

THE FORMATION OF SRZ ON A FOURTH GENERATION SINGLE CRYSTAL SUPERALLOY APPLIED WITH ALUMINIDE COATING

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Abstract

The formation behavior of Secondary Reaction Zone (SRZ) for a 4th generation nickel-base single crystal (SC) superalloy with aluminide coating was investigated. The growth of SRZ is supposed to be dominantly controlled by the inward diffusion of aluminum from the coating layer to the substrate. The outward diffusion of Ru from the substrate to the coating layer may also contribute to SRZ formation. A remarkable reduction of SRZ was accomplished by depositing thin films composed of Co and/or Ru on the alloy surface prior to aluminide coating, that is expected to restrict the diffusion of Al and Ru between the coating layer and the substrate.

Introduction

The 3rd generation Ni-base SC superalloys, containing high concentrations of rhenium, are used in jet engine turbine blades for their outstanding high-temperature mechanical strength. However, applying aluminide coating to these alloys, necessary to improve oxidation resistance, causes a harmful intermediate layer under the coating. This intermediate layer called SRZ, is believed to degrade mechanical properties of the alloys [1]. SRZ consists of Topologically Close Packed (TCP) phase, which contains the refractory elements such as Re or W, and needle-like gamma phase in a matrix of gamma prime [1]. Since SRZ formation does not occur in alloys with lower Re concentrations, the higher levels of Re may be important in SRZ formation. It is suggested that SRZ is derived from the local compositional changes due to diffusion of Al and other elements between the coating layer and the substrate [2]. The effect of stress is also suggested [1].

Recently the 4th generation SC superalloys[4] have achieved further thermal stability and remarkable creep strength by the addition of Ru, which is expected to restrict the formation of TCP [3]. Since these alloys also contain high concentrations of Re, as is the case of the 3rd generation SC superalloys, SRZ caused by aluminide coating may become a significant issue. We confirm that the application of aluminide coating degrades the creep-rupture strength of the 4th generation SC superalloy accompanied with the formation of SRZ. It is supposed that SRZ contributes considerably to this mechanical degradation.

This study investigated the formation behavior of SRZ caused by aluminide coating for a 4th generation SC superalloy. Moreover, some additional coatings to reduce SRZ by restricting the diffusion of elements between the coating layer and the substrate will be suggested.

Formation Behavior of SRZ Caused by Aluminide Coating

With the aim of clarifying the mechanism of SRZ growth, the formation behavior of SRZ and the diffusion behavior of the elements under several oxidation conditions were examined.

Experimental Procedures

A 4th generation Ni-base SC superalloy, TMS-138, was used as the substrate material, as shown in Table I. Aluminide coating was applied by conventional pack-cementation method.

Table I. Chemical Composition in wt.% of Alloy TMS-138

Ni	Cr	Co	Mo	W	Al	Ta	Re	Ru	Hf
Bal.	2.9	5.9	2.9	5.9	5.9	5.6	4.9	2.0	0.10

A static oxidation test in air at 1273K for 2000 hours was carried out for the specimen with aluminide coating to examine the time dependence of SRZ growth. Static oxidation tests in air at a variety of temperatures from 1173K to 1373K in 500 hours were also carried out to examine the temperature dependence. The geometry of the specimen was 20 mm in diameter and 3 mm in thickness. The cross-sectional microstructures were analyzed by optical microscopy and scanning electron microscopy (SEM). The X-ray intensities of the elements were measured by electron probe micro analyzer (EPMA). The diffusion behavior of an element was evaluated by the ratio of X-ray intensity to the substrate.

Results

Microstructures. The cross-sectional microstructure of the specimen with aluminide coating after the oxidation test at 1373K in 500 hours is shown in Figure 1. The gamma matrix has disappeared under the diffusion zone of coating, where large amount of precipitates composed of refractory elements such as Re, W, or Mo were formed. (This region is defined as SRZ in this paper.) Granular precipitates distributed in the upper part of SRZ, and needle-like precipitates perpendicular to the interface distributed below. SRZ expanded toward the substrate as the oxidation time became longer or the temperature became higher.

