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Hot-salt oxidation characteristics of titanium aluminides

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The oxidation and hot-salt corrosion of a Ti–46% Al, 1.8% Nb, 1.9% Cr (at%) alloy were investigated in the temperature range 700–800 °C. Oxidation tests were carried out using thermogravimetric analysis and show parabolic oxidation after 30 h for salt-coated and uncoated samples. Oxide-scale morphologies were examined using scanning electron microscopy and X-ray diffraction for various oxidation times. The X-ray data reveal the presence of rutile, alumina and $NaTiO_2$ as surface oxides. For quantitative analysis, the cross-sections of the specimens were analysed by energy dispersive X-ray analysis. © *1998 Kluwer Academic Publishers*

1. Introduction

Light-weight alloys based on gamma titanium aluminide intermetallics, are of interest as potential high-temperature structural materials for aircraft applications due to their high strength and excellent high-temperature properties. TiAl alloys exhibit good oxidation resistance due to their high aluminium content forming alumina, which is slow growing and highly resistant to further oxidation of the underlying layer.

At temperatures above 200 °C there is significant reaction for most metals in air and the rate of reaction increases with temperature. More complex corrosion processes occur when metals are exposed to aggressive environments containing components such as sodium chloride, moisture and sulphate species and the degradation is known as "hot corrosion". Alloys used in industrial environments are constantly subjected to such aggressive reactants and the magnitude of the resulting hot corrosion depends on several factors, such as deposit composition, temperature, temperature cycling, alloy composition and alloy microstructure. The oxidation and corrosion of titanium aluminide alloys have been studied by many authors [1–3] and suggest that TiAl intermetallic alloys do not form a protective alumina scale but a mixture of rutile and alumina due to the small difference in free energy of oxidation of aluminium and titanium, the high oxidation rate of titanium compared to aluminium, the high solubility of oxygen and the low diffusivity of aluminium. Although many investigations have been carried out on the effect of composition, alloy microstructure and mechanical properties [4–8], oxidation behaviour of this class of materials in the presence of NaCl is a serious problem at high temperatures. NaCl-induced oxidation tests carried out by Yao and Mark [9] reveal that the reaction of metal, oxygen and deposited salt causes the formation of non-protective scale and accelerated oxidation in titanium aluminide. The present study investigates the oxidation mechanism of NaCl-induced hot corrosion of titanium aluminide in the temperature range 700–800 °C using thermogravimetric analysis in air.

2. Thermogravimetric analysis

The material studied was a commercial alloy supplied by General Electric, USA, with composition Ti–46.6%Al, 1.9%Nb, 1.8%Cr, (0.127–0.3)% Fe (at%) which was verified by energy dispersive X-ray analysis. Specimens were prepared by standard grinding and polishing. In the present study, NaCl was coated on to the specimen by dipping in saturated salt water and drying. The amount of NaCl on the specimen surface was approximately $2.5\,\mathrm{mg\,cm^{-2}}$. Because the melting point of NaCl is 801 °C, the oxidation tests were conducted below this temperature by thermogravimetric analysis in the temperature range 700–800 °C for 100 h. After the oxidation tests, specimens were analysed by scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDX). The oxide phases were characterized by X-ray diffraction (XRD).

3. Results and discussion

3.1. Oxidation kinetics

Fig. 1 shows the weight gain against time for the uncoated alloy at 700, 750, 775 and 800 °C for 100 h oxidation. The data show that the weight gain increases as temperature increases. At 750, 775 and 800 °C, the first 30 h oxidation is found to be non-parabolic, and after that the oxidation is parabolic. The initial non-parabolic kinetics are attributed to the diffusion of oxygen ions inwards into the matrix [10].

