

IMPROVEMENT OF HOT CORROSION RESISTANCE OF Ti_3Al INTERMETALLIC COMPOUND BY SPUTTERED NiCrAlY COATING^①

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ABSTRACT The effects of sputtered NiCrAlY coating on hot corrosion resistance of Ti_3Al intermetallics in the presence of $(Na, K)_2SO_4$ salts film at 950 °C in air were studied. It was shown that Ti_3Al suffered from severe corrosion, forming a poor adhesive scale with an outer TiO_2 -enriched and inner Al_2O_3 enriched layer. The electrochemical mechanism was responsible for the corrosion process. The sputtered NiCrAlY coating can greatly improve corrosion resistance of Ti_3Al by the the formation of a good adhesive Al_2O_3 enriched scale. But a three-layer diffusion zone formed between coating and substrate alloy.

Key words: intermetallic compounds Ti_3Al NiCrAlY coating hot corrosion

Ti_3Al based intermetallic compounds have received increasing attention for its good high temperature properties but faces low room temperature ductility, and poor oxidation and hot corrosion resistances. Improving oxidation and hot corrosion resistances of Ti_3Al are important for its high temperature applications. Here, effects of sputter deposited NiCrAlY coating on hot corrosion resistance of Ti_3Al are studied.

1 EXPERIMENTAL

The chemical composition of the ingot Ti_3Al in atomic percent is Al 24 and Nb 11 with the balance being Ti. The specimens of 15 mm × 10 mm × 2 mm were cut from the ingot, followed by surface polishing and cleaning. The NiCrAlY coating of 40 μm thick on Ti_3Al was prepared by magnetron sputtering technique. The chemical composition of alloy for sputtering in weight percent is Ni-40Cr-10Al-1Y. A (0.9Na, 0.1K)₂SO₄ salt film of

2.8 mg/cm² was applied to the specimens surface after the specimens were heated to 300 °C. The samples in an Al_2O_3 crucible were put into furnace. After some time testing, the crucibles were removed out and weighted when being cooled down to room temperature. The test temperatre was 950 °C.

X-ray diffraction, EPMA and SEM techniques were employed to analyse the corrosion products.

2 EXPERIMENTAL RESULTS AND DISCUSSION

2.1 Hot Corrosion Kinetics

Hot corrosion kinetics of Ti_3Al and NiCrAlY coated Ti_3Al in the presence of $(Na, K)_2SO_4$ film at 950 °C are shown in Fig. 1. Ti_3Al has a rapid corrosion with the average mass gain of 0.27 mg/cm²·h in the 40 h testing. On the contrary, the mass gain rate for NiCrAlY coating is much slower than Ti_3Al . The average mass gain is 0.04 mg/cm²·h in

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the 40 h testing. Obviously, the sputtered NiCrAlY coating can greatly improve corrosion resistance of Ti₃Al.

2.2 Corrosion Products

XRD analysis revealed that TiO₂ is the primary oxide phase with some Al₂O₃ and Nb₂O₅ for Ti₃Al and Al₂O₃ is the main oxides with some Cr₂O₃ and little TiO₂ for NiCrAlY coated Ti₃Al. The examination of the cross section of the corroded samples indicated that the corrosion products for Ti₃Al is porous and multilayered with an outer TiO₂ enriched and inner Al₂O₃ enriched layer, as shown in Fig. 2. The Al₂O₃ doesn't form a continuous, protective layer. Some sulfides form along scale/substrate boundary. Fig. 3 gives the cross-sectional morphology and elements distribution of NiCrAlY coated Ti₃Al after corrosion at 950 °C for 60 h. It is shown that a protective Al and Cr oxides layer enriching in Al₂O₃ forms on the coating surface. Little TiO₂ also forms by the outer diffusion of Ti in the substrate alloy. Some Al oxide and sulfide form along the pores across the coating. A three-layer diffusion zone forms between coating and substrate with an outer Ti enriched, middle Ni enriched and inner complex Ti, Ni, Cr, Al and Nb-contained layer.

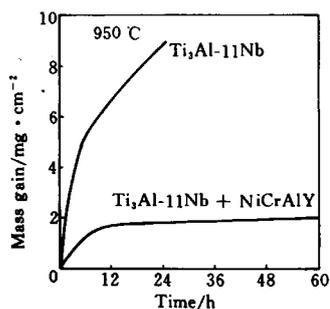


Fig. 1 Kinetics of hot corrosion at 950 °C for Ti₃Al based compound and the compound with NiCrAlY coating

