

Effect of Hf Addition on Oxidation Properties of Pt-Ir Modified Aluminide Coating

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In the present study, the effect of Hf addition on oxidation kinetics of Pt-Ir modified aluminide coatings was investigated. Pt-15 at%Ir and Pt-15 at%Ir with trace amount of Hf films with 7–8 μm thick were deposited on a Ni-based single crystal superalloy TMS-82+ using magnetron sputtering, followed by a diffusion treatment and conventional Al pack cementation. While there were no significant microstructural differences observed in as aluminized specimens, cyclic oxidation test at 1423 K revealed clear advantages of Hf addition. Hf containing coatings showed smaller mass change with retarded surface rumpling during cyclic oxidation test. These results confirmed the beneficial effects of Hf addition reported for other alloy systems such as Pt modified γ - γ' coatings and Pt modified aluminide coatings. [doi:10.2320/matertrans.MAW200723]

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1. Introduction

In order to increase the efficiency of gas turbines, turbine blades must be exposed at as high operating temperature as possible. It is thus essential to develop thermal barrier coatings (TBCs) on Ni-based superalloys having better thermal shock, oxidation and hot corrosion resistances. TBCs have widely been used for turbine blades since 1960s.^{1–3)} Typically, an aluminum enriched alloys such as PtAl⁴⁾ and MCrAlY are used as a bond-coat materials in TBCs. Among bond-coat materials, a PtAl has led to the widespread application for TBCs, and some excellent properties were reported, such as to promote protective Al₂O₃ formation, to suppress void formation along the scale, and to enhance adhesion between the scale and the coating.⁵⁾

Application of Ir based alloys for bond-coats has been proposed by the authors' group.^{6–13)} As one of these approaches, oxidation and hot corrosion resistances of Pt-Ir-Al alloy systems were evaluated, and Ir addition to PtAl bond-coat was revealed to enhance oxidation and hot corrosion resistances.^{11–13)}

On the other hand, proper addition of reactive elements such as Zr, Y, Hf to bond-coat is reported to minimize the detrimental effect of S and to enhance the scale adhesion.^{14–18)} Among them, Hf addition is of particular interest because it is known to reduce the scale growth rate and thus effective in enhancing oxidation resistance.

In this study, Pt-15 at%Ir and Pt-15 at%Ir with trace amount of Hf were deposited on a Ni-based single crystal superalloy TMS-82+ by the magnetron sputtering method, followed by the diffusion annealing and the Al pack cementation. The effect of Hf addition to Pt-Ir aluminide coating on oxidation resistance was investigated.

2. Experimental Procedures

As a substrate material, so-called “second generation” Ni-based single crystal superalloy TMS-82+^{19,20)} developed by

National Institute for Materials Science (NIMS) was prepared. Its nominal composition is Ni- 12.2Al- 8.2Co- 5.8Cr- 3.0W- 2.2Ta- 1.3Mo- 0.8Re- 0.6Ti- 0.01Hf in at% (Ni- 7.8Co- 4.9Cr- 1.9Mo- 8.7W- 5.3Al- 0.5Ti- 6.0Ta- 0.1Hf- 2.4Re in mass%). Substrates were cut into 8 mm \times 8 mm \times 2 mm plates, which were polished with SiC paper up to #800 and cleaned with acetone in an ultrasonic bath. Inverse sputtering for substrate cleaning and pre-sputter cleaning for the target were respectively conducted prior to alloy deposition. Alloys consisting of Pt-15 at%Ir and Pt-15 at%Ir with trace amount of Hf were then deposited with the thickness of 7–8 μm on superalloy substrates by the magnetron sputtering method. SEM analyses revealed that all the coatings were dense, flat, with no cracks. The coated specimens were then annealed at 1423 K for 1 h in vacuum. A conventional Al pack cementation process was subsequently carried out where samples were embedded in a retort containing 48.7Al+ 23.5Fe+ 25.8Al₂O₃+ 2NH₄Cl in at% (24.5Al+ 24.5Fe+ 49Al₂O₃+ 2NH₄Cl in mass%) powder mixture, and heated at 1273 K for 5 hours in atmospheric pressure under flowing Ar. Hereafter, these specimens are respectively denoted as Pt-15Ir and Pt-15Ir-Hf.

