Process Dependence of Ir-Based Bond Coatings*1

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The process dependence of Ir-based-alloy-coated Ni-based single crystal superalloys was investigated. An Ir-4 at% Ta alloy, 10 μm thick, was coated on a Ni-based single crystal superalloy TMS-82+, by means of magnetron sputtering deposition (SD) and electron beam physical vapor deposition (EB-PVD). X-ray analysis revealed that the grain size of the as-SD-coated layer (∼20 nm) has five times smaller than that of the as-EB-PVD coated layer (∼100 nm), and the SD-coated specimens showed more rapid outer diffusion of Ni and Al from the substrate after annealing, than the EB-PVD-coated ones. On the other hand, the aluminizing treatment reduces the differences between the SD coated and EB-PVD coated specimens in terms of compositional distribution and oxidation resistance. This study also revealed that even without aluminizing, the simple annealing treatment enhances the oxidation resistance of the Ir-4%Ta-coated TMS-82+.

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1. Introduction

In order to improve efficiency and performance of gas turbines, there is a constant effort being done to develop new components, which can be used at higher operating temperatures. Since modern gas-turbine engines used for airplanes or power generations are operated well above the melting temperature of Ni-based superalloy substrates, improvement of thermal barrier coating (TBC) systems is essential in realizing next-generation engines.1)

The performance of current YSZ-based TBCs can be considerably increased with the improved bond-coat materials because they essentially control the spallation failure of the TBC. The ideal bond coat should have the following characteristics: i) the thermally grown oxide (TGO), which forms on the surface of the bond-coat layer, is pure, defect-free, uniform α-Al2O3 and its growth rate is slow, ii) the adhesion between the TGO and the bond-coat is highly strong, and iii) the interdiffusion of solute elements between the superalloy substrate and the bond-coat, which promotes the precipitation of detrimental phases such as topologically close packed (TCP) phases and accordingly deteriorates the mechanical properties of substrates, is slow. A various kinds of approaches to obtaining such a bond-coat have been proposed, for instance, addition of reactive elements such as Si or Hf, to MCrAlY or PtAl alloys to strengthen the TGO adhesion,2) or incorporation of the σ phase diffusion barrier interlayer between the substrate and Al-rich outer layer to retard the microstructural deterioration of the substrates.3)

One of the authors has also proposed the application of Ir-Ta-based alloys to bond-coat materials, which demonstrated the improved oxidation and corrosion resistance with controlled TCP precipitation.4,5)

Characteristics of coated materials drastically vary depending on the coating process. The typical example is YSZ top-coatings by air-plasma-spraying (APS) and electron beam physical vapor deposition (EB-PVD). The properties of bond-coats will also differ by the coating techniques, even though the composition and the thickness of coated materials are almost identical. However little work has been carried out to investigate the process dependence of the bond-coatings, except one that discusses the characteristics of NiAl coatings.6)

With these as backgrounds, process dependence of Ir-based alloy coatings on a Ni-based single crystal superalloy TMS-82+ was examined in this study. Coatings, developed by the magnetron sputtering deposition (SD) and EB-PVD, are compared in terms of inter-diffusion behavior and oxidation resistance.

2. Experimental

Substrate coupons, 25 mm in diameter and 2 mm in thickness were cut along (100) direction from the Ni-based single crystal superalloy TMS-82+ bar, whose chemical composition is Co:7.7, Cr:4.5, Mo:1.8, W:8.6, Al:5.3, Ta:6.4, Hf:0.14, Re:2.5 and Ni as a balance (in mass%).7) The substrate material was solution heat treated at 1573 K for 1 h and 1593 K for 5 h followed by gas fan cooling, and the two step ageing treatment was conducted, i.e. 1373 K for 5 h, and 1143 K for 20 h, both followed by air cooling. These substrates were then metallographically polished with emery paper up to #600, buffed with 0.25 μm diamond paste, and subsequently cleaned with acetone in an ultrasonic bath. An Ir-Ta alloy was chosen as a coating material, since our preliminary investigation revealed that the Ir-Ta alloy coating followed by Al-pack cementation demonstrated good oxidation resistance with limited deleterious phase precipitation.4) There are several processing methods to develop Ir coatings, such as electrodeposition,8) metal organic chemical vapor deposition9) and physical vapor deposition.10) In this study, SD and EB-PVD were selected as typical physical vapor deposition processes because these methods are expected to provide dense and compact coatings with designed composition. Detailed deposition conditions by SD and EB-PVD are summarized in Table 1. The as-coated
specimens were then either annealed in Ar for 1 h and 5 h, or treated with a conventional aluminizing process for 5 h, both at 1273 K. Detailed procedure for aluminizing procedure is described elsewhere.4,5)

In order to investigate the effects of coating process and heat treatment on oxidation resistance, a cyclic oxidation test was carried out as-coated, annealed and aluminized specimens. In the cyclic oxidation tests, one heating cycle was defined as heating a sample at 1423 K for 1 h in air, followed by 20 min of air-cooling. The oxidation resistance of the specimens was evaluated by measuring the mass change of the sample in the passage of oxidation cycles.