2.3 Discussion

Just as oxidation behaviour^[1], a protective Al₂O₃ scale can't form on the salts-coated Ti₃Al alloy surface, which may be ascribed to that the activity of Al obviously deviates from its solubility in Ti₃Al system^[1]. Furthermore, Ti oxides have relatively high grown rates^[2]. Just as mentioned above, Ti₃Al has a relatively more rapid corrosion, especially in the initial stage (the average mass gain rate is 2.35 mg/cm²·h in the initial 2 h testing). But, the mass gain for oxidation in air is only 1.92 mg/cm² after testing at 950 °C for 20 h. It can be concluded that the (Na, K)₂SO₄ deposites can accelerate corrosion of Ti₃Al. Hot corrosion mechanisms mainly include sulfidation, fluxing and electrochemistry models, which have been excellently discussed in reference [3]. The sulfidation and fluxing mechanisms can't be responsible for the corrosion behaviour of Ti₃Al. Firstly, the oxides scale on Ti₃Al is formed by direct growth, not by fluxing and reprecipitation. Secondly, oxygen solubility in molten salts is rather small, and its diffusion rate is very slow, which can't account for the rapid mass gain of Ti₃Al. Hot corrosion of Ti₃Al is an electrochemical process, which mainly includes anodic oxidation, cathodic reduction and ions diffusion. Reduction reaction is mainly the reduction of O₂²⁻, produced by the chemical solution of oxygen in molten salts (O²⁻ + 1/2O₂ = O₂²⁻). O₂²⁻ in strong-electroly-



Fig. 2 Microstructure of Ti₃Al after hot corrosion at 900 °C for 20 h

te molten salts has a relatively fast diffusion rate, and may diffuse to alloy surface and be reduced ($O_2 + 2e = 2O^{2-}$). The formed O^{2-} may react with anodic oxidation products, mainly Ti^{4+} , and contribute to the growth of oxides. The formation of TiO_2 may cause the enrichment of Al and the formation of Al_2O_3 enriched layer, produced by the reaction of Al^{3+} with O^{2-} . So, an outer TiO_2 enriched and inner Al_2O_3 enriched scale can keep growing. The formed Al_2O_3 may dissolve, reprecipitate in the TiO_2 layer, and can't provide

protection^[4]. The existence of TiO_2 in the inner Al_2O_3 enriched layer may increase the vacancy number of Al or interstitial number of O^{2-} , which can cause the Al_2O_3 enriched layer to lose its protection function^[5]. On the other hand, the rapid outward diffusion of Ti^{4+} to the alloy surface may produce a strong reduction condition, and cause the reduction of SO_4^{2-} ($SO_4^{2-} + 2e = SO_2 + 2O^{2-}$). SO_2 or SO_4^{2-} may diffuse inward, and cause the formation of sulfides. Sulfides may provide rapid diffusion way for the anodic ions, and accelerate

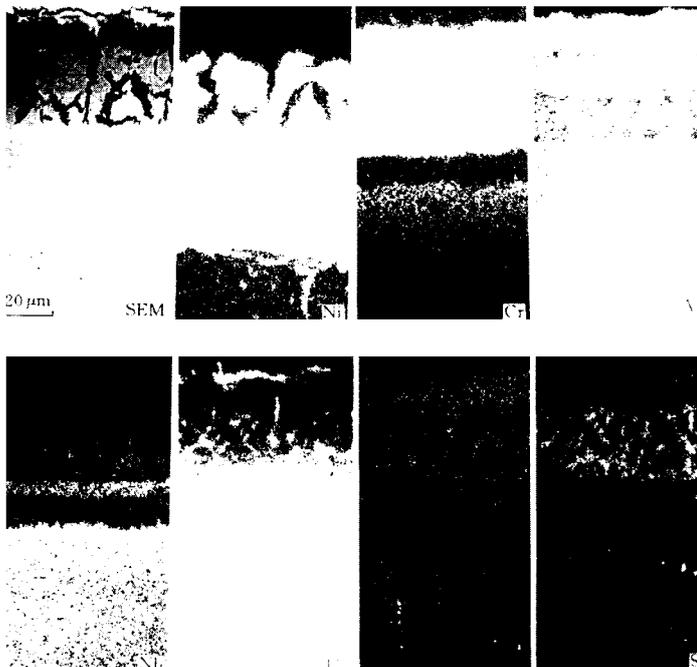


Fig. 3 Microstructure and X-ray mapping of Ti_3Al with NiCrAlY coating after hot corrosion at 950 C for 60h

corrosion of Ti₃Al.

The sputtered NiCrAlY coating can provide good corrosion resistance for Ti₃Al by the preferential formation of a protective Al₂O₃ scale. The outward diffusion of Al in the substrate alloy can also keep the growing and rehealing of Al₂O₃ scale, which is superior to the aluminides coating. Of course, the NiCrAlY coating still can't inhibit the outward diffusion of Ti. More study should be done to know how to inhibit the diffusion of Ti.

3 CONCLUSIONS

Ti₃Al intermetallic compound in the presence of (Na, K)₂SO₄ salts film at 950 °C suffers from severe hot corrosion. A protective Al₂O₃ scale doesn't form, but a TiO₂ enriched complex scale of Ti, Al and Nb oxides be

formed. Some sulfides form across the scale, especially along scale/substrate alloy boundary. The corrosion is an electrochemical process. The sputtered NiCrAlY coating may greatly improve corrosion resistance of Ti₃Al by the formation of a protective Al₂O₃ scale. A three-layer diffusion zone forms between the coating and substrate alloy.

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