

Hot Corrosion of Aluminide Coated Ti-Al-Cr-Nb-Zr-Y Intermetallic Alloys

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Abstract. Pack aluminide coatings were performed on a Ti-Al-Cr-Nb alloy doped with zirconium and yttrium having two phase of α_2 -Ti₃Al and γ -TiAl microstructure. The high activity TiAl₃-based coating was developed from aluminizing process carried out at 850°C for 25 hours in a pack containing 20%-wt Al, 2%wt NH₄Cl, and 78%wt Al₂O₃. During applications at high temperatures, the coating can degrade due to the interaction between the coated system and the environment exhibit high corrosion potentials. This study investigates the hot corrosion behavior of high-activity aluminide coated Zr-Y doped α_2 -Ti₃Al/ γ -TiAlCrNb intermetallic alloy at 700°C, 800°C, and 900°C in a mixture of 90% Na₂SO₄ and 10% NaCl. The experimental results showed that the addition of Zr and Y in the alloy reduces significantly the hot corrosion rate of the coating as resulted from the interdiffusion of these elements from the alloy to the coatings and influence the behavior of the TiAl₃-based coatings.

Introduction

Intermetallic alloys of the Ti – Al system have been developed to have combination of properties suitable for high temperature applications. However, it is generally accepted that the applications of γ -TiAl alloys faced problems as the materials are relatively brittle and prone to hot cracking. Reducing slightly the aluminium content of the alloy to give two phase of α_2 -Ti₃Al and γ -TiAl (simplified as α_2 -Ti₃Al/ γ -TiAl) has been reported provide better mechanical properties at room as well as high temperatures [1]. Nevertheless, this reduces the high temperature corrosion resistance of the alloys [2,3]. To solve this problem, two methods are available, i.e., alloying with elements that increase oxidation resistance of α_2 -Ti₃Al/ γ -TiAl, such as chromium, and applying aluminide based coatings.

At elevated temperatures, the structural stability of an aluminide coating is primarily affected by: (i) selective oxidation and hot-corrosion processes; and (ii) interdiffusion between the coating and the substrate. Study to investigate the effect of aluminide coatings on substrate of α_2 -Ti₃Al/ γ -TiAl doped with rare earth elements, i.e., Y and Zr have not been intensively carried out. This study investigated the effects of small amount addition of Zr and Y on the aluminide coated α_2 -Ti₃Al/ γ -TiAl substrate at high temperatures. In this study a diffusion aluminide coating having layers of TiAl₃ and TiAl₂ based intermetallic compounds was developed using pack aluminizing method on a substrate of Ti-Al-Cr-Nb alloys doped with Zr and Y at 700°C, 800°C, and 900°C in a mixture of 90% Na₂SO₄ and 10% NaCl.

Experimental Works

A two phase α_2 -Ti₃Al/ γ -TiAl with nominal chemical compositions of Ti-40Al-2Cr-2Nb doped with 0.5Zr and 0.6Y was produced from high purity Ti, Al, Cr, Nb, Zr and Y metals using a Centorr 5 SA single-arc furnace with high purity argon atmosphere. The alloy buttons were homogenized at 1000°C for 18 hours in a tube furnace purged with argon. The homogenized alloy was then sectioned to obtain 2.0 mm thick coupons. Prior to the pack cementation process, the samples were ground to a 1200-grit finish and ultrasonically cleaned in acetone. Aluminum-rich TiAl₃ coating was applied to the

substrate coupons using a high- activity pack cementation process at 900°C for 10 hours. The pack composition consisted of a mixture of 20 wt.% aluminum powder, 2 wt.% NH₄Cl and 78 wt.% Al₂O₃ powders. The pack aluminised samples were tested in a mixture of 90% Na₂SO₄ + 10% NaCl melt at 700°C, 800°C and 900°C for 5 hr, up to 200 hrs. After removed from liquid salt, the specimens were cleaned in boiling water and dried. The samples were then weighed in a microbalance to obtain the weight gain and weight loss of each sample.

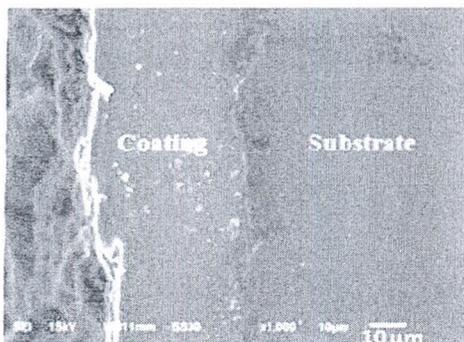
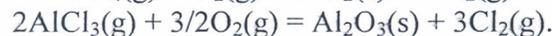
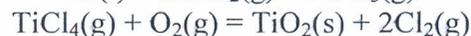
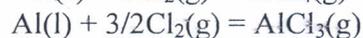
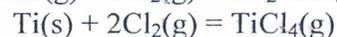
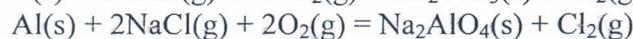
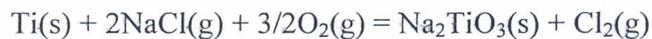
Microstructural analysis using optical and scanning electron microscope (SEM) were carried out on the cross section samples. Energy dispersive x-ray spectroscopy (EDX) analysis was conducted to identify the phases occurred in the samples based on the chemical contents resulted from the EDX analysis. To support the finding obtained from the EDX analysis, x-ray diffraction (XRD) analysis was conducted on the surface of the tested samples. In order to compare the performance of the coating and the role of the doped element Zr and Y, bare TiAlCrNb and TiAlCrNbZrY samples were also tested in the same salt solution and temperatures.

