Cyclic Oxidation Behavior of Iridium-Modified Aluminide Coatings for Nickel-Base Single Crystal Superalloy TMS-75*1

Feng Wu1,*2, Hideyuki Murakami2 and Hiroshi Harada1

1High Temperature Materials 21 Project, Materials Engineering Laboratory, National Institute for Materials Science (NIMS), Tsukuba 305-0047, Japan
2Department of Materials Engineering, Graduate School of Engineering, The University of Tokyo, Tokyo 113-8656, Japan

The oxidation behavior of iridium-modified aluminide (Ir–Al) coating obtained by a two-step process was investigated. A pure Ir layer was first electrodeposited on the nickel-base single crystal superalloy TMS-75, and then the Ir-coated TMS-75 was treated by a conventional low activity pack-cementation aluminizing process. The oxidation resistance of the Ir–Al coated TMS-75 and the simply aluminized TMS-75 was evaluated by a cyclic oxidation test at 1373 K in air. The results showed that the Ir–Al coated TMS-75 had better thermal cyclic oxidation resistance than the simply aluminized TMS-75. The existence of Ir in the Ir–Al coatings may promote the formation of dense and adherent Al2O3 scale and thus retard the degradation of β-(Ir, Ni)Al phase during oxidation process.

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1. Introduction

For many years, nickel-base superalloy blades and vanes used in the hot sections of land-based gas turbines have shown resistance to high temperature oxidation and hot corrosion due to the application of aluminide coatings to their external surfaces, primarily via the well-known pack cementation (aluminizing) route.1,2) Aluminide coatings have been regarded as the most basic and the most 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, and they have been found to exhibit excellent oxidation resistance and hot corrosion resistance.3–5) However, one disadvantage of Pt is the cost of the material, which has led to the assessment of the other platinum-group-metals (PGMs) such as Pd, Ir, Rh etc and their alloys. More recently, Ir–Ta modified aluminized coatings have also been proposed by the authors’ group.6) In our research, Ir is selected because it has the highest melting temperature (2716 K) among PGMs, excellent chemical stability and low oxygen diffusivity,7) and Ir addition also increases the melting temperature of Ni-base superalloys.8) These results suggest that Ir may retard the growth rate of thermally grown oxide, and the interdiffusion between substrates and coatings without drastically deteriorating the mechanical properties of substrates. It is thus of utmost importance to evaluate the Ir- or Pt–Ir-modified aluminide (Ir–Al, or (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 may be advantageous in terms of reducing the cost of airfoils.9) Recently, we have succeeded in the electrodeposition of Ir and Ir–Pt alloys on Ni-base single crystal superalloys.10) Our next step is to develop and characterize the Ir- or Ir–Pt-modified aluminide coatings. In this work, a comparative study on the oxidation behavior of Ir-modified aluminide TMS-75 and simply aluminized TMS-75 is reported. The effect of Ir on the change in microstructure after oxidation was also discussed.

2. Experimental

A nickel-base single crystal superalloy TMS-7511) was used as a substrate material, whose nominal composition (in mass pct) is 6.0Al, 12.0Co, 3.0Cr, 6.0Ta, 6.0W, 5.0Re, and Ni as balance. The basic electrolyte used for the pure Ir electrodeposition was composed of 4–12 g/l IrCl3·4H2O and 35–50 g/l HOSO3NH2. The electrodeposition was conducted at a solution temperature of 353 K, and pH value 2.0 with stirring using a magnetic drum.10) Disc specimens (2 mm in thickness × 12 mm in diameter) of TMS-75 were used as substrate for electrodeposition. Typically, Ir coatings of 6 μm in thickness were obtained for 60 minutes of electrodeposition.

The Ir-coated TMS-75, together with the uncoated TMS-75 (18 × 18 × 2 mm3) were then treated by a conventional pack-cementation aluminizing process, where these specimens were embedded in an alumina retort containing the mixture of Al2O3, Al and Fe powder, and NH4Cl. The pack-cementation aluminizing treatment was carried out at 1273 K for 5 h under flowing Ar under one atmosphere. Hereafter, these Ir-coated, Al-pack cemented samples are denoted as Ir–Al coated TMS-75, and uncoated, Al-pack cemented samples are denoted as simply aluminized TMS-75, respectively.