The microstructure, concentration profile of elements and the crystallinity of the specimens was investigated by scanning electron microscopy equipped with energy dispersive spectroscopy (SEM-EDS), electron-probe microanalysis (EPMA) and X-ray diffractometry (XRD).

3. Results

The surface and cross sectional morphologies of the as-deposited specimens were investigated by SEM-EDS analysis. It is confirmed that both the coatings have dense, compact with identical thickness of about 10 μm, except for the fact that the EB-PVD coated specimen has a slightly rougher surface. In addition, both the films were found to have identical composition, Ir-4 at% Ta from SEM-EDS analysis. However, XRD analysis revealed a considerable difference in the growth orientation and crystallinity between the as SD-coated and EB-PVD-coated specimens, as in Fig. 1. While both the coated layers were identified as the fcc solid-solutioned Ir single phase, the layers showed different preferred growth orientation. The SD-coated layer was strongly oriented to (220) direction whilst the EB-PVD-coated layer did not exhibit such tendencies.

From the X-ray profiles, the grain size \( d_g \) of the as-deposited films were roughly estimated using the Scherrer formula\(^{11} \)

\[
d_g = \frac{k\lambda}{B \cos \theta}
\]

where \( \lambda \) is the wavelength (0.15418 nm), \( k \) is the correction factor (\( k = 0.9 \)), \( \theta \) is the Bragg angle, \( B \) is the full width at half maximum (FWHM) of the (220) diffraction line of the films, excluding instrumental broadening. This estimation indicated that the average grain size in the SD coated layer (~20 nm) is approximately five times smaller than that in the EB-PVD coated layer (~100 nm).

These coated samples were then annealed in Ar atmosphere at 1273 K. As shown in Fig. 2, dramatic interdiffusion between the coated layer and the substrate was observed after 1 hour’s annealing treatment, and both the specimens can be categorized into four layers; i) the Ir-enriched outer layer, about 12 μm thick, ii) the Ir-Ni-Al-enriched brightest layer, about 3 μm thick, iii) the diffusion layer and iv) the substrate. While SEM cross-sectional images do not show distinctive morphological differences between the annealed specimens, the SD specimen exhibited more significant outer diffusion of Ni and Al from the substrate than the EB-PVD specimen. Figure 3 shows the change in XRD profiles as a function of annealing time. After annealed for 1 h, strong diffraction peaks of IrAl were observed in the SD specimen, while in the EB-PVD specimens, Ir peaks were dominant. The differences in XRD profiles become smaller after annealed for 5 h, consisting of IrAl main peaks together with substrate and Ir peaks. On the other hand, as shown in Fig. 4, EDX analysis revealed that the SD specimen has higher Ni concentration and lower Ir concentration in the surface layer. It should be noted that there are no such distinctive differences in terms of concentration profile and XRD peaks observed in the aluminized specimens.

In order to evaluate the oxidation resistance of these as-deposited, 5 h annealed, and aluminized specimens, the cyclic oxidation test was conducted and the result is shown in Fig. 5. In the as-deposited specimens, spallation or evaporation of surface layers started soon after the first heating cycle and following considerable mass loss occurred. Annealed specimens exhibited very similar oxidation kinet-

![Fig. 1 X-ray diffraction profiles of (a) as-SD-coated and (b) as-EB-PVD-coated TMS-82+.](image-url)
ics up to 20 oxidation cycles, and then rapid mass loss occurred for the SD specimen. Aluminized specimens both have highest oxidation resistance. They demonstrated very similar oxidation kinetics up to 30 oxidation cycles and then mass loss rate became slightly higher in EB-PVD specimens. The mass loss is almost two times higher in the EB-PVD specimen than in the SD specimen. However, this difference in mass change is much smaller compared with annealed specimens.

4. Discussion

4.1 Characteristic differences between SD and EB-PVD coatings

This study revealed that the main differences between the SD coated and EB-PVD coated specimens lie in i) the growth orientation of the coated layer and ii) the grain size of the films. The reason for the preferred (220) orientation in SD coated specimens would be discussed elsewhere. On the other hand, the difference in grain size can alter the diffusion behavior of solute elements. In this study, the as-SD-coated layer has almost two times higher in the EB-PVD specimen than in the SD specimen. However, this difference in mass change is much smaller compared with annealed specimens.

