Microstructural Characterization of Sputtered Pt–Ir Coatings on Ni-Base Single Crystal Superalloy

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Characterization of Pt–Ir alloy coatings on a Ni-base single crystal superalloy was carried out. Pt–Ir alloys with varied composition were sputter-deposited on TMS-82\textsuperscript{+}, which were then subjected to annealing and Al-pack cementation treatments. It was found that all the as-deposited films consisted of Pt–Ir solid solutioned fcc single phase, while the annealing treatment at 1423 K for 1 h drastically changed the microstructure, depending on the composition of coated layers. On the other hand, concentration profiles of alloying elements were not drastically changed by the Al-pack cementation process. It was also revealed that Ir addition increases the surface hardness of all the as-deposited, annealed, and aluminized specimens.

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1. Introduction

In the development of protective coatings for use in combustion-type energy conversion systems such as gas turbines and diesels, primary emphasis has been put on oxidation and hot corrosion resistance. For many years, aluminide coatings have been regarded as the most basic but important among various kinds of high-temperature coatings. To improve performance of the aluminide coatings, Pt-modified aluminide coatings have been applied for turbine blades and vanes. However, the high price of the platinum pre-deposition may limit their industrial use. Pt-modified aluminide coatings also suffer from so-called ‘rumpling’ mainly due to the phase transformation under oxidizing atmosphere.\textsuperscript{1)}

Addition of Ir to Pt in the coatings is of great interest because Ir has the highest melting temperature (2716 K) among platinum-group-metals (PGMs), excellent chemical stability and low oxygen diffusivity,\textsuperscript{2)} which suggests that Ir addition may retard the growth rate of thermally grown oxide, and may retard the interdiffusion between substrates and coatings. It is thus of utmost importance to understand the microstructure of Pt–Ir-modified aluminide ((Pt,Ir)–Al) coatings which are expected to prolong the life of components exposed under high-temperature environments. In addition, since Ir is cheaper than Pt, Ir deposition would reduce the production cost of airfoils.

To overcome the ‘rumpling’ problem, a simple annealing treatment has recently noticed. In fact, Pt-coated and simply annealed superalloys are reported to demonstrate improved TBC spallation lives.\textsuperscript{3)} Since Pt–Ir coated and annealed superalloys may further prolong the spallation lives, it is also important to understand the microstructural variation of Pt–Ir coated and annealed superalloys.

Above these as backgrounds, five kinds of Pt–Ir films with different compositions, coated on a Ni-base single crystal superalloy were prepared by the sputtering method. The effects of film composition and surface treatment, such as annealing and aluminizing, on changes in the microstructure of coated alloys were investigated.\textsuperscript{4)}

2. Experimental

A so-called second generation Ni-base single crystal superalloy TMS-82\textsuperscript{+},\textsuperscript{5)} which was developed by National Institute for Materials Science (NIMS) in Japan, was selected as a substrate material. Its nominal composition is Ni–7.8Co–4.9Cr–1.9Mo–8.7W–5.3Al–0.5Ti–6.0Ta–0.1Hf–2.4Re in mass\%. The substrate material was supplied as a (100) oriented single crystal bar with 25 mm in diameter, which was cut into discs with 2 mm in thickness. These discs were then polished up to #800 SiC paper, and cleaned ultrasonically in an acetone bath.

In order to control Pt–Ir film composition, triangular sections of Ir or Pt are placed on a Pt or an Ir target, respectively. Sputter-deposition was conducted in the following conditions; substrate temperature: 873 K, output power: 800 W, vacuum: 5.0 \times 10^{-1} Pa in Ar. In this way, five kinds of films with different composition were prepared. These Pt–Ir-coated specimens are hereafter denoted as Pure Pt, Pt–30Ir, Pt–50Ir, Pt–80Ir and Pure Ir, based on their atomic compositions. Each of the as-deposited specimens was annealed at 1423 K for 1 h in vacuum, and some of the annealed samples were treated by a conventional pack-cementation aluminizing process, where they were embedded in an alumina retort containing the mixture of Al\textsubscript{2}O\textsubscript{3}, Al, Fe, and NH\textsubscript{4}Cl powders. The pack-cementation aluminizing treatment was carried out at 1273 K for 5 h under flowing Ar. Hardness, crystal structure, cross-sectional microstructure and composition of the specimens were analyzed by a Micro-Vickers hardness tester, X-ray diffractometer (XRD) and a scanning electron microscope (SEM) with energy dispersive spectrometer (EDS), respectively.

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3. Results and Discussions

3.1 Microstructural changes of Pt–Ir films

Figure 1 shows the cross-sectional microstructure of the as-deposited Pt–80Ir. The dense and flat coating without any internal cracks was obtained. Crystal structures of as-deposited Pt–Ir alloy coatings were examined by X-ray diffractometry. As shown in Fig. 2, all the X-ray peak profiles showed single phase fcc structure, indicating that Pt and Ir in the as-deposited coatings formed a completely miscible solid solutioned fcc structure. According to the Pt–Ir binary alloy phase diagram, phase separation should occur at lower temperatures, however, the sputtering process caused the supersaturated single phase formation in the films due to the inherently high cooling rate of sputtered particles depositing on the substrate.