Results and Discussion

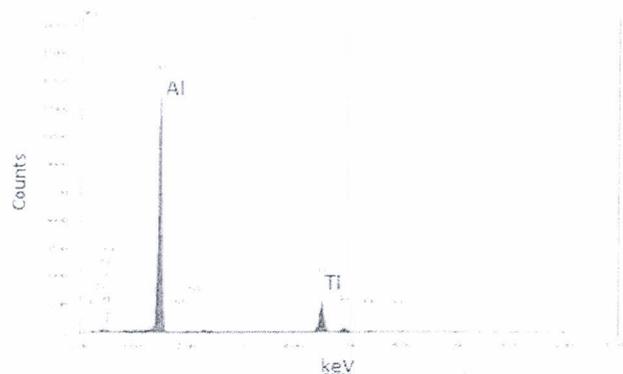
The microstructure of an as-coated $\gamma+\gamma'$ substrate and corresponding EDX pattern are shown in Figure 1.a and 1.b, respectively. It is clearly seen from Fig. 1.a that the outer layer about 35 μm in thickness in average. From the concentration analysis taken EDX in $10 \times 10 \mu\text{m}^2$ on the coating cross section of the sample, it is seen that the coating in the as-coated samples possessed an aluminium concentration between 52 %at and 63 %at. It is therefore concluded that the coating is primarily aluminium-rich β , as also clearly seen from the EDX pattern of the outer layer shown in Fig. 1.b.

Figure 2 shows the kinetic plot of hot corrosion test on bare and coated samples. It is seen that slight weight gain at early of hot corrosion test was identified, but then for certain samples it followed by significant weight loss at longer times, especially at higher temperatures, e.g., 800°C and 900°C. The figure also indicates that severe corrosion was observed in samples tested for 200 hrs. with the corrosion products consisted mainly of oxide mixtures of TiO₂ and Al₂O₃. Nevertheless, few amounts of other oxides of Cr and Nb, probably in the forms of Cr₂O₃ and NbO, are also identified. Surprisingly, no sulfides were found in all tested samples.

It is believed that severe weight loss indicates metal chlorides responsible for the degradation of the coatings, with possible reactions as follow:



(a)



(b)

Fig. 1 (a) Cross section microstructures of as coated sample, and (b) corresponding EDX pattern of the coating layer.

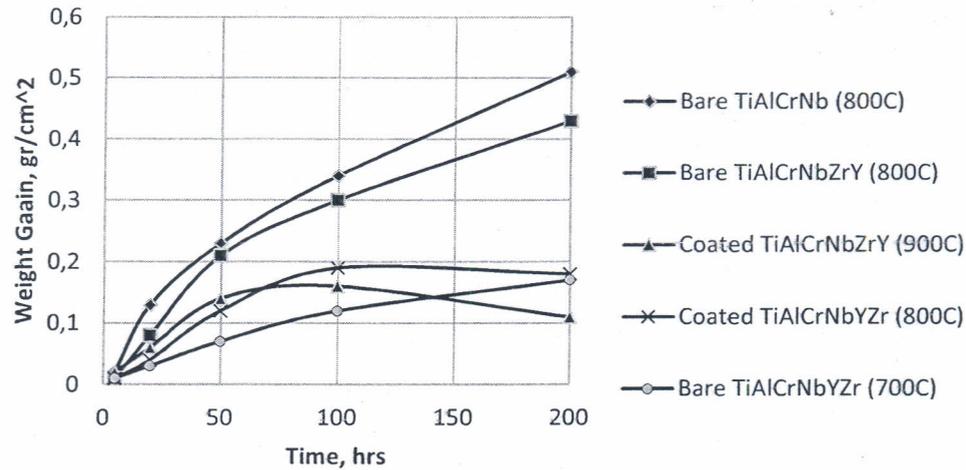


Fig. 2 Hot corrosion kinetics curves of different bare and aluminide coated samples.

Even though there was no EDX results indicated the occurrence of chromium and niobium oxides, it is believed that similar reactions might also apply for Cr and Nb but with small quantity. The reactions indicate self catalysis of Cl_2 as also reported by other researchers [6,7].

Due to limited space available, only view microstructures are presented in this paper. The microstructure of the sample corrosion tested at $900^\circ C$ for 200 hrs. and corresponding EDX pattern of the corrosion product are shown in Figure 3.a and 3.b, respectively, taken using windows of electron beam in the size of about $1\mu m^2$. Pitting type corrosion was clearly seen as the main mode of the corrosion attack on the coated samples at high temperature ($900^\circ C$). The XRD analysis on the surface of the samples shows predominant oxides of TiO_2 and Al_2O_3 , as shown one of which in Figure 4, and this support the finding based on EDX analysis on the cross section of all corrosion tested samples.