Fig. 2 Cross sectional microstructure and corresponding concentration profiles of (a) SD-coated and (b) EB-PVD coated TMS-82+ after annealed at 1273 K for 1 h. Both consist of (i) the Ir-enriched outer layer, (ii) the Ir-Ni-Al-enriched layer, (iii) the diffusion layer and (iv) the substrate.

Fig. 3 Change in X-ray diffraction profiles as a function of annealing time at 1273 K. (a) SD-coated TMS-82+ and (b) EB-PVD coated TMS-82+. The intensity profiles for (a) SD-coated TMS-82+ and (b) EB-PVD coated TMS-82+.
substrate temperatures of the two specimens are almost identical to each other.

The higher concentration of Ni and Al in the surface layer in the SD specimen indicated that compositional change after the annealing can be mainly controlled by grain boundary diffusion.

When the annealing time increases, interdiffusion of elements, formation of the IrAl phase, and grain growth simultaneously occurred. Consequently, the difference in movement of elements did not become distinctive. Therefore, the reason for the smaller difference in XRD profiles after 5 hours’ annealing can be attributed to the grain growth and formation of the IrAl phase in the layer. However, outer diffusion of Ni from the substrate in the SD specimen at the very initial stage of annealing is so quick that Ni easily reaches the surface. When the sample having a certain amount of Ni on the surface is exposed under oxidizing atmosphere, it will form brittle oxides such as NiAl2O4, which promote the exfoliation of surface layers. The rapid decrease in mass in the annealed SD specimen can thus be explained by the rapid formation of brittle oxides such as NiAl2O4.

Once aluminizing is carried out, the differences in the distribution of elements become much smaller. This result indicates that reactions between Al-containing gases and the substrate surface and subsequent diffusion of Al into the substrate are the governing reaction in the aluminizing process, rather than the solid-phase interdiffusion between the substrate and the coated layer. Consequently, they exhibited similar oxidation kinetics during cyclic oxidation tests.

However, changing aluminizing conditions can make the process dependence more distinctive, especially when the aluminizing treatment is followed by the annealing treatment. In this study, aluminizing treatment is conducted for 5 hours at 1273 K without annealing. In some Pt-coated and aluminized coatings, the annealing treatment is sometimes conducted before aluminization in order to increase the adhesion of Pt-coatings. The combination of annealing and aluminizing treatments in the case of Ir-coated specimens may further enhance the properties, which is discussed below.

4.2 The effect of annealing treatment

In this study, simply annealed samples demonstrated higher oxidation resistance than the as-deposited samples. Since Ir forms gaseous oxides such as IrO2 and IrO3 at elevated temperatures, the rapid mass loss observed for the as-deposited specimens may have been caused by the evaporation and/or exfoliation of these oxides from the surface. On the other hand, annealed specimens have a certain amount of Al in the surface layer, caused by the outward diffusion of Ni and Al. Rapid outer diffusion of Ni can be related to its small atomic radius. As for the outer diffusion of Al, the binary Al-Ir phase diagram shows the high melting point of IrAl β-phase, suggesting the high
binding energy of Ir-Al. Although further investigation should be required, it is speculated that due to this strong bonding of Ir and Al, Ir in the coated layer may have attracted aluminum atoms in the substrate, resulting in the outward diffusion of Al and the enhancement of oxidation resistance of specimens by forming stable Al$_2$O$_3$ on the surface. Unfortunately, it is expected that this annealing treatment for improving oxidation resistance is only available when the aluminum content is sufficiently high. The outward diffusion of Ni as well as Al should be controlled also. Nevertheless, this annealing treatment could become more effective when combined with the aluminizing process. It is reported that addition of Ni to IrAl expands the single β-phase region. Therefore, to form Ir-Ni-Al-enriched layer by annealing can contribute to the formation of the stable (Ir, Ni)Al β-phase surface layer by the aluminizing treatment, which is expected to have better oxidation resistance with better phase stability than Ir-coated and aluminized specimens without annealing. Optimization of annealing and aluminizing treatments may be promising and will be investigated in the future.

5. Conclusions

(1) The smaller grain size of the as sputter-deposited specimen exhibited the more rapid outward diffusion of Ni and Al after 1 h annealing treatment at 1273 K, than the as EB-PVD coated specimen.

(2) The aluminizing treatment reduces the process dependence of coated samples.

(3) Simple annealing promoted the oxidation resistance of specimens, suggesting that the optimum combination of annealing and aluminizing will further increase the oxidation resistance of the specimens.

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