Lattice parameters of Pt–Ir alloy films can be determined using the peaks of X-ray diffraction patterns, and the relationship between lattice parameter and composition of the coatings can be depicted as Fig. 3. The reported lattice parameters of bulk Pt and Ir are also plotted in the figure. Measured lattice parameters decrease linearly with the increase of Ir content, suggesting that the changes in lattice parameters in the Pt–Ir binary system follows the Vegard’s law.

The as-deposited specimens were then annealed at 1423 K for 1 h. It was revealed that the annealing treatment drastically changes the microstructural morphologies of the coated specimens. In addition, there is a significant difference between Pt-enriched coatings and Ir-enriched coatings in microstructure and phase constitution, as in Fig. 4. On the Pt-enriched side, there is no drastic change in the concentration profile of each element. Also, it is shown in Pt–30Ir that the inward diffusion of Ir terminates at approximately 25–30 µm from the surface, whereas Pt diffuses further down to 35 µm, confirming the lower diffusivity of Ir into Ni-base superalloy substrates than that of Pt.

On the Ir-enriched side, however, drastic microstructural change took place. As shown in Fig. 4(b), Ir-enriched layers were observed at 15–20 µm from the surface. In addition, some precipitates with a bright contrast, whose sizes ranged from 1 to 3 µm, were present just beneath the surface. EDX composition analysis revealed that these brightly contrasted precipitates were Al-enriched (Ir,Ni)Al phase as seen in Fig. 4(c), which was also confirmed by the X-ray analysis. Figure 5 shows the change in X-ray profiles of annealed specimens as a function of Pt–Ir composition. On the Pt-enriched side, two fcc peak patterns with different lattice parameters were observed. It is suggested one fcc peak profile may originate from the surface which constitutes mainly of coated Pt, Ir and outwardly diffused Ni, and the other peak may come from the layer just beneath the surface, which consists mainly of Ni together with inwardly diffused Pt and Ir. On the other hand, when the Ir content exceeds 80 at%, B2 structured (Ir,Ni) aluminide and fcc γ phases were identified. These results agree well with the microstructural observations. This microstructural evolution in Ir-rich alloy coated specimens by the annealing treatment can be explained by the following sequence. Before annealing, Ir-rich alloy coated specimens had consisted of fcc single phase in the coating layer and γ + γ’ two phase structure in the substrate. However, Ni and Al in the substrate diffused outwardly to the surface, and they passed through the Ir-rich alloy coated layer. Part of the Ni and Al atoms that penetrated through the coated layer would react with Ir to form B2 structured (Ir,Ni) aluminide phase in the vicinity of the surface. Consequently, a layer consisting of an Ir–Pt–Ni solid solutioned fcc phase with small precipitates of (Ir,Ni) aluminide were formed at the surface. As time passes, coarsening of the (Ir,Ni) aluminide precipitates occurred.
closer to the surface, while continuous formation of Ir–Ni–aluminide particles took place at the interface between the top surface and the Ir-enriched layer, due to the continuous outward diffusion of Ni and Al from the substrate, and the formation of $\beta$-aluminide can be attributed to the strong interaction between Ir and Al.

A part of the annealed specimens was subjected to Al-pack cementation. Figure 6 shows the cross-sectional microstructure and corresponding concentration profiles of annealed and aluminized specimens. All the images showed some similarities to the annealed specimens, for instance, Ir-enriched layers in the coatings, which were formed by the annealing process, can be seen even in the aluminized specimens, as shown in Fig. 6(b). In addition, thickness of the Al-enriched layer is almost identical to each specimen. From these results, it can be concluded that the amount of Al deposited by the Al-pack process is not drastically affected by film compositions, and Al can diffuse into all the specimens in a similar manner.

3.2 Hardness of specimens

Mechanical properties of films are also one of the pivotal factors to determine the longevity of films. In this section, surface hardness of specimens was measured by means of the Micro-Vickers hardness tester. Figure 7 shows the changes in Vickers hardness as a function of film compositions and surface heat treatments. In the case of as-deposited films, Vickers hardness almost linearly increases with the increase of Ir content, confirming that Ir strengthens the film surface. The annealing treatment and the aluminizing treatment further harden the specimens and in both cases and up to 80 at% of Ir addition increases the hardness. The reason for the drop in hardness of annealed specimens when Ir content exceeds 80 at% has not been elucidated yet and will be investigated in the future.

The softer surface may promote the rumpling phenomenon under the oxidizing atmosphere, therefore, hardened surfaces by the Ir addition can be expected to retard the surface rumpling, and accordingly improve the oxidation resistance. However, further investigation should also be required to confirm this hypothesis.

4. Conclusion

From the present study, the following conclusions were obtained.
All the as deposited films consisted of Pt–Ir solid solutioned fcc single phase.

Annealed Ir-enriched coatings indicated high interaction between Ir and Al whereas annealed Pt-enriched coatings did not show any phase transformation.

Concentration profile of alloying elements was not drastically changed by aluminizing.

Ir addition into Pt coatings is effective in strengthening the hardness of films, and would be beneficial in retarding the rumpling on the surface.

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