Cyclic oxidation tests were carried out in a programmed muffle furnace (YAMADA DENKI: MSFT-1500) at 1373 K in still air. Each thermal cycle consisted of 20 h at 1373 K and 4 h at room temperature. The tests were conducted for up to 10 cycles. The periodic mass change of the specimens was measured by a precision analytical balance.

The phase identification of the coatings and oxides was conducted using CuKα radiation in a Rigaku RINT 2500 X-ray diffraction (XRD) system operating at 40 kV and 300 mA.
Surface morphology and composition of the coated layer were analyzed using a Philips XL-30 scanning electron microscopy (SEM) equipped with an energy dispersive X-ray (EDX) analyzer.

3. Results and Discussions

3.1 Microstructure of as-aluminized specimens

Figures 1 and 2 show the cross-sectional microstructure and the concentration distribution of the elements for the Ir–Al coated TMS-75 and simply aluminized TMS-75, respectively. It can clearly be seen from Fig. 1(a) that the Ir–Al coated TMS-75 has a triplex layer structure. XRD and EDX analyses revealed that the Ir–Al coating has a B2 ordered structure, consisting of continuous three layers: a dense and uniform outer layer of $\beta$-(Ir, Ni)Al with $\sim$14 µm thick, an intermediate layer of $\beta$-NiAl with $\sim$50 µm thick, and an inner Al-diffusion zone with $\sim$5 µm thick. While for the simply aluminized TMS-75 (Fig. 2(a)), only a duplex layer structure is observed, i.e., $\sim$60 µm $\beta$-NiAl as the outer layer and $\sim$8 µm Al-diffusion zone as the inner layer.

Figures 1(b) and 2(b) illustrate the concentration distribution of the elements measured along the entire cross-section of the sample shown in Fig. 1(a) and Fig. 2(a), respectively. For the Ir–Al coated TMS-75 (Fig. 1(b)), the outer $\beta$-(Ir, Ni)Al layer contains approximately 56 at% of Al, 32 at% of Ir together with a small amount of Ni (10 at%) and Co (1 at%) which may be attributed to the outward-diffusion from the substrate. The intermediate layer is mainly composed of $\beta$-NiAl with a small amount of Co. A part of Ir could have diffused inwardly from the coating during the pack-cementation aluminizing process. The inner layer below the $\beta$-NiAl layer is enriched with Ta and Cr, forming an Al-diffusion zone accompanied by a coarsened $\gamma'/\gamma'$ structure. Although having slightly thicker intermediate and inner layers, the simply aluminized TMS-75 (Fig. 2(b)) demonstrates a similar concentration profile to that of the Ir–Al coated TMS-75, except for the presence of Ir–Al enriched layer in the latter.

3.2 Cyclic oxidation kinetics

In order to evaluate the stability of oxides formed on the coated specimens under cyclic thermal stresses, a cyclic oxidation test was performed. The mass change during cyclic oxidation at 1373 K for the Ir–Al coated TMS-75 is compared with the simply aluminized TMS-75 given in Fig. 3. The mass gains of both Ir–Al coated TMS-75 and simply aluminized TMS-75 increase almost linearly at the first 6
or 7 oxidation cycles and then slow down to stay at certain values (former) or decrease slightly (latter). For each oxidation cycle, the simply aluminized TMS-75 shows larger mass gain than the Ir–Al coated TMS-75. The maximum mass gain of the Ir–Al coated TMS-75 is about half as large as that of the simply aluminized TMS-75, suggesting that the growth rate of thermally grown oxide (TGO) in Ir–Al coated TMS-75 is lower than that in the simply aluminized TMS-75. In addition, the mass gain of the simply aluminized TMS-75 slightly decreases after up to 7 oxidation cycles, inferring a spallation of the oxide scale from the surface. The observation by optical microscopy also confirmed that the oxide scale spallation for the simply aluminized TMS-75 was more serious than that for the Ir–Al coated TMS-75.

