Submicron Structure of Rhenium-Base Diffusion Barrier Coating Layer on a Nickel-Base Superalloy

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Cross sectional structure of a Re-based diffusion barrier layer coated on a Ni-based single-crystal superalloy has been investigated in sub-micron scale. The barrier layer was prepared by electroplating of a Ni-30 at% Re film onto the alloy substrate, followed by a Cr-pack cementation in a mixture of Ni-30Cr and Al₂O₃ powders at 1573 K for 36ks in vacuum. The diffusion barrier containing 38 at% Re, 35 at% Cr, 16 at% Ni and few amount of Al was identified to be topologically close-packed σ-phase using electron backscattered diffraction method. Voids formed with precipitates in the diffusion barrier layer. Poly-crystallization and γ′-phase coarsening occurred in the superalloy substrate close to the Re-based alloy layer.  [doi:10.2320/matertrans.48.526]

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1. Introduction

Thermal barrier coatings (TBC) are a key technology for advanced gas turbine materials to provide thermal insulation from the hot gas stream, because of their outstanding thermo-mechanical properties. The TBC structure is composed of two main layers; an aluminum-rich bond coat and a ceramic top coat as a thermal insulator. By increasing the turbine inlet temperature, 1973 K for the next generation gas turbine engines, microstructural degradation of the substrate and layers can be enhanced by interdiffusion between them.1,2) Recently, a novel diffusion barrier bond coat, having a duplex structure of Al reservoir and Re-based alloy layers, has been developed for improving high temperature properties. It has been shown that the Re-based alloy layer can suppress mutual diffusion efficiently and improve the life span of a TBC.3) However, fundamental formation mechanism and structures of the barrier layer has not been sufficiently understood.

In this paper, the cross-sectional structures of the Re-based barrier layer were investigated in micron and submicron scales. The cross section of the Re-based barrier layer coated specimen was prepared by a new method. The phase identification of the Re-based alloy and orientation analysis of the substrate/layer interface region were carried out by means of electron backscatter diffraction (EBSD) method.

2. Experimental

A diffusion barrier layer was formed by two steps: electrolytic plating and Cr-pack cementation. A nickel-based single-crystal superalloy TMS-82+4 was used as the alloy substrate, where the nominal composition is Ni-7.8Co-4.9Cr-1.9Mo-8.7W-5.3Al-0.5Ti-6.0Ta-0.1Hf-2.4Re (mass%). The superalloy was cut into a disk of 1.2 mm in thickness and 15 mm in diameter. The formation process of the Re-based diffusion barrier is summarized as follows:3)

(1) Multi-layer plating: A Ni layer of 1 μm in thickness was electroplated on the substrate with a current of 500 mA/cm² at room temperature. Then, a 7 μm-thick Ni-73 at%Re layer and another 7 μm-thick Ni layer were sequentially electroplated at 323 K. In the process, the Re-Ni layer contained about 10 at% oxygen, detected by energy dispersive spectrometry (EDS).

(2) Pack cementation: The Cr-pack cementation was carried out using Ni-30 at% Cr powder at 1573 K for 10 h, followed by cooling in vacuum to form a two-layered structure on the substrate; a Re-rich layer on the substrate to act as the diffusion barrier, and a top Ni-based alloy layer which can be further changed to an Al reservoir layer by an additional Al-pack cementation.3)

The cross-sectional structure of the diffusion barrier layer was firstly investigated by a scanning electron microscope (SEM) equipped with an electron probe micro analyzer (EPMA, JEOL JXA-8900M). In this case, the specimen was prepared by conventional mechanical polishing. In order to obtain a flat cross-section with minimal mechanical damage, a new method of cross-section polishing (CP, JEOL SM-09010) utilizing Ar ion beams was employed. The specimen cross-sectioned by CP method was suitable both for high-resolution SEM observation and EBSD analysis. A field emission scanning electron microscope (FE-SEM, JEOL JSM-6500F) was used for high-resolution cross-sectional observation. EDS (JEOL JED-2300) and EBSD (TSL OIM Data Collection system) equipments attached to the FE-SEM were employed for chemical composition and crystal structural analysis, respectively.

