] Cu-Ti [19] and Cu-Be, [20] There have been several reports of cellular precipitation in superalloys, mainly involving either carbides [21-23] or eta phase [24] at grain boundaries. The presence of grain boundary serrations in superalloys has also been attributed to cellular precipitation of γ' at the grain boundaries. [25] These serrations are reported to improve fatigue crack growth rate. It has also been

observed in turbine disk alloys that additions of Hf promoted a cellular precipitation reaction. Pollock has previously reported on the occurrence of the cellular colonies along grain boundaries in alloy 5A, <sup>[4]</sup> but there have been no other reports of cellular precipitation in single crystal superalloys.

Cellular precipitation consists of the transformation of a supersaturated  $\alpha'$  phase into a structurally identical  $\alpha$  phase plus a lamellar  $\beta$  phase. The reaction visually resembles a eutectoid decomposition, such as pearlite in steels. The initial nucleation and growth theories originally proposed by Smith, [27] Turnbull [28] and Cahn [29] have only been modified slightly [30-32] since their inception in the 1950's. Nucleation of the cellular reaction occurs at grain boundaries, or more specifically, on favorably oriented precipitates along the grain boundaries. The driving force for nucleation is the supersaturation in the matrix adjacent to the nucleating particle. The presence of stress also aids the nucleation process.

Following the nucleation of a small grain boundary precipitate, the reaction grows in a cell morphology with lamellar precipitates. The growth of the cell boundary is driven by the difference in chemical potential between the supersaturated matrix ahead of the cell boundary and the matrix within the cell which contains the equilibrium structure. The lead interface is an incoherent boundary, while the lamallae boundaries within the cell are partially coherent. Thus, the dominant diffusion mechanism occurs along the advancing cell boundary. Volume diffusion in the supersaturated matrix is negligible. Growth of the cell can be slowed by precipitation in the matrix ahead of the cell, and growth will stop when the supersaturated condition driving the reaction have dissipated.

Comparison of the SRZ and the cellular colonies in superalloys with the observations in other systems leads to some interesting points. The observation that the lead interface is incoherent helps to explain the cracking in the cellular colonies in the dendrites that had such a detrimental effect on properties. Also, the fact that growth of the cellular precipitation reaction will stop when the driving force has been eliminated is observed in these superalloys. Under a coating, the growth of SRZ corresponds closely to the interdiffusion zone between the coating and substrate. The SRZ is rarely observed to extend deeply into the microstructure. The cellular colonies in the dendrites also are confined to the dendrite core, because there is little driving force outside of the supersaturated core.

The SRZ and cellular colonies shown in this paper differ in two important ways from the classical cellular precipitation discussed in the literature. First, in cellular precipitation the matrix ahead of the advancing cell is structurally identical to the matrix within the cell. In this paper, the matrix ahead of the cell is a  $\gamma$  matrix, while the matrix inside the cell is  $\gamma'$ . Theories on cellular precipitation state that the structure within the cell represents the equilibrium structure for the alloy. Thus, under certain conditions, the equilibrium microstructure in high  $\gamma$  volume fraction superalloys with high refractory contents is a  $\gamma'$  matrix with  $\gamma$  and P phase precipitates. The other difference between

the observations in this paper and classical cellular precipitation is the structure within the cells. Three phases co-exist in the SRZ and cellular colonies, while only two phases have previously been observed in cellular precipitation colonies. This is likely due to the complex phase relationships in these superalloys versus the simpler phase relationships in many of the alloys previously studied.

Cellular precipitation is described in the literature as occurring along grain boundaries. In the single crystal alloys described in this paper, the only grain boundaries present are those defects that form during solidification. It has been shown that cellular colonies form along these grain boundaries in the same manner as described in the literature on cellular precipitation. The SRZ beneath coatings also likely nucleates along a grain boundary in the coating or the coating primary diffusion zone. However, there are no apparent grain boundaries in the dendrite cores to serve as nucleation sites for the cellular colonies observed in this paper. Thus, while these cellular colonies structurally appear similar to the cellular colonies along grain boundaries of the SRZ under coatings, the nucleation mechanism may be different than classical cellular precipitation. Nucleation of the cellular colonies in the dendrite cores likely occurs from a heterogeneous site rather than undergoing homogeneous nucleation. The heterogeneous site could be a small TCP phase that has nucleated in this refractory-rich region. Other heterogeneous sites, such as carbides and  $\gamma/\gamma'$  eutectic, are confined to the interdendritic regions due to segregation of elements during casting. It appears that the nucleation barrier for the cellular colonies is very high because nucleation only occurs under special circumstances of high levels of supersaturation or high levels of strain energy. More work needs to be done to understand the nucleation of cellular colonies in the dendrite cores.