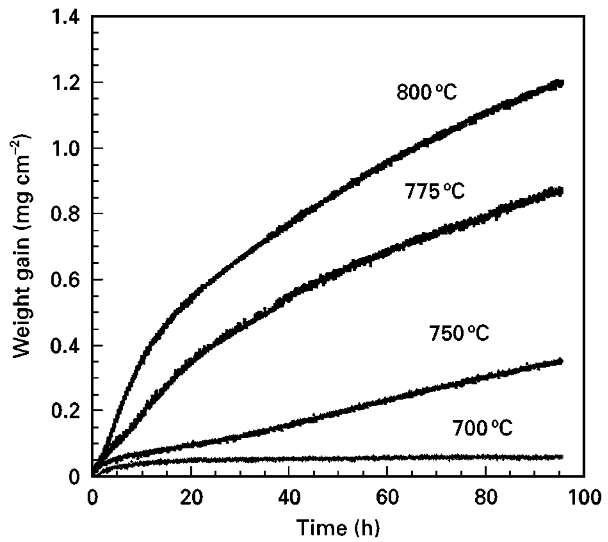

Figure 1 Weight gain versus time for the oxidation of Ti–46.6%Al, 1.9%Cr, 1.8%Nb, (0.127–0.3)%Fe at 700, 750, 775 and 800 °C.

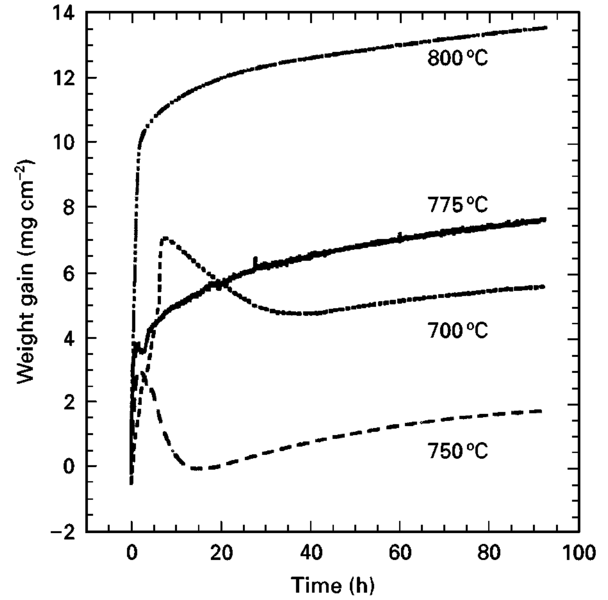

Figure 2 Weight gain versus time for the oxidation of Ti–46.6%Al, 1.9%Cr, 1.8%Nb, (0.127–0.3)%Fe with NaCl coating at 700, 750, 775 and 800 °C.

Fig. 2 shows the weight gain of salt-coated specimens at 700, 750, 775 and 800 °C. The total weight gain increases almost ten-fold for salt-coated compared with uncoated specimens. During the first 3.5 h, there is a rapid increase in weight which then drops off drastically for 700 and 750 °C. After approximately 16 h the specimen starts to oxidize parabolically. Also, as the temperature increases from 700°C to 775 °C this drastic change decreases and at 800 °C a steady increase in weight gain with time is observed. The initial fast oxidation at 700, 750, 775 and 800 °C is due to the reaction of salt with the alloy and the decrease after 3.5 h is due to the evaporation of salt and moisture remaining on the coated specimen. The initial oxidation of the alloy (for NaCl-coated samples) happens rapidly and so a steady increase in weight gain is observed during the initial oxidation period at 800 °C. The evaporation of salt from the specimen is confirmed by the dentritic growth of salt observed on the inside wall of the furnace next to the sample after the test. The oxide scale formed on the salt-coated specimens was very thick and brittle, and greenish immediately after the test, turning grey on cooling. No spalling of oxide was found during the tests for either NaCl-coated or uncoated samples. The brittle oxide observed is due to the aluminium in the aluminide reacting with the moisture present in the salt and generating atomic hydrogen which will penetrate through the oxide layer causing cracks on the oxide surface [11].

3.2. X-ray diffraction and oxide morphology

The X-ray diffraction data of oxidized samples at different temperatures with and without NaCl coatings are shown in Table I. At all temperatures, α-Al_2O_3, TiO_2 and Ti_3Al are the compounds detected for uncoated samples. Because the oxides formed at 700 °C were very thin, the X-ray intensities observed at this temperature were weak.

