HOT CORROSION PERFORMANCE OF

AMORPHOUS Al₂O₃ COATING⁽¹⁾

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ABSTRACT

The amorphous Al_2O_3 coatings were prepared on superalloy GH30 by dc reactive sputtering. Hot corrosion behaviors of the coated and uncoated specimens were studied in $75\% Na_2SO_4 + 25\% K_2SO_4$ melt at 1 123 K by either immersing the samples half in sulphate or applying sulphate deposit. The Al_2O_3 coatings reduced the hot corrosion rates by about one magnitude, and the internal sulphidation was not observed in the Al_2O_3 coated specimens.

Key words: Al₂O₃ coating hot corrosion reactive sputtering

1 INTRODUCTION

It is generally accepted that the hot corrosion resistances of alloys rely on the stable and protective oxide scales forming on the surfaces of the alloys. Coatings such as aluminide coatings and MCrAlY (where M—some metallic elements overlay coatings are applied to alloys in order to improve the hot corrosion resistance. Recent experimental results^[1-4] showed that the compact Al₂O₃ coatings deposited on alloys were beneficial to the oxidation resistance of alloys, and these kinds of coatings exhibited excellent adherence to the substrates.

2 EXPERIMENTAL

Superalloy GH30(Ni-20Cr-0. 2Ti) was used as substrates. Its chemical composition was Ni- 20Cr-0. 2Ti (wt.- $\frac{9}{0}$). The specimens with the dimensions of 20 mm \times 10 mm \times 2 mm were ground by SiC papers, blasted by glass balls, and then cleaned ultra-

sonically in detergent.

The Al₂O₃ coatings of $6 \sim 8 \, \mu m$ were deposited by means of dc reactive sputtering. The target used was 99. 99wt. - % Al target. The average distances between the specimens and the target were about $10 \, \text{cm}$. The residual pressure in chamber was $5 \times 10^{-3} \, \text{Pa}$. The working gas was the mixture of Ar + O₂ where argon and oxygen partial pressures were 0.3 and 0.25 Pa respectively. Electron diffraction of the Al₂O₃ coating indicated that the as-sputtered Al₂O₃ coatings were amorphous^[5]. Post annealing was carried out for the as-sputtered Al₂O₃ coating in vacuum at $1.73 \, \text{K}$ for 3 h in order to improve the protectiveness of the Al₂O₃ coatings^[2].

The corrosion experiments were carried out for 100 h at 1123 K by immersing the specimens half in the sulphite molten or by applying sulphate deposit on the specimens. The compostions of the salt molten were 75% Na₂SO₄ + 25% K₂SO₄ (wt. - %). The corrosion products were analyzed by various

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methods and the corrosion depth was measured.

3 RESULTS AND DISCUSSIONS

The mass gains vs time curves of the coated and uncoated specimens at various conditions are shown in Fig. 1. The mass decrease of the Al₂O₃ coated GH30 specimens was about one order of magnitude lower than without Al₂O₃ coating under the same test conditions. Much severe corrosion occurred on the uncoated GH30 in half-immersion test than in the test by sulphate deposit. However, the corrosion rates of the Al_2O_3 coated GH30 half immersed in sulphate melt were even below those of the uncoated GH30 with sulphate deposit. These results indicated that the Al_2O_3 coatings are protective. The colors of the salt films and of the salt in the crucibles after tests became rather yellow, so it is deduced that the ions of CrO_1^{2-} were dissolved in the salt melt during tests. It is proposed that basic fluxing of the oxide scales on the specimens occurred. Because salt on the specimens was cleaned in boiling water before the specimens were weighed, the mass decrease of the specimen represented the oxide dissolved to some extent.

No spallation of Al_2O_3 coatings occurred on the coated specimens. According to the X-ray diffraction results, the scales formed on the uncoated GH30 were Cr_2O_3 and a little $NiCr_2O_4$, whereas the scales on the Al_2O_3 coated specimens composed of Al_2O_3 and a little Cr_2O_3 .

