O U R N A L O F

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High temperature oxidation characteristics of NiCoCrAlY coating for gas turbines

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About 200 μ m-thick 32.5Ni-38.5Co-21Cr-8Al-0.5Y (wt.%) coatings were sprayed onto Hastelloy-X using a high velocity oxyfuel spraying (HVOF) method, and were oxidized between 900 and 1100°C in air to study their oxidation behavior. The coating consisted mainly of Ni₃Al with some Ni. Relatively thin scales were formed on the coating, due mainly to the formation of α -Al₂O₃. Additionally, some CoCr₂O₄ and Al₅Y₃O₁₂ formed. Beneath the oxide layer, an Al-depleted zone existed.

Key words: Oxidation, NiCoCrAlY, Spraying, Coating.

Introduction

Plasma sprayed MCrAIY alloys (M=Ni,Co) are widely used in commercial gas turbine engines as protective coatings. They form an Al_2O_3 -rich scale in an oxidative atmosphere at high temperatures. The scale thickens very slowly because diffusion through Al_2O_3 is very slow. The oxygen reactive element, Y, improves scale adhesion. Many attempts have been made to further improve scale adhesion, increase the oxidation limit, and obtain strain-tolerant scales by modifying the MCrAIY alloy composition and spraying methods [1, 2].

In this study, gas-atomized NiCoCrAIY alloy powders were sprayed onto a Ni-based substrate via a high velocity oxy-fuel (HVOF) process, oxidized at high temperatures, and the oxide scales formed were investigated. The results obtained serve to understand the oxidation of MCrAIY coatings, thereby ultimately leading to the development of an optimum coating having reasonable oxidation resistance.

Experimental

Gas atomized 32.5Ni-38.5Co-21Cr-8Al-0.5Y (wt.%) (hereafter, termed as NiCoCrAlY) having particle sizes of 11-62 μ m was HVOF-sprayed to about 200 μ m-thickness using Metco DJ 2600 equipment onto Hastelloy-X (49.0Ni+22.0Cr+15.8Fe+9.0Mo+1.5Co+2.0Al+0.6W+ 0.15C, wt.%) plate. Before spraying, the substrate was grit blasted with grade 60 alumina powders. Detailed spraying parameters are listed in Table 1. For stress relaxation, the HVOF-sprayed coatings were heated for

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Table 1. HVOF deposition conditions

Spray distance	300 mm
Transverse speed	750 mm/s
Fuel gas type	H_2
Fuel gas flow	1600 SCFH
Oxygen gas flow	380 SCFH
Air cap flow	800 SCFH
Carrier gas	N_2
Carrier gas flow	29 SCFH

24 h at 845°C, and 2 h at 1120°C in a vacuum furnace, followed by furnace-cooling. They were cut into $10 \times 10 \times 15 \text{ mm}^3$ -size pieces, and oxidized.

Oxidation tests were performed in a muffle furnace at 900, 1000 and 1100°C in an atmospheric air for up to 300 h. The specimens before and after oxidation were inspected by an X-ray diffractometer (XRD), a scanning electron microscope (SEM), and an electron probe microanalyzer (EPMA).

Results and Discussion

Figure 1 shows the top view, an unetched crosssectional image, elemental line profiles, an XRD pattern, and an etched cross-sectional image of a prepared NiCoCrA1Y coating. The rough surface shown in Fig. 1(a) was caused by both the molten splat bombardment and the turbulent cooling jet. During spraying, the coating is built up splat by splat. As splats move at supersonic speed with considerable force, a low level of porosity was attained, as shown in Fig. 1(b). Although a small amount of pores and internal oxide particles were seen along the coating-substrate interface, the coating-substrate adhesion was good. The HVOF method employed is better than the air plasma spray (APS) method which is more susceptible to the formation of internal oxide stringers [3, 4]. The elemental line pro-

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Fig. 1. NiCoCrAIY coating. (a) SEM top view, (b) unetched EPMA cross-sectional image, (c) EPMA line profiles, (d) XRD pattern, (e) etched SEM cross-sectional image.