The data show that the oxide scale formed on NaCl-coated samples consists of TiO_2, Al_2O_3 and $NaTiO_2$. Because the oxide scales formed on the NaCl-coated samples are very thick and porous, the relative intensity of the peaks was low compared to that of uncoated samples. The oxide scales formed on the uncoated samples were very thin, and quantitative analysis of the cross-sections of the oxide scale shows that, at 700 °C the oxide scale is a single layer consisting of an oxide containing predominantly rutile, indicating the outward diffusion of titanium ions. The Ellingham diagram for oxides shows that alumina should form in preference to TiO_2, but TiO_2 forms more rapidly than Al_2O_3 [12]. Fig. 3a shows an SEM picture of the cross-section of the alloy after oxidation for 100 h at 750 °C. The matrix has a lamellar twin structure at all temperatures studied. Fig. 3b shows the backscattered image of the same specimen showing a two-layer structure. EDX analysis of the oxide scale shows that the oxide is an intermixed layer of Al_2O_3 and TiO_2 and is rich in rutile close to the outer

TABLE I XRD data of Ti–46.6%Al, 1.9%Cr, 1.8%Nb, (0.3–0.127)%Fe alloy after oxidation at different temperatures for 100 h with and without a salt coating

Alloy	Oxide	Relative intensities[a] at different temperatures		
		700 °C	750 °C	800 °C
Without NaCl	α-Al_2O_3	W	S	S
	TiO_2	S	VS	VS
	Ti_3Al	–	S	S
With NaCl	α-Al_2O_3	S	S	S
	TiO_2	VS	VS	VS
	$NaTiO_2$	S	S	S

[a] VS, very strong; S, strong; W, weak.

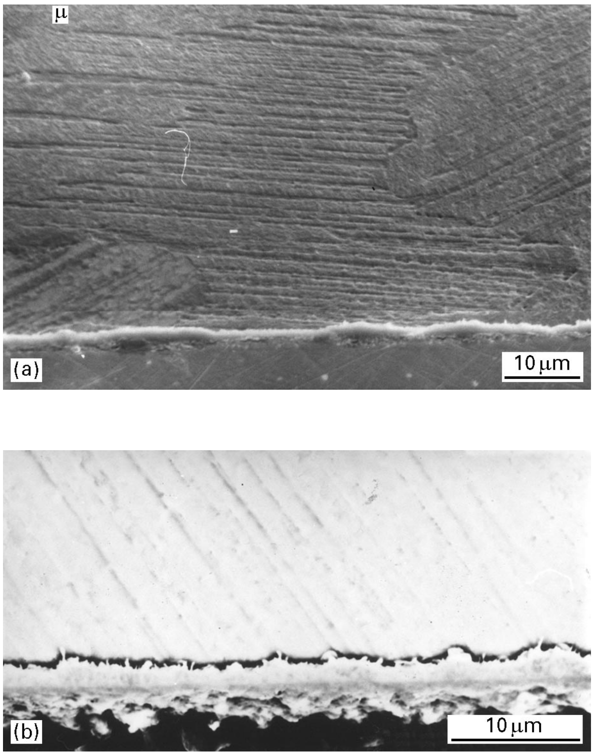

Figure 3 Scanning electron micrograph of a cross-section of the Ti–46.6%Al, 1.9%Cr, 1.8%Nb, (0.127–0.3)%Fe alloy oxidized for 100 h 750 °C (a) secondary image, (b) backscattered image.