Al was distributed from the coating layer to the SRZ after the oxidation test at 1173-1273K. This indicates that Al had diffused inward from the coating layer to the substrate during the oxidation test. The X-ray intensity of Al just under the coating layer had increased to about 1.8 times as high as that in the substrate after 1000 hours at 1273K. After the highest temperature oxidation test at 1373K, Al scarcely remained in the coating layer. Its X-ray intensity in the coating layer had decreased to as low as about 60% of that in the substrate. On the other hand, Ru was concentrated in the coating layer while it was depleted under the coating layer after the oxidation tests. This indicates that Ru had diffused outward from the substrate to the coating layer. The X-ray

intensity of Ru in the coating layer had increased to about twice as high as that in the substrate after 1000 hours at 1273K. While that under the coating layer had decreased to as low as about 20% of that in the substrate.

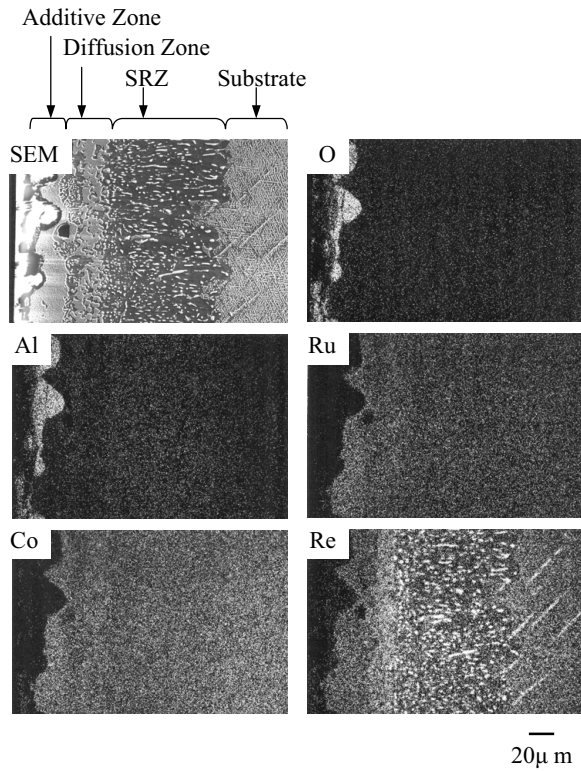


Figure 1. Cross-sectional microstructure and characteristic X-ray images of the specimen with aluminide coating after the oxidation test in air at 1373K in 500 hours.

SRZ Thickness. The layer thickness of SRZ, d , was defined as the average thickness from just under the diffusion zone to the bottom of the SRZ, was measured as shown in Figure 2. The dependence of SRZ thickness d on the oxidation time at 1273K and the oxidation temperature in 500 hours were examined.

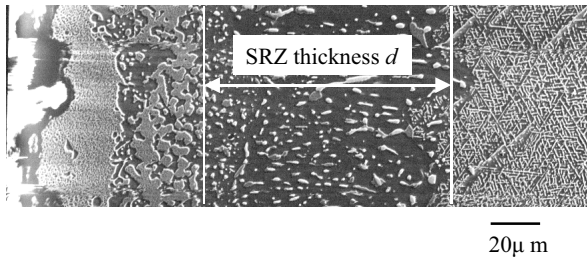


Figure 2. Definition of SRZ thickness d

Time dependence: The time dependence of SRZ thickness d at 1273K is shown in Figure 3. It is confirmed that d increases in proportion to the square root of time \sqrt{t} .

Temperature dependence: The temperature dependence of SRZ thickness d in 500hours is shown in Figure 4. The linear

relationship is observed between $\ln(d)$ and $1/T$ in the temperature ranged from 1173K to 1323K. The growth rate of thickness d tends to decrease at higher temperature than 1323K.