3. Results and Discussion

3.1 Cross-sectional surface structure

Figure 1 shows the cross-cut view of the Re-based barrier coating with a duplex layer structure. The concentration profiles of major elements (Re, Ni, Cr and Al) measured by EPMA are superimposed. The barrier layer of Re-based alloy, composed of 38 at% Re, 35 at% Cr, 16 at% Ni and few amount of Al, formed with ~10 μm in thickness. Concentrations varied sharply at the interfaces between the outer layer, barrier layer and substrate. The barrier layer is known to be an effective diffusion barrier for Al and other alloying elements of the substrate.3)
Figure 2 shows a secondary electron image (SEI) of the cross section prepared by the CP method. Comparison of Fig. 2 and Fig. 1 demonstrated that the combination of CP method and FE-SEM observation provided more detailed information about the cross-sectional structure. The interface between the barrier layer and substrate showed no cracks, but many voids which were sometimes accompanied by precipitates were visible in the Re-based barrier layer. Although further investigation should be required, the Kirkendall effect would unlikely explain the void formation on the basis of low diffusivity of Re in the Re-Cr-Ni system. O and H would dissolve into the Re-Ni layer during the electroplating processes, and probably contribute to the formation of voids during the Cr-pack cementation at 1573 K.

Figure 3 shows a micrograph of precipitates inside a void. EDS analysis indicated that the barrier layer contained a little amount of Al (about 1 ~ 2 at%) and free oxygen, while the precipitate included ~39 at% Al and ~42 at% O. Therefore, the precipitates could be alumina. On the basis of the Richardson-Jeffes diagram, it is predicted that Al₂O₃ would be more stable than the oxides of Cr, Ni and their mixtures at 1573 K. During the Cr-pack cementation at 1573 K, Al diffused into the Re-based alloy layer from the substrate might preferentially react with oxygen, resulting in oxygen activity in the Re-based alloy layer lowering below the levels for forming Cr₂O₃, NiO and spinel oxides. Dopings of Ni and Cr to the Al₂O₃ may be possible, but it is impossible for the precipitates to obtain an accurate measurement of composition by EDS in SEM, since the sampling depth (~1 μm) and lateral resolution (~1 μm) of EDS are much larger than the size of the precipitates.

Figure 4 shows a magnified SEI of the barrier layer/substrate interface region. The distribution of γ' precipitates, visible as dark spots in the substrate, can be categorized into two areas. In area II, the γ' precipitate was similar in size to that in the bulk substrate. In area I, the γ' precipitate showed obvious coarsening, indicating that this area is a transient region. It has been widely accepted that directional coarsening of γ' precipitate, known as rafting phenomenon, occurs under applied external stresses at elevated temperatures. In contrast to the rafting, the coarsening of γ' precipitate in the area I appears to be isotropic. There should be little stresses introduced in the coated specimen during the Cr-pack cementation at 1573 K. However, thermal residual stress due to mismatch in the thermal expansion coefficients would be introduced during the cooling process. The thermal expansion coefficient of the barrier layer is believed to be lower than that of the substrate, since the barrier layer composed of a brittle topologically close-packed (TCP) phase (refer to section 3.2). Therefore, a tensile thermal stress would developed in the area I during the cooling process and resulted in re-crystallization and the coarsening of γ' phase.

Referring to a Ni-Cr-Al ternary diagram, the co-existed γ'-phase tends to disappear with increasing of Cr content in the γ-phase, and then, β-phase joins with the γ-phase with over 20 at% Cr. Although the substrate containing multi elements might not be fully subject to the ternary Ni-Cr-Al system, it is suggested that the γ'-phase should become
unstable with increasing of Cr content in the alloy substrate. In the present case, therefore, re-crystallization and the coarsening in the transient area could be also related to the change in local composition due to Cr-penetration and depletion of Al during the Cr cementation process.