3.3 Comparison of Ir–Al coated TMS-75 and simply aluminized TMS-75 after ten oxidation cycles

3.3.1 Morphology of oxide scales

The surface morphology of the oxide scales on the Ir–Al coated TMS-75 and simply aluminized TMS-75 after ten oxidation cycles are shown in Fig. 4. It can be seen that the surface of the Ir–Al coated TMS-75 is still covered by a continuous oxide scale with slight spallation (Fig. 4(a)), which is identified by EDX analysis to be nearly pure α-Al2O3. Whereas for the simply aluminized TMS-75, serious oxide spallation (as indicated by arrows B) and some cracks (as indicated by arrows A) are observed (Fig. 4(b)). The oxide scales on both the specimens contain α-Al2O3 and some unidentified ones are observed in addition to α-Al2O3, β-NiAl and γ’-Ni3Al, suggesting that the surface of Ir–Al coated TMS-75 is more stable and resistant to oxidation than that of simply aluminized TMS-75. This may be attributed to the presence of Ir in the coating layer. While diffusivity of Ni in the α-Al2O3 is very low, outward diffusion of Ni may be accelerated by the presence of NiAl2O4. Ir seems to retard the outward and inward diffusion of solute elements such as Ni and Al. As a consequence, Ir–Al coated TMS-75 preserves a fairly pure α-Al2O3 layer after cyclic oxidation tests and offers better oxidation resistance than the simply aluminized TMS-75. The detailed mechanism of oxidation and beneficial effects of Ir in the Ir–Al coated TMS-75 will be discussed elsewhere.

3.3.2 Cross-sectional microstructures

Figure 5 shows the SEM images of the cross-sectional microstructures of the Ir–Al coated TMS-75 and simply aluminized TMS-75 after ten oxidation cycles, respectively.

It can be seen that the oxide scale formed on the Ir–Al coated TMS-75 is uniform and dense with a thickness of ~3 μm, whereas the oxide scale formed on the simply aluminized TMS-75 is thick (~10 μm), rough and porous. The amount of γ’-phase formed under the oxide scale in the Ir–Al coated TMS-75 is much smaller than that in the simply aluminized TMS-75, suggesting that the transformation from the β-NiAl phase to the γ’-phase was decelerated due to the presence of (Ir, Ni)Al layer. Because the γ’-phase has a poor oxidation resistance, the deceleration of the γ’-phase formation is beneficial in improving the oxidation resistance.

3.3.3 Phase identification

Figure 6 shows the XRD patterns of (a) Ir–Al coated TMS-75 and (b) simply aluminized TMS-75 after ten oxidation cycles, respectively. As seen from the figure, both the specimens contain β-NiAl (or β-(Ir, Ni)Al) and α-Al2O3 as the major phases. Some amount of γ’-Ni3Al phase is also detected. However, while for Ir–Al coated TMS-75, almost all the peaks are identified and they are mainly from β-(Ir, Ni)Al and α-Al2O3, for simply aluminized TMS-75, peaks possibly from NiAl2O4 and some unidentified ones are observed in addition to α-Al2O3, β-NiAl and γ’-Ni3Al, suggesting that the surface of Ir–Al coated TMS-75 is more stable and resistant to oxidation than that of simply aluminized TMS-75. This may be attributed to the presence of Ir in the coating layer. While diffusivity of Ni in the α-Al2O3 is very low, outward diffusion of Ni may be accelerated by the presence of NiAl2O4. Ir seems to retard the outward and inward diffusion of solute elements such as Ni and Al. As a consequence, Ir–Al coated TMS-75 preserves a fairly pure α-Al2O3 layer after cyclic oxidation tests and offers better oxidation resistance than the simply aluminized TMS-75. The detailed mechanism of oxidation and beneficial effects of Ir in the Ir–Al coated TMS-75 will be discussed elsewhere.
4. Conclusions

An iridium-modified aluminide (Ir–Al) coating on the nickel-base single crystal superalloy TMS-75 was successfully achieved by the electrodeposition of iridium followed by a conventional low activity pack-cementation aluminizing process, and its oxidation behavior was compared with simply aluminized TMS-75. The Ir–Al coated TMS-75 showed higher thermal cyclic oxidation resistance than that of simply aluminized TMS-75. This can be attributed to the existence of Ir in the coating, which not only improved the adherence of oxide scale but also delayed the degradation of β-(Ir, Ni)Al phase during oxidation.

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REFERENCES