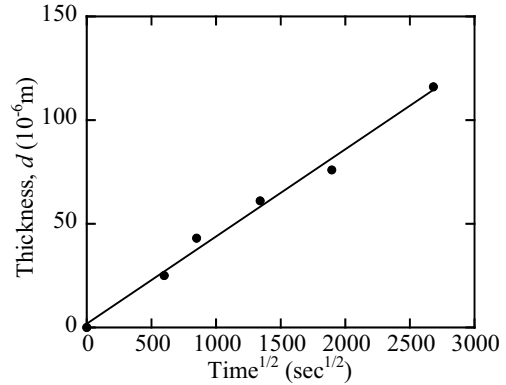


Figure 3. Time dependence of SRZ thickness d of the specimen with aluminide coating at 1273K.

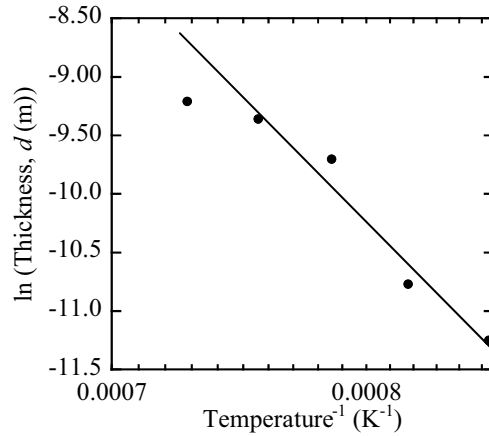


Figure 4. Temperature dependence of SRZ thickness d of the specimen with aluminide coating in 500hours.

Discussion

The growth kinetics of SRZ will be discussed here on the assumption that the oxidation test can be regarded as purely thermal exposure. Namely the effects of oxidation reactions or inward diffusion of oxygen are not included in following discussions.

The results of EPMA analysis shows that Al diffuses inward from the coating layer to the substrate and Ru diffuses outward from the substrate to the coating layer during high temperature exposure. The increase of Al content in the substrate due to its inward diffusion from the coating layer may cause phase transformation from gamma into gamma prime, leading to the formation of SRZ. Also, the decrease of gamma phase may oblige the refractory elements such as Re or W in it to be supersaturated and separate into TCP. So it can be said that the growth of SRZ is predominantly controlled by the inward diffusion of Al from the coating layer and the presence of refractory elements in the substrate. On the other hand, the decrease of Ru content in the

substrate due to its outward diffusion into the coating layer may cause local phase instability [3, 4]. It may also promote the formation of SRZ.

SRZ thickness d increases in proportion to the square root of time \sqrt{t} until 2000 hours at 1273K, as shown in Figure 3. This indicates that the growth of SRZ is dominantly controlled by the diffusion process. The linear relationship is also observed between $\ln(d)$ and $1/T$ in the temperature ranged from 1173K to 1273K, as shown in Figure 4. This indicates that the growth of SRZ is subject to the thermal activation process. At higher temperatures than 1323K, the growth rate of SRZ tends to decrease. Al in the coating layer is consumed to form oxide scale and also diffuses into the substrate. This results in the depletion of Al in the coating layer. Both the oxidation reaction rate and the diffusion rate increase as the temperature becomes higher, accelerating the Al depletion rate. Therefore Al is exhausted in a shorter time at higher temperature. Since the chemical potential of an element is related to its concentration, this Al depletion in the coating layer reduces the driving force for diffusion. This may be the main reason for the reduction of the growth rate of SRZ.

Generally, when the growth of an internal reaction layer is controlled by the diffusion process of element i , the thickness of that layer, d_i , can be described by the following equation (1) as a function of the diffusion coefficient D_i ($\text{m}^2 \text{sec}^{-1}$) and the diffusion time t (sec) [5]:

$$d_i \propto \sqrt{D_i t} \quad (1)$$

D_i can be described by the following equation (2) as a function of absolute temperature T (K) [6]:

$$D_i = D_0 \exp(Q_i/RT) \quad (2)$$

Where D_0 is the frequency factor ($\text{m}^2 \text{sec}^{-1}$), Q_i is the activation energy of diffusion of element i (J mol^{-1}), and R is the gas constant ($\text{J K}^{-1} \text{mol}^{-1}$).