# Cellular Precipitation versus Cellular Recrystallization

The cellular precipitation observed in alloy 5A closely resembles cellular recrystallization commonly observed in superalloys.<sup>[33]</sup> In fact, it is very difficult to determine the difference based on microstructural features. In high volume fraction γ' superalloys, both cellular precipitation and cellular recrystallization have  $\gamma'$  matrices with  $\gamma$ precipitates and sometimes a TCP phase precipitate. Both have a cellular structure with the precipitates within the cell aligned perpendicular to the growth front. The major difference is in the driving force for nucleation and growth. While cellular recrystallization is driven primarily by residual stress, cellular precipitation is driven by stress and composition (supersaturation). In the three cases of cellular precipitation presented in this paper, supersaturation plays a key role in their nucleation and growth. In the failed creep rupture specimens in which cellular colonies were observed very close to the fracture surface, the contribution of strain energy to the cell formation was very high. In this case, the distinction between cellular precipitation and cellular recrystallization becomes less clear.

#### Implications of SRZ

The presence of SRZ and cellular colonies is a serious issue for all advanced directionally solidified superalloys. The combination of a segregated solidification structure, high levels of refractory elements

and a high volume fraction of  $\gamma'$  make these alloys especially susceptible to cellular precipitation. This phenomenon has been observed in a large number of third generation single crystal alloys, including alloy 5A, René N6 and CMSX-10 to varying degrees. SRZ under coatings has even been observed in alloys with Re contents as low as 3 weight %.

The amount of SRZ under coatings can vary widely depending upon coating characteristics, surface preparation and exposure conditions. For these reasons, it is necessary to fully understand the effects of these variables and how they affect the processing window for each alloy. While PtAl coatings tend to promote the most SRZ, all aluminide coatings and MCrAlY coatings can cause SRZ. While drastic reductions in properties have not been observed for SRZ beneath coatings, there is a concern due to loss of load bearing cross section and the potential for crack initiation.

It has been found that cellular colonies along grain boundaries in directionally solidified or single crystal superalloys reduce rupture strength across the boundary. In single crystals, this effectively reduces the acceptable limit for low angle grain boundaries in castings. Traditional limits may not apply unless extensive testing across grain boundaries has been performed. Such testing was performed on alloy 5A, and it was found that the acceptable limit for grain boundary misorientation decreased by several degrees due to the presence of cellular colonies.

Cellular colonies in dendrite cores represent the most serious concern for advanced turbine airfoil alloys. It is difficult to screen for the presence of these colonies, and their dramatic impact on rupture strength may only be evident in long-time tests in certain temperature ranges. For alloy 5A, the loss in rupture strength was only observed in a small fraction of the total tests conducted. This experience and knowledge of the cellular precipitation reaction led to the successful development of René N6, which is free of cellular colonies in dendrites and has shown no property degradation in extensive testing. [9]

## Prevention of SRZ

Some of the prevention methods for SRZ and cellular colonies discussed earlier are summarized in Table 4. For SRZ under coatings, there are several alternative prevention methods. Coating parameter changes, surface preparation and carburization all can be successfully employed. Prevention of cellular colonies along grain boundaries is difficult, except by changing alloy composition or screening castings based on grain misorientations. A balanced alloy composition is key to preventing the cellular colonies in the dendrite cores. Once a balanced alloy composition has been obtained, an extended solution heat treatment cycle to reduce the Re segregation is effective in ensuring the absence of this reaction.

Table 4. Summary of Prevention Methods for SRZ & Cellular Colonies.

Microstructural Instability	Method of Prevention
SRZ Under Coating	Change Alloy Composition  Modify Coating Parameters  Surface Carburization <sup>[14]</sup> Reduce Surface Stresses
Cellular Colonies Along Grain Boundaries	Change Alloy Composition Screen Castings for Grain Misorientation
Cellular Colonies in Dendrite Cores	Change Alloy Composition  Extended Solution Heat Treatments [11]

# Conclusions

- A new type of instability in superalloys has been observed in alloys containing high levels of refractory elements. This instability can occur beneath coatings, along grain boundaries or in dendrite cores
- 2. The instability has been termed secondary reaction zone (SRZ) for its occurrence under the primary diffusion zone of coatings. SRZ and the cellular colonies elsewhere in the microstructure are a form of cellular precipitation previously reported in a wide variety of alloy systems.
- Cellular colonies in dendrite cores can reduce creep rupture properties over 50% at temperatures around 1100°C. SRZ under coatings can lower properties by reducing load-bearing area and serving as crack initiation sites.
- Methods to reduce or eliminate SRZ under coatings have been developed, such as altering coating parameters or carburizing a thin layer of the substrate prior to coating.
- Prevention of the cellular colonies in the dendrite cores is best accomplished by developing a balanced alloy composition, although an extended solution heat treatment cycle can reduce colony occurrence.

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