files shown in Fig. 1(c) indicate a rather uniform distribution of coating elements. The XRD pattern shown in Fig. 1(d) indicates that the major phase is γ' -Ni₃Al and the minor one is y-Ni. The other coating elements were absent due mainly to their dissolution or distribution in the coating, or their small amount. Since the coating consists of rapidly solidified molten droplets, nonequilibrium prevails so that different coating phases have been reported, depending on the investigators. For example, phases of $(\gamma$ -Co+ β -NiAl) [5], and phases of $(\gamma - Ni + \gamma' - Ni_3Al + \sigma - CrCo)$ [6] were previously found in similar NiCoCrAlY coatings. The crosssectional image shown in Fig. 1(e) was etched with (60 ml, 90% lactic acid + 10 ml, 37% hydrochloric acid + 65 ml, 70% nitric acid) solution that etches γ' -Ni₃Al and leaves γ -Ni unetched. It is noted that the coating consists of fine grains due to the rapid solidification.

Figure 2 shows the SEM top views of the NiCoCrAIY coatings after oxidation at 1000°C. Although the oxide particles at the outermost surface tended to be looser to a certain extent as oxidation progressed, the general surface morphology of agglomerated, flattened splats is preserved.

Figure 3 shows EPMA results of cross sectional scales formed on NiCoCrAlY coatings. The scale shown in Fig. 3(a) was about 4 μ m-thick. Figure 3(b) shows that the scale is embedded in the epoxy mount up to a



Fig. 2. SEM top views of NiCoCrAIY coatings after oxidation at 1000°C. (a) for 150 h, (b) for 300 h.

thickness of about 24 μ m, due to the looseness of oxide particles. Since the active element of Al is abundant, Al is rich in the scale, but is depleted beneath the oxide



Fig. 3. EPMA cross-sectional images and line profiles of cross sectional scales formed on NiCoCrAIY coatings after oxidation at 1000°C. (a) for 150 h, (b) for 300 h.



Fig. 4. XRD patterns of NiCoCrAlY coatings after oxidation. (a) at 1000°C for 300 h, (b) at 1100°C for 150 h.

layer. The other oxygen active element of Y is weakly segregated in the oxide layer. The scale is depleted in Co, Ni, and Cr, because of their nobility. The concentration profiles of Ni, Co and Cr are similar to each other, indicating that their activities and diffusivities are similar. In Fig. 3(b), micropores formed during spraying are seen in the unoxidized coating.

Figure 4 shows XRD patterns of NiCoCrAlY coatings after oxidation. Because of the thinness of the scales formed, the γ' -Ni₃Al coating phase is seen. To produce any discernable oxide phase in the XRD pattern, oxidation at 1000°C for 300 h was at least required, due to the superior oxidation resistance of the coating.

The major oxide phase was α -Al₂O₃. Since Al was active, Al₂O₃ formed preferentially to cover the coating surface. Cobalt is noble so that CoCr₂O₄ is a minor oxide, which was formed by the reaction of CoO with Al₂O₃. Al₂O₃ also had a strong tendency to react with Y₂O₃ to form Al₅Y₃O₁₂ (yttria-alumina garnet or YAG), whose transition phase was AlYO₃. Some Al₅Y₃O₁₂ is seen in Fig. 4(b). No Ni-oxides were detected despite the considerable amount of Ni in the original coatings. This may be explained in terms of the weak affinity of Ni for oxygen, together with some dissolution of NiO in the other oxide phases if NiO were ever formed. The significant consumption of Al in the oxide scale led to the formation of the Al-depletion zone beneath the oxide scale.

Conclusions

The major phase was γ '-Ni₃Al, and the minor one was γ -Ni for the NiCoCrAlY coating having a rapidly solidified structure. The major oxide phase formed was α -Al₂O₃, and the minor ones were CoCr₂O₄ and Al₅Y₃O₁₂. Aluminum oxidized preferentially from the coating surface. The consumption of the active Al element to make the oxide scale resulted in the depletion of Al in the unoxidized coating.

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