When temperature is constant, D_i is constant from the equation (2). Then d_i is proportional to \sqrt{t} from the equation (1). When time is constant, the equations (1) and (2) arrived at the following equation (3):

$$\ln(d_i) = -Q_i/2RT + \text{Const.} \quad (3)$$

The equation (3) shows the linear relationship between $\ln(d_i)$ and $1/T$. The gradient of $\ln(d_i)$ - $1/T$ line equals to the value of $-Q_i/2R$.

The experimental result shows $d \propto \sqrt{t}$ at 1273K. The diffusion coefficient calculated from the gradient of regression line of the d - \sqrt{t} plot in figure 3 is $1.87 \times 10^{-15} (\text{m}^2 \text{sec}^{-1})$. This is very similar to the diffusion coefficient of Al in gamma prime, $6.03 \times 10^{-15} (\text{m}^2 \text{sec}^{-1})$ at 1187-1513K, calculated from the reported value of the activation energy [7]. The experimental result also shows the linear relationship between $\ln(d)$ and $1/T$. The gradient of the regression line of the $\ln(d)$ - $1/T$ plot through the points from 1223K to 1323K in Figure 4 is about -2.1×10^4 . The value of Q_i calculated from this is about $3.5 \times 10^5 (\text{J mol}^{-1})$. This is also similar to the reported value of the activation energy of diffusion of Al in Ni, $Q_{\text{Al}}=2.7 \times 10^5 (\text{J mol}^{-1})$ at 1372-1553K [8], and in gamma prime, $Q_{\text{Al}}=1.6 \times 10^5 (\text{J mol}^{-1})$ at 1187-1513K [7]. The quantitative evaluation of the influence of Ru diffusion is difficult

because of the lack of data.

From the above results and discussions, it can be said that the growth of SRZ is predominantly controlled by the diffusion of Al from the coating layer to the substrate and by the outward diffusion of Ru from the substrate to the coating layer.

SRZ Reduction by Additional Coating

Since SRZ is supposed to be caused by the diffusion of Al and Ru between the coating layer and the substrate, it is expected that the existence of an internal layer at the coating/substrate interface preventing the diffusion of these elements can reduce SRZ. Thus, an additional coating was applied prior to aluminide coating in an attempt to form the internal layer.

Experimental Procedures

A thin film composed of Co and/or Ru was deposited on the specimen surface by sputtering, as an additional coating. The composition and thickness of the deposited films are shown in Table II. Then aluminide coating was applied following a heat treatment. Static oxidation tests were carried out in air at 1373K in 500 hours for these specimens. The cross-sectional microstructures before and after the oxidation tests were analyzed by optical microscopy, SEM, and by EPMA. The layer thickness of SRZ was measured and compared to that of the specimen with aluminide coating, that means without additional coating.

Table II. The variation of sputter deposited films

	Name	Composition (at.%)	Thickness
A	Ru / 5 μm	Ru 100%	5 μm
B	Ru / 1 μm	Ru 100%	1 μm
C	Co50-Ru50 / 5 μm	Co 50% - Ru 50%	5 μm
D	Co80-Ru20 / 5 μm	Co 80% - Ru 20%	5 μm
E	Co / 5 μm	Co 100%	5 μm

Results

SRZ Thickness. The ratio of SRZ thickness d of the specimens with additional coatings to the specimen with aluminide coating after the oxidation test is shown in Figure 5. SRZ thickness of the specimens A:Ru/5 μm , C:Co50-Ru50/5 μm , and D:Co80-Ru20/5 μm were no more than half of that of the specimen with aluminide coating. Those of the specimens B:Ru/1 μm and E:Co/5 μm were only slightly thinner than that of the specimen with aluminide coating.