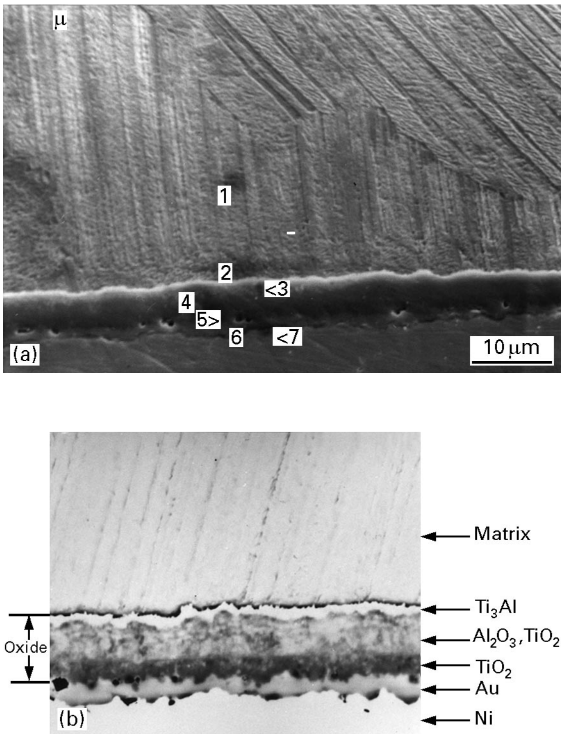

Figure 4 Scanning electron micrograph of a cross-section of a Ti–46.6%Al, 1.9%Cr, 1.8%Nb, (0.127–0.3)%Fe alloy oxidized for 100 h at 800 °C; (a) secondary image, (b) backscattered image.

scale, although from X-ray data the presence of Ti_3Al could also be detected.

Fig. 4a and b show the secondary and backscattered images of the cross-section of the alloy oxidized at 800 °C for 100 h. The oxide scale consists of three layers:

1. close to the matrix, a layer of Ti_3Al (1.2 μm);
2. an intermixed layer of Al_2O_3 and TiO_2 (4.8 μm);
3. a layer of TiO_2 (0.9 μm).

During the initial oxidation, the Ti_3Al layer is formed due to the higher diffusion rate of titanium ions compared to aluminium ions. The depletion of aluminium in the alloy/scale interface promotes internal oxidation producing TiO_2 due to the diffusion of oxygen ions inwards. As the time of oxidation increases, a heterogeneous oxide layer of TiO_2 and Al_2O_3 is formed. The outer rutile layer results from the outward diffusion of titanium through rapid diffusion paths in the oxide scale. Fig. 5a and b show the surface morphologies of the scale after oxidation for 100 h at 750 and 800 °C with crystals of TiO_2 dispersed in Al_2O_3. The oxide grows on the twin lamellae and the crystallite size increased with increasing oxidation time, scale thickness and temperature, indicating that these crystals grew by outward diffusion.

Fig. 6a–c show the oxide scale formed on the NaCl-coated alloy after oxidation and display similar features at all the temperatures studied with regions of Al_2O_3 and TiO_2. The thermogravimetric tests showed that salt promoted the oxidation, giving much thicker oxide scales which, when examined by EDX, indicated titanium- and aluminium-rich phases containing less than 3 at % NaCl. The microstructure and EDX analysis of the scale and the alloy reveal that during oxidation, metal ions diffuse outwards through the initial NaCl layer and react with oxygen forming an

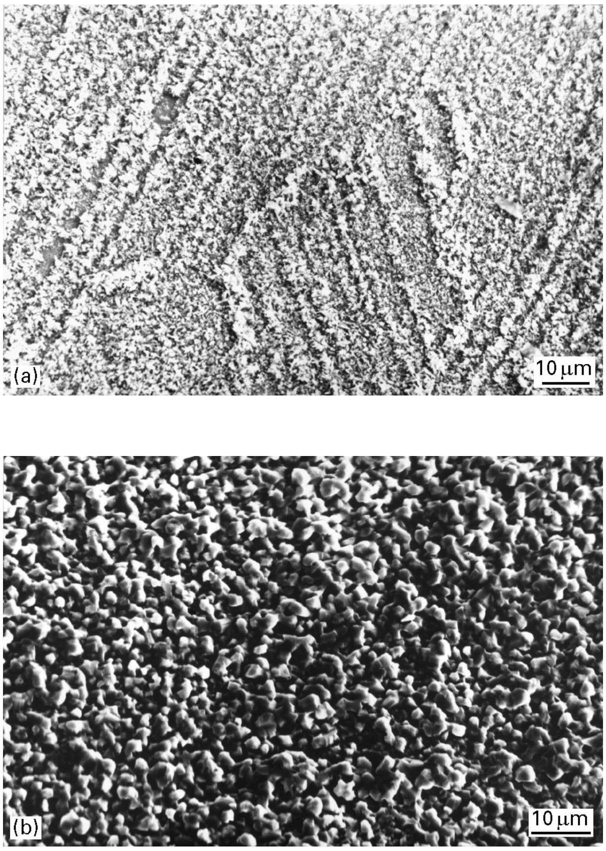

Figure 5 SEM microstructure of Ti–46.6%Al, 1.9%Cr, 1.8%Nb, (0.127–0.3) Fe alloy oxidised for 100 h at (a) 750 °C and (b) 800 °C.