Oxidation resistance of the specimens was evaluated by a cyclic oxidation test, where 1 cycle was defined as heating at 1423 K for 1 hour followed by air cooling for 10 min. A hole, 1 mm diameter, was drilled in a specimen in which a Pt wire was penetrated to suspend the specimen. Sample mass was measured after a certain period of cycles, while measurement of spalled scales was not conducted for technical reasons. The test was carried out up to 500 cycles.

Phase constitutions of the specimens were identified by an X-ray diffractometer (XRD). Surface and cross sectional images and local element concentrations were analyzed by a scanning electron microscope (SEM) equipped with an X-ray energy dispersive spectrometer (EDS). Surface roughness was measured by a laser microscope.

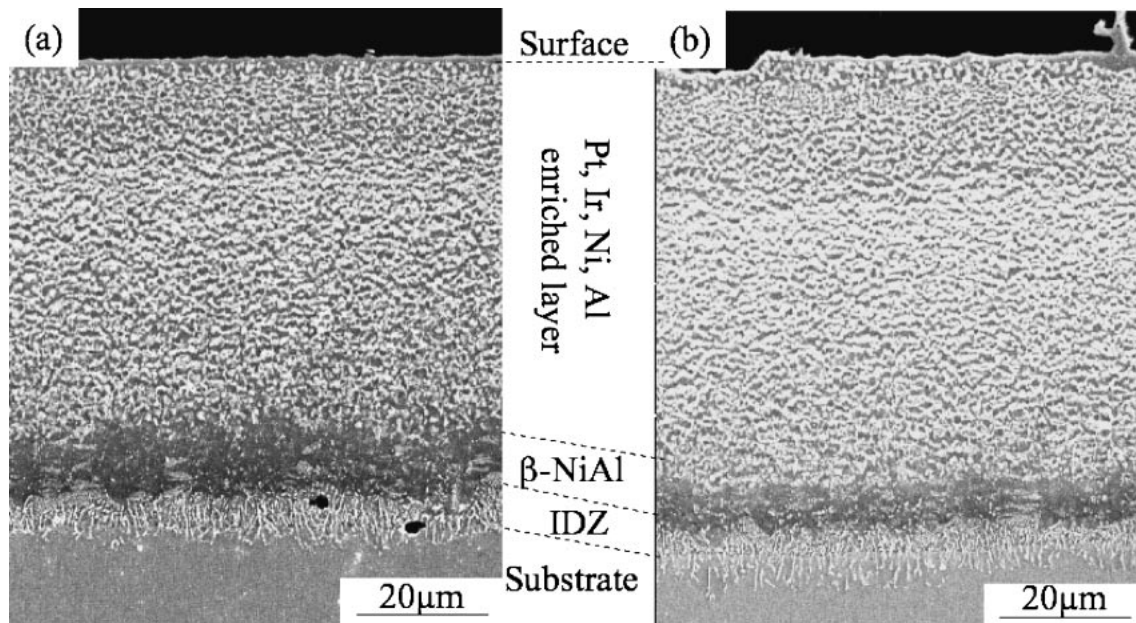


Fig. 1 Cross sectional microstructures of as aluminized (a) Pt-15Ir and (b) Pt-15Ir-Hf.

3. Results and Discussions

3.1 Microstructure of aluminized specimens

SEM observations confirmed that the diffusion annealing was successfully fabricated for both the specimens with coating layers being intact to substrates and the number of voids was negligibly small.