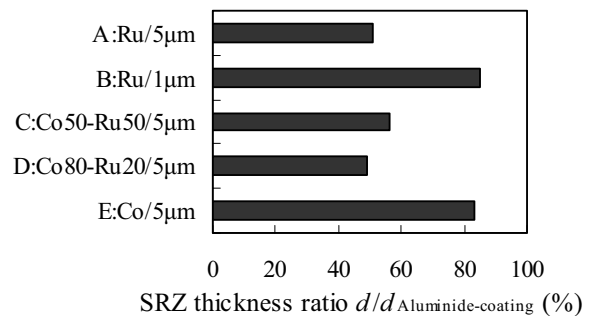


Figure 5. SRZ thickness ratio of the specimens with additional coatings to the specimen with aluminide coating after the oxidation test in air at 1373K in 500 hours.

Oxidation Resistance. The weight changes of the specimens with additional coatings during the oxidation test in air at 1373K in 500 hours is shown in Figure 6. The specimens with aluminide coating and without coating are also plotted for reference. All the specimens with additional coatings showed good oxidation resistance equivalent to that of the specimen with aluminide coating. The specimen without coating showed large weight decrease due to scale separation. It was confirmed that the oxidation resistance is improved by the application of these coatings.

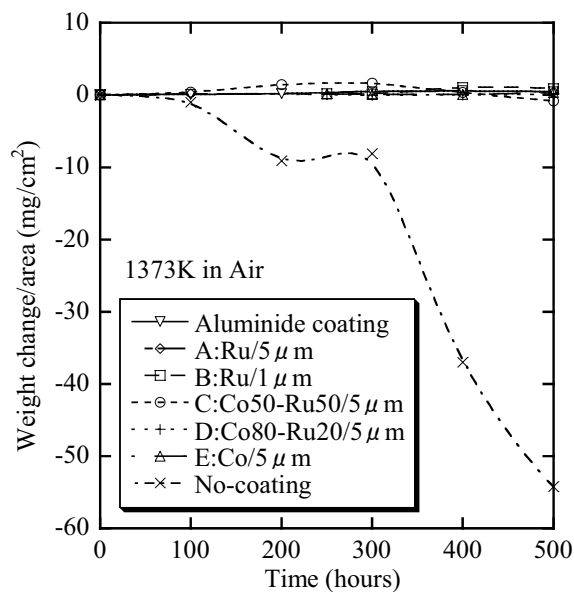


Figure 6. Weight changes of the specimens at 1373K in air.

Microstructures. In the case of pure Ru deposition: The cross-sectional microstructure of the specimen A:Ru/5μm before the oxidation test is shown in Figure 7-(a). Ru concentrated in the upper part of the additive zone and also in the bottom part slightly. Ni was distributed in the middle part and Al was distributed in the entire additive zone. The diffusion zone was much thinner than that of the specimen with aluminide coating. It consisted of granular or needle-like precipitates.

The microstructure after the oxidation test is shown in Figure 7-(b). The diffusion zone had transformed into a line of granular precipitates and SRZ were formed below. Fine granular precipitates as small as about 0.5-1μm in diameter distributed in the most part of SRZ. A few needle-like precipitates were also formed in SRZ, however most of them were thin and as short as about 3-5μm. A secondary phase was formed in the additive zone. Ru and Al concentrated in this phase. The content of Al under the coating layer had scarcely increased, whose X-ray intensity was no more than 1.05-1.1 times as high as in the substrate. Ru was distributed from the coating layer to the upper part of SRZ. Its X-ray intensity just under the coating layer was about 2.5 times as high as that in the substrate.