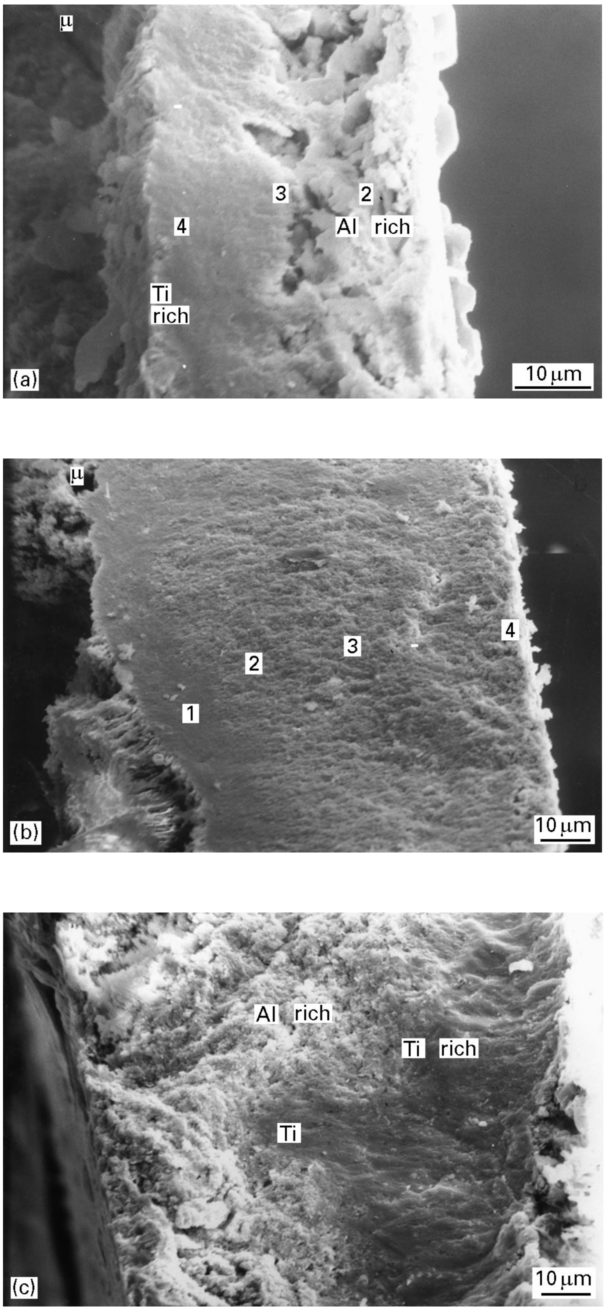

Figure 6 Scanning electron micrograph of the cross-section of Ti–46.6%Al, 1.9%Cr, 1.8%Nb, (0.127–0.3)%Fe alloy with NaCl coating after oxidation for 100 h at (a) 700 °C, (b) 750 °C and, (c) 800 °C.