Figure 1 shows the cross sectional BSE Images of as aluminized (a) Pt-15Ir and (b) Pt-15Ir-Hf. As shown in Fig. 1, there were no significant microstructural differences observed in the two specimens, similar to the microstructure previously reported.¹³ Both the coatings consisted of a 70–80 μm thick Pt, Ir, Ni, Al enriched layer consisting of PtAl_2 and β - (Pt, Ir, Ni) Al phases beneath the surface, followed by a 10 μm thick intermediate Ni, Al enriched layer, a 10 μm thick interdiffusion zone (IDZ) and the substrate. Both the specimens near (5 μm beneath) the surface showed no significant compositional differences either, which were 57Al- 22Ni- 9Pt- 2Ir- and other trace elements (at%). The difference of Hf content between these coatings could not be observed due to the limit of detection capability of EDS.

3.2 Oxidation resistance

Figure 2 shows the oxidation mass change of the specimens as a function of oxidation cycles. In the cyclic oxidation test, a mass gain is mainly caused by the formation of oxide scales on the surface, whereas a mass loss mainly being caused by the spallation of the oxides, respectively. Hence, a specimen which exhibits smaller mass change is generally regarded to have better oxidation resistance. Both the specimens showed similar kinetic curves up to 200 cycles. After 200 cycles, Pt-15Ir showed continuous mass gain, and then accelerated from 400 cycles. Finally, net mass gain of 0.84 mg/cm^2 was observed after 500 cycles in comparison to the initial stage. Whereas, mass change of Pt-15Ir-Hf from 200 to 300 cycles was much smaller than that of Pt-15Ir. A sudden mass loss was observed between 320 to 340 cycles.

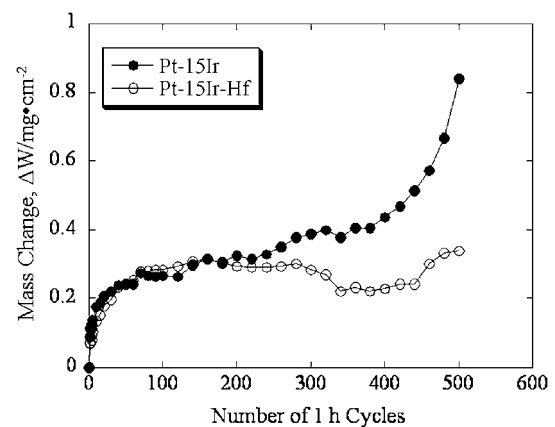


Fig. 2 Oxidation kinetic curves of the specimens during cyclic oxidation test at 1423 K.

Then the continuous mass gain was observed up to 500 cycles, with the net mass gain of 0.34 mg/cm^2 . The side surface was deposited only within 1 μm due to a technical reason. It is thus speculated that spallation of the scales could occur more easily on the side surface of the specimens. Although quantitative analysis of spalled scales from the specimen was not carried out in this study, it is very likely that occasional mass loss can be mainly attributed to the scale spallation from the side surface of the specimens. Subsequent microstructural analysis can support our hypothesis.

While significant differences were not observed in mass change of the specimens up to 200 cycles, changes in surface morphologies became clear from the earlier stage as shown in Fig. 3. This difference in surface roughness became more significant with increasing oxidation cycles.

Figure 4 shows the change in average surface roughness of the specimens during the passage of oxidation cycles derived from laser microscope. While both the specimens demonstrated increasing of surface roughness, Pt-15Ir showed an