The microstructure of the specimen B:Ru/1μm before the oxidation test was almost the same to that of the specimen with aluminide coating, except that Ru concentrated in the upper part of the additive zone. After the oxidation test, needle-like precipitates as long as about 10-15μm were formed obliquely in SRZ. A

secondary phase composed of Ru and Al was formed in the additive zone like in specimen A. Al was distributed from the coating layer to SRZ decreasing gently, whose X-ray intensity under the coating layer had increased to 1.5 times as high as that in the substrate.

In the case of Co-Ru deposition: The microstructure of the specimen C:Co50-Ru50/5μm before the oxidation test is shown in Figure 8-(a). Co concentrated in the upper part of the additive zone and in the diffusion zone. Ru concentrated in the lower part of the additive zone. Thin diffusion zone consisted of needle-like precipitates perpendicular to the interface.

The microstructure after the oxidation test is shown in Figure 8-(b). Fine granular precipitates were distributed in most of the SRZ. The diameters of these granular precipitates were about 1-2μm in the upper part and as small as about 0.5μm in the lower part of SRZ. Needle-like precipitates perpendicular to the interface were formed under SRZ in the substrate. A secondary phase composed of Ru and Al was formed in the additive zone like in specimen A. Ru was distributed from the coating layer to the upper part of SRZ. Its X-ray intensity just under the coating layer was about 2.2 times as high as in the substrate.

The structure of the specimen D:Co80-Ru20/5μm before the oxidation test was similar to the specimen C. Needle-like precipitates as large as about 10-20μm were observed in SRZ after the oxidation test, however its amount was very small. The gamma matrix remained to a large extent except in the very neighborhood of these needle-like precipitates.

In the case of pure Co deposition (the specimen E:Co/5μm): Co and Al were distributed in the entire additive zone. The diffusion zone was relatively thick and consisted of granular or needle-like precipitates. After the oxidation test, granular precipitates which were about 1-3μm in diameter were distributed in the upper part of SRZ. Needle-like precipitates were distributed below, which became longer in the lower part. Both Co and Al had diffused inward so that they were distributed from the coating layer to the substrate almost uniformly.

Discussion

Effect of pure Ru deposition. Ru deposition prior to aluminide coating proved to be effective on the reduction of SRZ as shown in Figure 5. The mechanism of SRZ reduction is thought to be as follows: First, the presence of a sufficient amount of Ru in the coating layer reduces the driving force for its outward diffusion from the substrate. It prevents the depletion of Ru content under the coating layer, maintaining the phase stability. Thus SRZ formation is restricted. Second, the formation of a secondary phase of Ru-Al compound in the coating layer keeps Al from diffusing into the substrate. It restricts the increase of Al content under the coating layer, so that SRZ formation is restricted. It is reported that RuAl has a considerably higher melting point than NiAl so that RuAl will be stable for a substantial time [9].

In the case of the specimen B:Ru/1μm, most of deposited Ru had diffused to the coating surface after aluminide coating treatment. So the amount of Ru at the coating/substrate interface was insufficient to prevent the diffusion of Al and Ru. It may be the reason of the failure in SRZ reduction. Therefore it can be said that a certain amount of Ru is necessary to reduce SRZ.