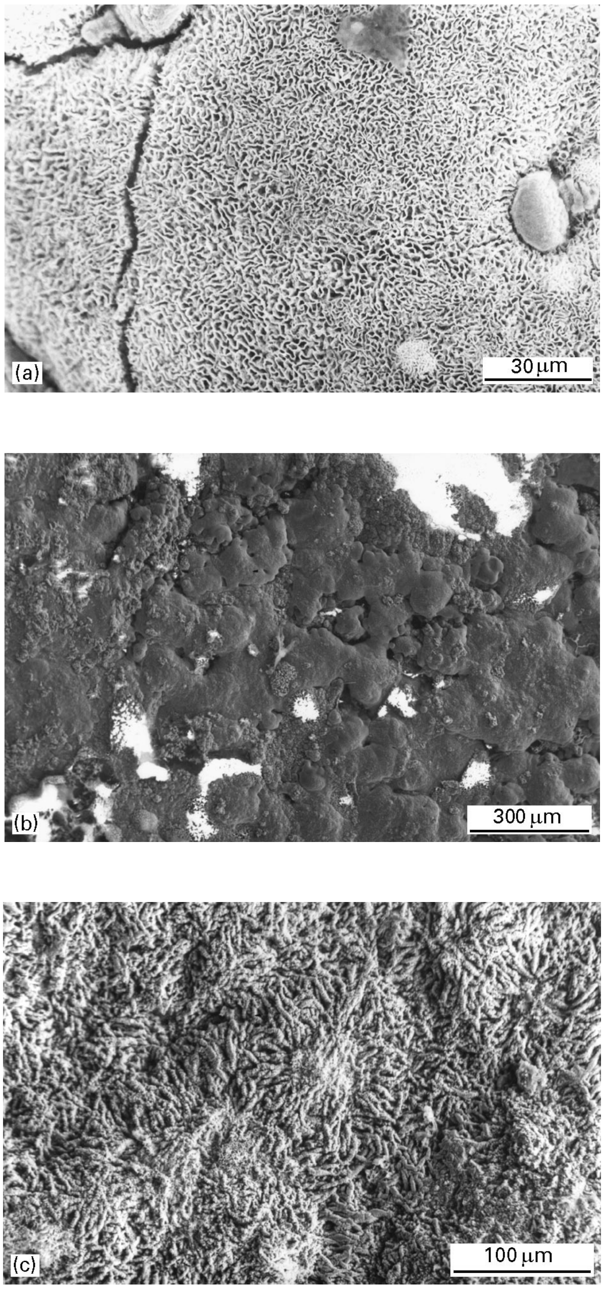

Figure 7 Scanning electron micrograph microstructure of Ti–46.6%Al, 1.9Cr%, 1.8%Nb (0.127–0.3)%Fe alloy with NaCl coating oxidized at (a) 700 °C, (b) 750 °C, and, (c) 800 °C for 100 h.

outward growing oxide scale. The presence of $NaTiO_2$ in the NaCl-coated specimens must indicate the early formation of this compound when the specimens are first exposed to air. Subsequent growth of Al_2O_3 cannot provide a continuous layer which means the protection afforded by the alumina is lost. Furthermore, this disruption of the initial oxide appears to enhance subsequent diffusion of titanium ions through the oxide, leading to enhanced oxidation giving higher weight gain at all temperatures for the coated specimens. Also, the reaction with NaCl will release chlorine [9]

$$2NaCl + Ti + 2O_2 \rightarrow Na_2TiO_4 + Cl_2$$

which will decrease the solubility and diffusivity of oxygen in the early stages of the reaction leading to enhanced external oxidation [13, 14]. The porosity of the oxide scale may be attributed to the formation of volatile phases, such as chlorine and atomic hydrogen generated by moisture.

Fig. 7a–c show the nodular growth of oxides on the surfaces of NaCl-coated samples at 700, 750, and 800 °C, respectively, for 100 h oxidation. At 700 °C, the surface is covered with a net-like oxide growth with small nodules and at 750 °C highly porous nodules are seen. These nodules grow outward and coalesce on some parts of the scale (Fig. 7c). The oxide scale was thick and adherent to the alloy, but showed large cracks (Fig. 8), which may have occurred on cooling due to the difference in thermal expansion of the alloy and the oxide scale. Subsequent handling of the specimens caused large areas of scale to spall.

Figure 8 Scanning electron micrograph of Ti–46.6%Al, 1.9Cr%, 1.8%Nb, (0.127–0.3)%Fe alloy showing cracks on the oxide surface.

4. Conclusion

Oxidation kinetics were non-parabolic for the first 35 h uncoated and NaCl-coated specimens and then became parabolic. The weight gain was found to be almost ten times greater for NaCl-coated samples. For uncoated samples, XRD and EDX analysis show that the oxide scale consists of three layers comprising Ti_3Al, a mixture of TiO_2 and Al_2O_3 and an outer scale rich in rutile. For NaCl-coated samples, the oxide has two layers of Al_2O_3 and TiO_2, but in addition $NaTiO_2$ is also detected.

Acknowledgements

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