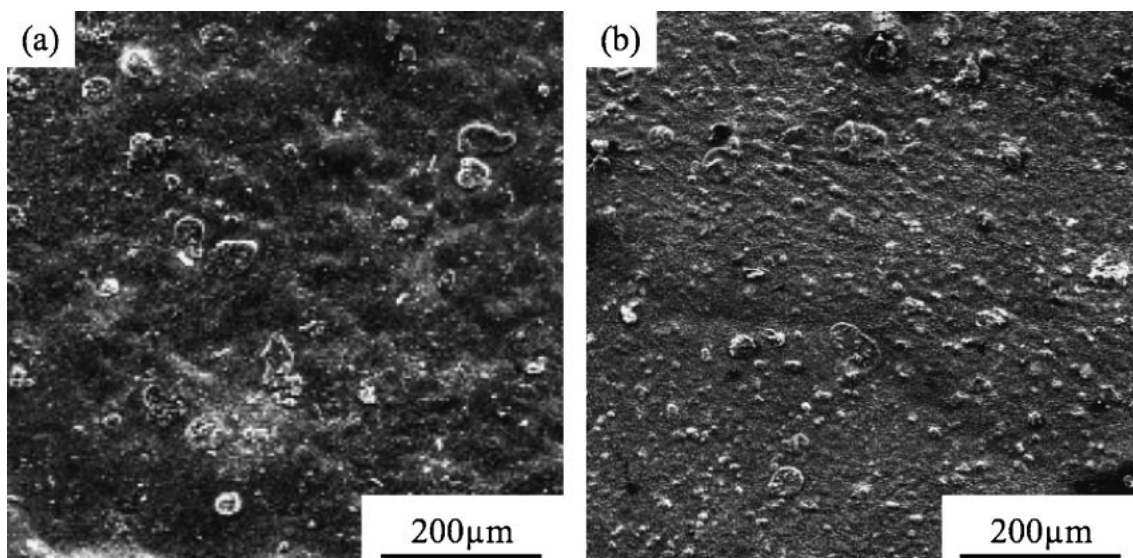


Fig. 3 Surface morphologies of the specimens after 80 oxidation cycles. (a) Pt-15Ir and (b) Pt-15Ir-Hf.

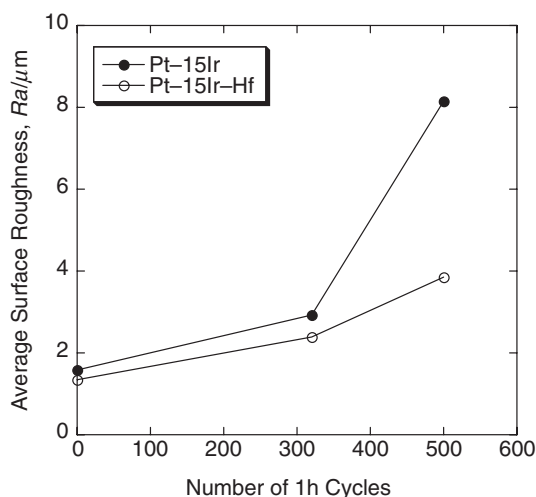


Fig. 4 Change in average surface roughness of the specimens as a function of heating cycles.

accelerated change in surface roughness, and after 500 cycles, roughness of Pt-15Ir became twice as large as that of Pt-15Ir-Hf.

Figures 5 and 6 show XRD patterns and surface morphologies after 500 cycles respectively. As shown in Fig. 5, α - Al_2O_3 , NiAl_2O_4 and $\gamma + \beta$ phases were identified on both the specimens. However, relative intensity ratio of (104) α - Al_2O_3 /(311) NiAl_2O_4 on Pt-15Ir-Hf was higher than that on Pt-15Ir. In Fig. 6, a number of spalled regions were observed on Pt-15Ir, whereas they were few on Pt-15Ir-Hf. On both the specimen surfaces, NiAl_2O_4 oxides were observed around the spalled spots. The lower relative α - Al_2O_3 / NiAl_2O_4 XRD intensity ratio of Pt-15Ir could be attributed to the larger number of spalled spots which would lead to the formation of the NiAl_2O_4 spinel. It is thus indicated that Pt-15Ir-Hf kept the Al_2O_3 scale with good adhesion.