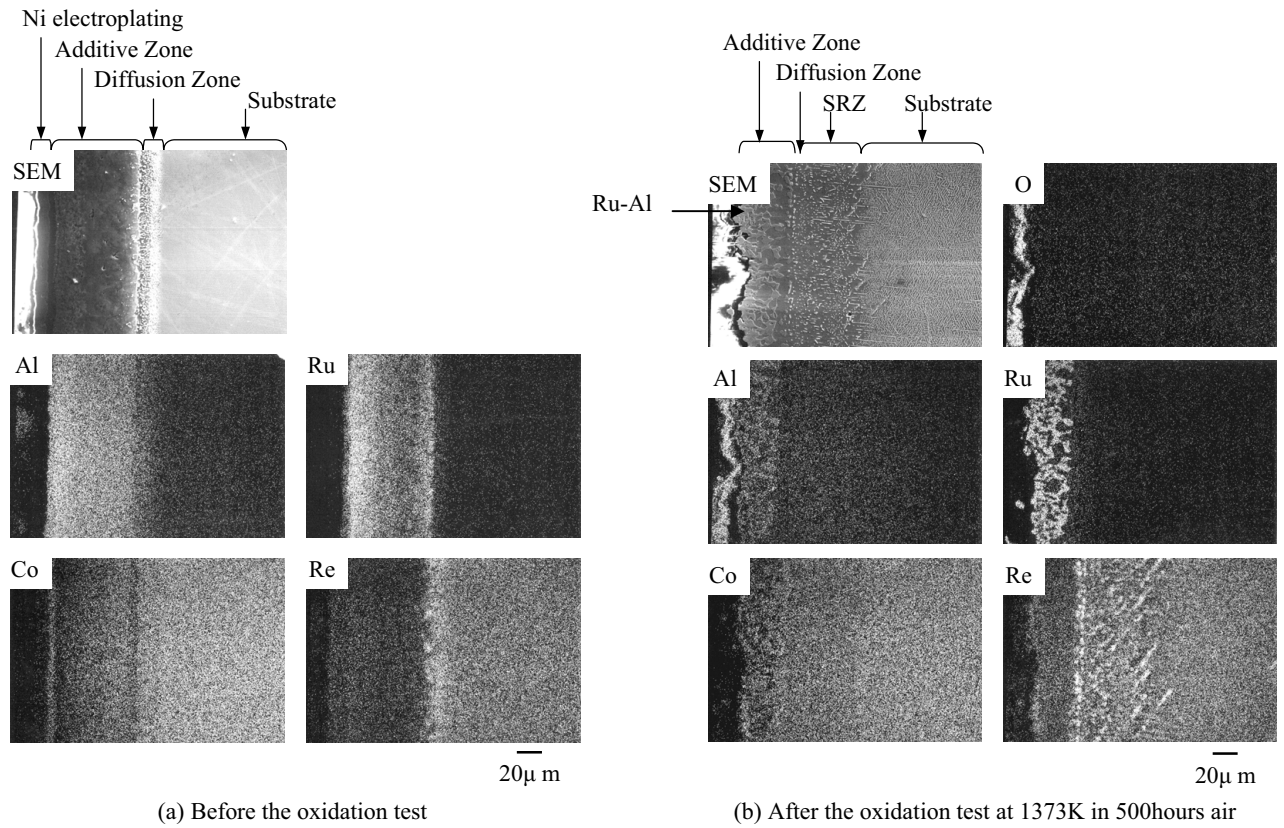


Figure 7. Cross-sectional microstructure and characteristic X-ray images of the specimen A:Ru/5 μ m.