Fig. 2 shows the surfaces morphologies of the coated and uncoated GH30 after 100 h half-immersion corrosion. Cracks were observed with the Al_2O_3 coating. In fact, the Al_2O_3 coating cracked in the vacuum annealing^[2]. EDAX indicated that Cr_2O_3 formed within the cracks of the Al_2O_3 coatings.

Loose external oxide scale and internal oxidation and the internal sulphidation with depth of 60 μm were observed in the uncoated GH30 after 100 h corrosion, as shown in Fig. 3(a). But there were neither internal

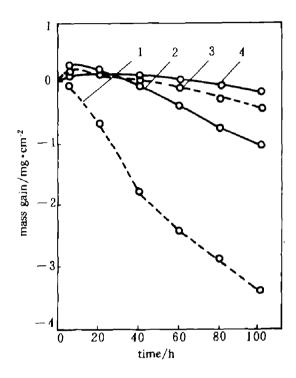


Fig. 1 Kinetics curves for hot corrosion at 1 123 K

- 1—GH30 half immersed in sulphate;
- 2—GH30 with sulphate deposit;
- 3-GH30+Al₂O₃ half immersed in sulphate;
- $4-GH30+Al_2O_3$ with sulphate deposit

oxidation nor internal sulphidation in the Al_2O_3 coated GH30, as shown in Fig. 3(b). Fig. 3(b) also indicated that the cracks within the Al_2O_3 coatings were blocked by Cr_2O_3 . The cracks within the Al₂O₃ coatings have harmful influences on the corrosion behaviors of the coated specimens because the cracks allow salt melt direct access to the underlying metals. The uncoated zones due to cracking of the Al₂O₃ coatings are attacked as in the uncoated specimens. But because their areas were rather smaller than those protected by Al_2O_3 , the basicity deviation in the salt films on the coated specimens are far less than on the uncoated specimens. So Cr_2O_3 formed within the cracks in the Al2O3 coatings can successfully obstruct the sulphur intrusion into metals.

The micrograph and X-ray images of Cr, O and S on the cross section of uncoated GH30 after 100 h half-immersion corrosion are presented in Fig. 4. Cr_2O_3 formed on the surfaces of the uncoated specimens. A band of internal sulphidation with the width of about $60~\mu\text{m}$, where Cr was depleted, was observed on metals beneath the oxide scale. These results indicated that sulphidation-oxidation reactions besides basic fluxing involved into the hot corrosion of the uncoated specimens.

The premise for basic fluxing is that the reaction

$$SO_4^2 \rightarrow SO_2 + (1/2)O_2 + O^{2-}$$
 (1) proceeds, to result in the increase of basicity

of the salt. The salt melt was direct access to the metals without the Al_2O_3 coatings. The SO_2 and O_2 were consumed in sulphidation-oxidation process, so reaction (1) proceeds, and the basicity in salt increased. Thus the basic fluxing of the oxide scales occurred on the uncoated specimens. The Al_2O_3 coatings prepared by reactive sputtering separate the underlying metals and the salt melt, and alleviate the fluxing of the oxide scales by suppressing the reactions which may result in the increase of the basicity in the salt films near the salt/scale interface.

4 CONCLUSIONS

(1) The reactively sputtered Al₂O₃ coatings on GH30 exhibited excellent hot corrosion resistances and adhesion to substrates.

Fig. 2 Surface micrographs of specimens after 100 h half-immersed corrosion
(a)—GH30; (b)—GH30+Al₂O₃

Fig. 3 Metallographs of cross-sections of specimens after 100 h half-immersed corrosion.

(a)—GH30; (b)—GH30+Al₂O₃

Fig. 4 X-ray images of Cr, O and S on cross section of GH30 after 100 h half-immersed corrosion

- (2) The corrosion rates of the Al_2O_3 coated specimens were about one order of magnitude lower than those of the uncoated specimens. The Al_2O_3 coatings eliminated internal oxidation and internal sulphidation.
- (3) The cracks within the Al_2O_3 coatings were blocked by Cr_2O_3 , which obstructed the salt melt from attacking the underlying metals through these cracks.

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