Figure 7 shows the cross sectional SE images of (a) Pt-15Ir, (b) Pt-15Ir-Hf after 500 oxidation cycles. In Pt-15Ir, a

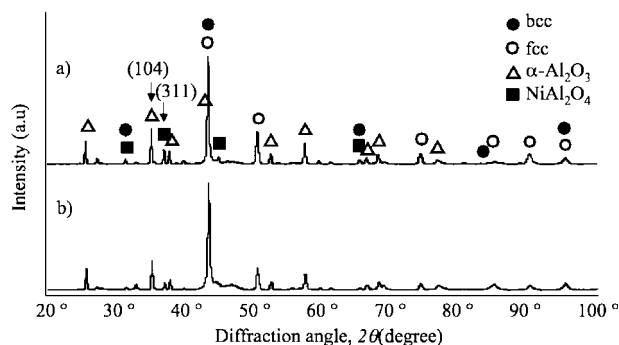


Fig. 5 XRD profiles of the specimens after 500 oxidation cycles. (a) Pt-15Ir and (b) Pt-15Ir-Hf.

number of voids were observed in the subsurface, and the voids were covered with Al_2O_3 based-oxides, indicative of internal oxidation. Thickness of oxide layer is also larger (20 μm) in Pt-15Ir than that in Pt-15Ir-Hf (3 μm). The accelerated mass gain of Pt-15Ir in Fig. 2 can be attributed to the progressive internal oxidation with the accelerated growth of surface oxide scale. On the other hand, as Pint *et al.* proposed in the previous study,¹⁷⁾ Hf could tend to segregate in the grain boundary of Al_2O_3 and retard the outward diffusion of Al, leading to the formation of uniform and smooth α - Al_2O_3 scales, which could also prevent the internal oxidation. Although further investigation is required to confirm, it is suggested that similar mechanism took place in Pt-15Ir-Hf.

As reported for other alloy systems such as Pt modified γ - γ' coatings and Pt modified aluminide coatings,^{14–18)} these results indicate that trace amount of Hf addition into Pt-Ir alloy coatings played a roll in suppressing surface rumpling and void formation, resulting in the enhanced oxidation resistance. On the other hand, under thermal cycles Hf-free coatings are more prone to form undulated surfaces. It is thus speculated that a more undulated surface may lead to form a surface oxide scale with localized internal stress, resulting in