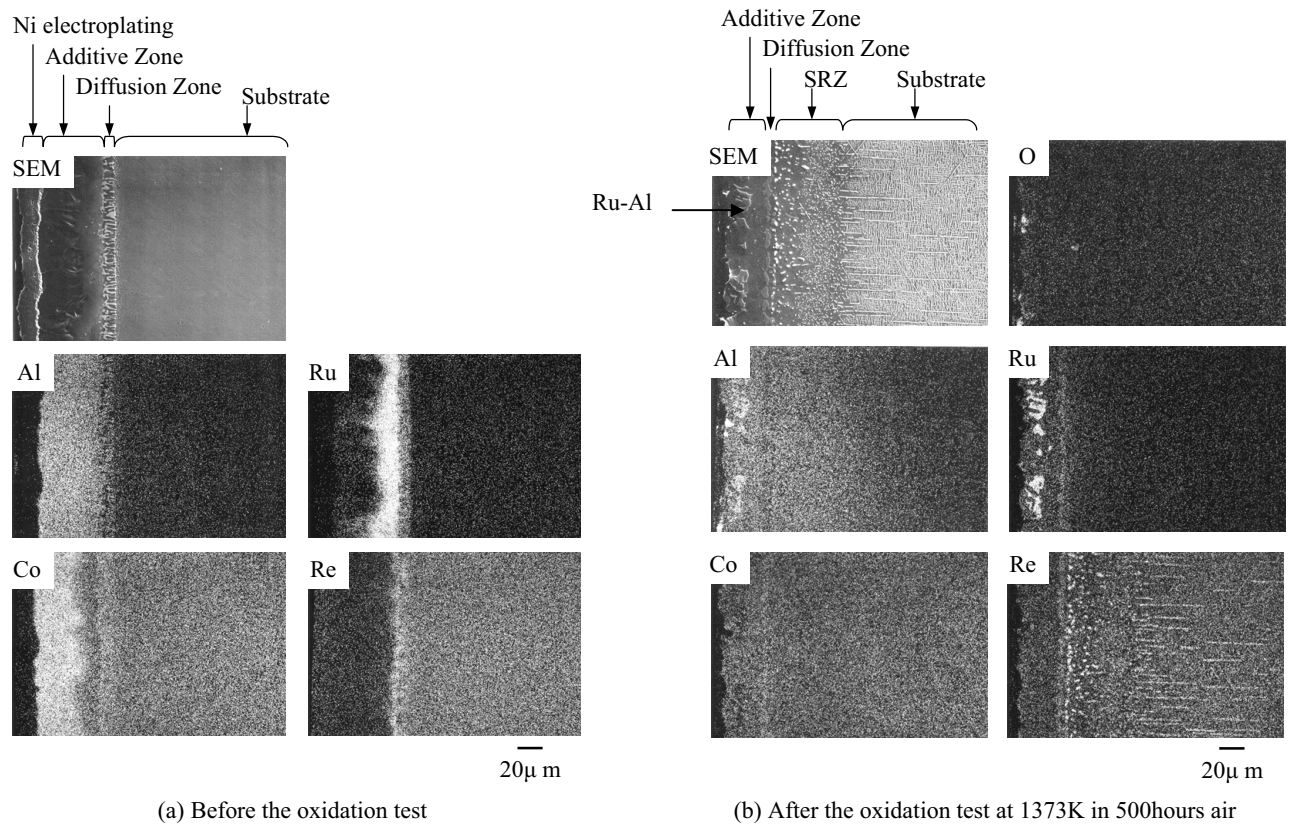


Figure 8. Cross-sectional microstructure and characteristic X-ray images of the specimen C:Co50-Ru50/5 μ m.

Effect of Co-Ru deposition. Co-Ru deposition is also effective for SRZ reduction. Moreover the effect is equivalent to pure Ru deposition in 5µm thickness in spite of the fact that the total amount of deposited Ru is smaller. Therefore it is said that Co-Ru deposition can reduce SRZ with a smaller amount of Ru than pure Ru deposition. When Ru is deposited with Co, Ru concentrates in the lower part of the additive zone and Co concentrates in the upper part after aluminide coating treatment. It is supposed that Co diffuses outward preferentially compared to Ru and combines with Al to form the additive zone of Co-Al compound during aluminide coating treatment. The Al that diffused further inward combines with Ru to form the lower part of the additive zone of Ru-Al compound, as the internal layer. It is thought that the existence of this internal layer with a high concentration of Ru at the coating/substrate interface contributes to a more effective SRZ reduction than pure Ru deposition.

Conclusions

The followings conclusions can be drawn from the results obtained in this investigation:

- 1 The growth of SRZ is predominantly controlled by the inward diffusion of Al from the coating layer and the presence of refractory elements in the substrate, such as Re. This study further revealed that the outward diffusion of Ru from the substrate to the coating layer destabilized the microstructure and lead to SRZ formation.
- 2 A certain amount of Ru deposition prior to aluminide coating can reduce SRZ.
- 3 Co-Ru deposition prior to aluminide coating can reduce SRZ with a smaller amount of Ru than pure Ru deposition.

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