3.2 Crystal structure of the barrier layer

According to the ternary phase diagram of the Re-Cr-Ni system\(^8\) and results of EPMA analysis, the barrier layer would be composed of \(\gamma^\prime\) phase. The \(\sigma\) phase has a body centered tetragonal structure and is a TCP phase. Several different types of TCP have been observed in advanced Ni-based alloys containing high amount of refractory elements such as W, Mo and Ta, as well as Re.\(^9,10\) These TCPs include \(\mu\), \(P\), \(R\) and \(\sigma\) phases, and Table 1 summarizes their basic crystallography.\(^10\) The present barrier layer also includes those refractory elements (Ta\(\approx\)0.9 at%, W\(\approx\)6.0 at% and Mo\(\approx\)1.4 at%), which diffused from the substrate during Cr-pack cementation. Therefore, we identified the phase of the barrier layer in this experiment.

The phase identification was carried out by the means of EBSD. EBSD is a useful technique for the characterization of crystalline materials, not only for orientation map fabrication, but also for phase identification. Phase identification procedure utilizes a “confidence index” (CI) parameter and a “fit” parameter,\(^11\) in comparing the unknown material with candidate phases, to determine the best solution. The CI parameter ranges in value from 0 to 1, and a greater value means higher confidence. The fit parameter defines the average angular deviation between the simulated bands and the detected bands, thus, it also provides some indication of how reliably the pattern has been indexed, and a good fit should be smaller than \(1^\circ\).\(^11\) In this experiment, the fcc (\(\gamma\)-Ni), bcc (\(\alpha\)-Cr) and hcp (Re) phases were also taken into account as the candidate phases, along with the TCPs.

Figure 5(a) shows an EBSD pattern obtained from the barrier layer. The Kikuchi pattern was generated at an acceleration voltage of 20 kV, and recorded by means of a DigiView™ camera system, where the specimen was at a tilt angle of 70°. This Kikuchi pattern was indexed with the candidate phases, and the results are listed in Table 1. The best match was achieved for \(\gamma^\prime\) phase structure with a CI of 0.70 and a fit of 0.59°. Figure 5(b) shows the simulated EBSD pattern overlaid on the experimental pattern that demonstrates the quality of the match. As the result, the crystal structure of the barrier layer was identified as TCP \(\sigma\) phase.

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3.3 Crystal orientations of the barrier layer and substrate

Figure 6 shows a SEI and an orientation map (inverse pole figure, IPF) for typical interface area between the substrate and barrier layer, where the IPF was obtained from the box area in the SEI. The transient area shown in Fig. 4 seems to be a single crystal, except an embedded belt-like grain. From the misorientation profile overlaid on the IPF, it could be concluded that orientation of this region was slightly different from that of the substrate, and the misorientation (or alternatively orientation difference) was about 3°. However, the belt-like grain was clearly different from the surrounding area in crystal orientation, and the misorientation was close to 60°.

Figure 7 shows a SEI from an irregular interface area between the substrate and barrier layer, and IPF from the box area in the SEI. The SEI revealed that the interface had complex interlocking structures. The barrier layer of σ phase indicated by bright-contrast in the SEI appears poly-crystalline as shown in the IPF. Although the transient region slightly differed from the substrate in orientation, the intrusive regions surrounded by σ phase composed of typical poly-crystals.
4. Summary

To elucidate formation mechanisms of a Re-based alloy as a diffusion barrier layer on the Ni-based single-crystal superalloy TMS-82+, the structural characterizations was carried out using EPMA, FE-SEM and EBSD. The CP method was used for preparing a flat cross section with little damage. The following are the main results obtained in the present investigation.

1) The Re-based alloy layer contains 38 at% Re, 35 at% Cr, 16 at% Ni and few amount of Al.

2) Voids and Al₂O₃ precipitates were observed in the Re-based alloy layer. The Al₂O₃ could be formed by the reaction of oxygen in the electroplated Ni-Re film and Al diffused from the substrate.

3) The crystal structure of the Re-based alloy layer was identified as TCP/C₂7 phase by EBSD method.

4) Poly-crystallization and coarsening of γ’-phase were observed in the substrate, in the vicinity of the interface.

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REFERENCES