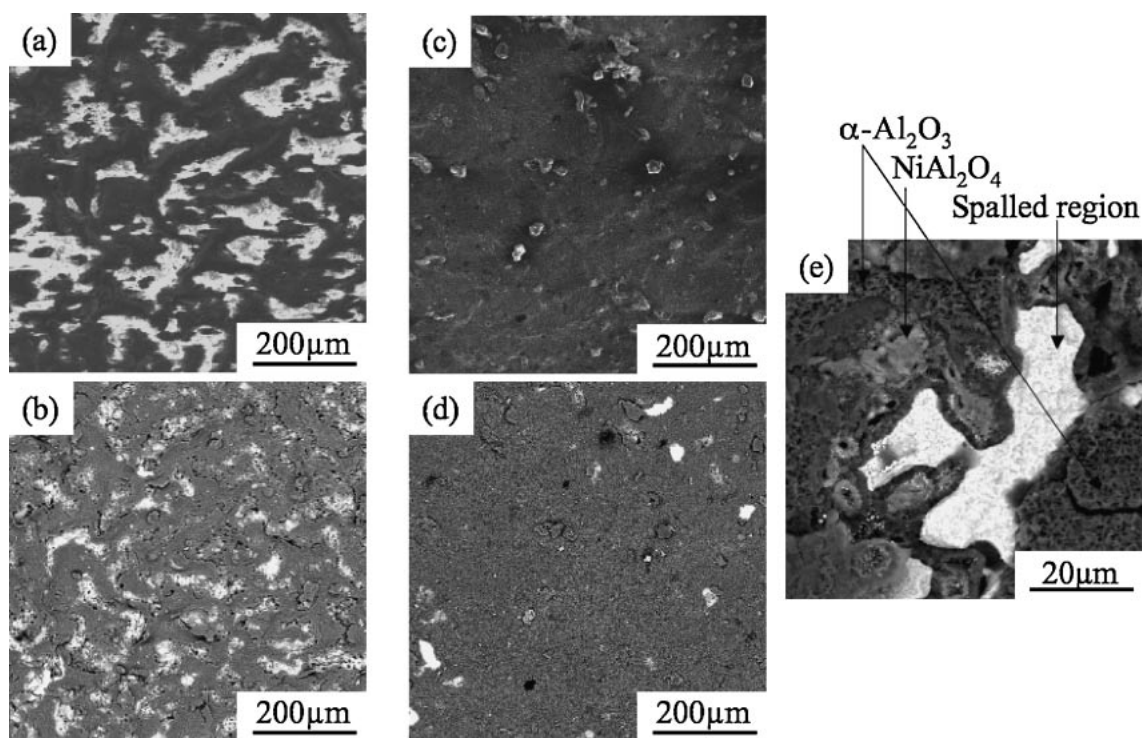


Fig. 6 Surface morphologies of (a) SEI, (b) BEI of Pt-15Ir and (c) SEI, (d) BEI of Pt-15Ir-Hf after 500 oxidation cycles. Close view of spalled region in Fig. 6(b) is also shown in (e).

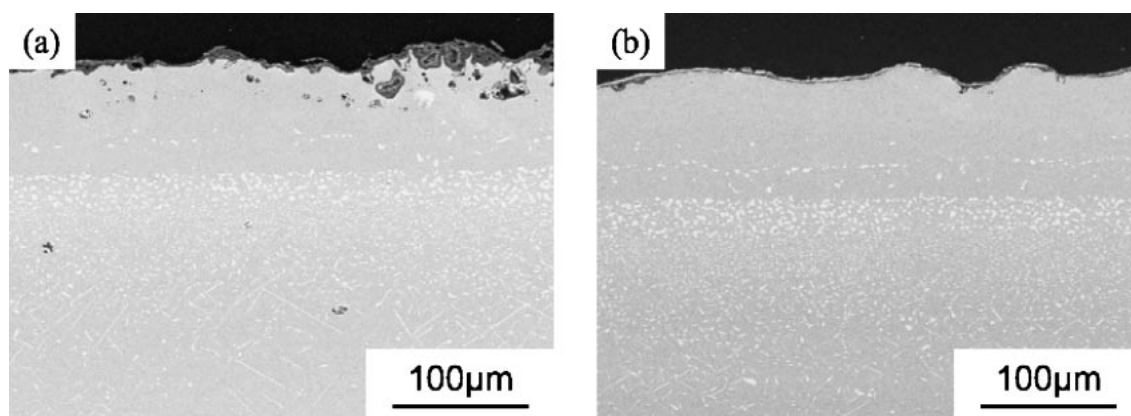


Fig. 7 Cross sectional microstructures of the specimens after 500 oxidation cycles. (a) Pt-15Ir and (b) Pt-15Ir-Hf.

the scale spallation or crack formation in the scale. Spallation of surface oxides consumes Al in the coated layer for rehearing the surface scale, which could lead to the formation of voids caused by the outer diffusion of Al. However, further investigation should be required to elucidate this hypothesis.

4. Conclusion

In this study, the effect of Hf addition on the oxidation resistance of Pt-15 at%Ir aluminide coating were investigated by conducting cyclic oxidation test at 1423 K. The results obtained are as follows.

(1) The Pt-15 at%Ir with trace Hf modified aluminide coating showed small mass change up to 500 hours of oxidation cycles.

(2) Trace Hf addition retarded surface rumpling and formation of internal voids, also forming thin Al_2O_3 scales with uniform thickness on the surface.

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