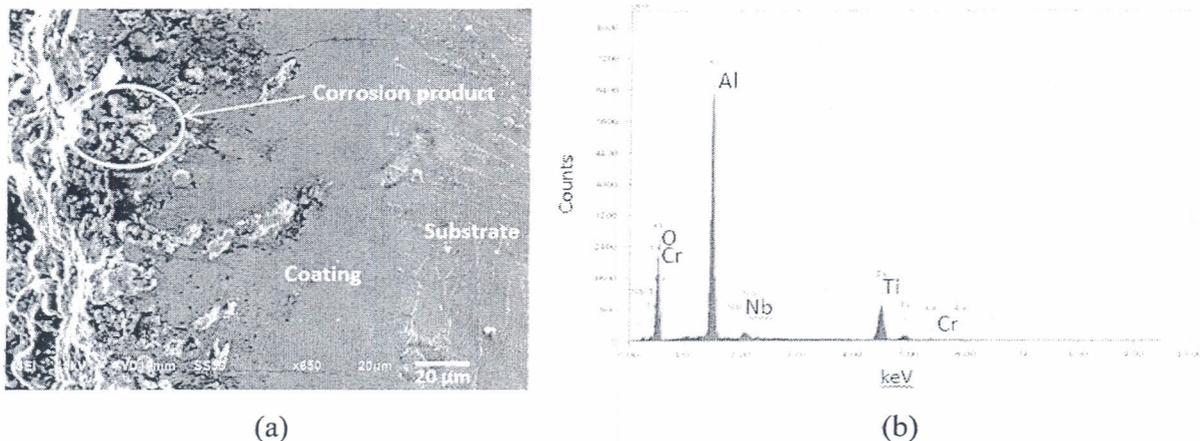


Fig. 3. (a) Cross section microstructure of the coated sample tested at $900^\circ C$ for 200 hrs, and (b) corresponding EDX pattern of the corrosion product.

The co-presence of TiO_2 and Al_2O_3 in the scale layer has been reported accelerate the hot corrosion attack known as synergistic hot corrosion as reported previously [8,9]. Nevertheless, it is found in this study that the role of Zr and Y that has been generally accepted to increase the oxidation resistant of the coated layer also play similar role in the hot corrosion, and this probably occur by reducing the diffusion of Ti outwardly from the substrate into the coating and diffusion of Al inwardly from the coating to the substrate.

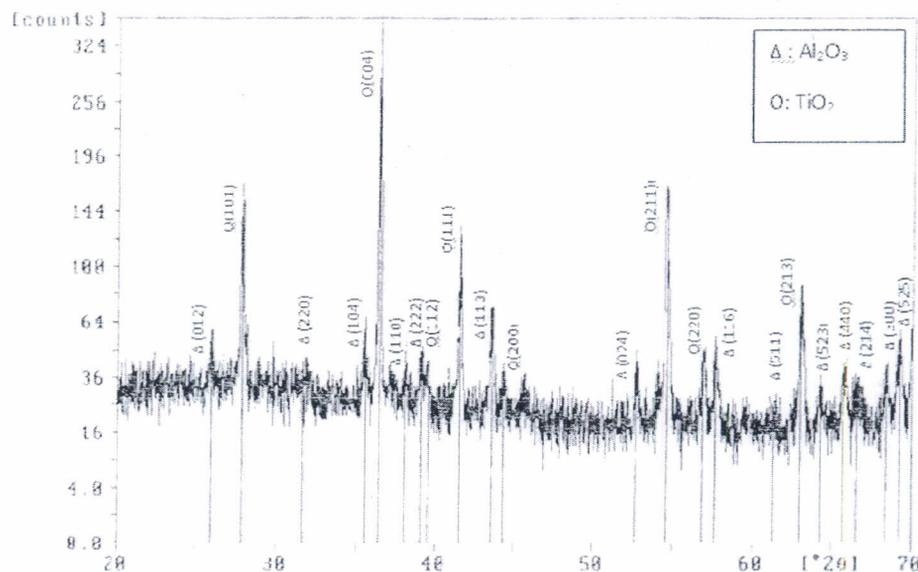


Fig. 4. XRD pattern for a sample subjected to corrosion test at 900°C for 200 hours.

Conclusions

The experimental results show that the hot corrosion of coated samples mostly exhibits pitting type corrosion. The XRD and EDX analysis confirm that the corrosion products consists mainly the mixture of TiO_2 and Al_2O_3 and no sulfide phase were found in corrosion products. Significant weight loss at longer times occurs especially at higher temperatures, e.g., 800°C and 900°C. Metal chlorides formation is believed responsible for this degradation of the aluminide coatings. The study shows that the addition of small amount of Zr and Y reduce the hot corrosion attack of the coating and this is predicted due to the reduction of interdiffusion behavior of Ti and Al in the coating as well as in the substrate.

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