Cyclic oxidation of aluminized Ti–14Al–24Nb alloy

J. SUBRAHMANYAM
Defence Metallurgical Research Laboratory, Kanchanbagh, Hyderabad 500258, India

Titanium aluminides are considered as replacements for superalloys in applications in gas turbine engines because of their outstanding properties. Ti_3Al has a superior creep strength up to 815° C, but has poor oxidation resistance above 650° C. Two approaches can be followed to improve the oxidation resistance of Ti_3Al above 650° C. One is alloying and the other obtaining a protective surface coating. Niobium was found to improve the oxidation resistance, when added as an alloying element. Recent investigations showed that a $TiAl_3$ surface layer considerably improves the oxidation resistance of titanium. In the present work, a $TiAl_3$ layer was obtained on a Ti–14Al–24Nb (wt%) alloy using a pack aluminizing process. The cyclic oxidation behaviour of aluminized and uncoated samples was evaluated.

1. Introduction

Ordered intermetallic compounds such as Ti_3Al and TiAl possess outstanding properties: high strength to weight ratio, high elastic modulus, higher elevated temperature creep rupture strength, etc. Because of these properties, development of these alloys has received increasing attention in recent years as replacements for nickel-base superalloys. It has been demonstrated that the titanium aluminides have competitive properties compared to nickel-base superalloys with 50% reduction in density [1].

Table I, from Lipsitt [2], compares the properties of titanium aluminides with conventional titanium- and nickel-base superalloys. It can be seen that Ti_3Al has good creep properties up to 815° C but poor oxidation resistance above 650° C. Lipsitt even suggests that either alloying or coating is necessary to improve the oxidation resistance of Ti_3Al. Chowdary *et al.* [3] and Mendiratta and Chowdary [4] added several alloying elements to Ti_3Al and found that niobium as well as tungsten improves the oxidation resistance of Ti_3Al considerably. In recent work [5, 6], $TiAl_3$ and TiAl layers were obtained on the surface of pure titanium and their cyclic oxidation behaviour was studied. It was found that $TiAl_3$ layers show superior oxidation resistance compared to TiAl. In the present work, a $TiAl_3$ coating is obtained on Ti–14Al–24Nb (wt %) alloy by pack cementation. The cyclic oxidation behaviour of coated and uncoated samples was studied at 1000 and 1100° C.

2. Experimental details

Ti–14Al–24Nb alloy was prepared by vacuum arc melting; 1 cm × 1 cm × 0.5 cm coupons were used for aluminizing and subsequent oxidation. Pack aluminizing was carried out using NiAl as the aluminium source, NH_4Cl as the activator and Al_2O_3 as diluent at a temperature of 1000° C. Further details have been presented earlier [5, 6]. Cyclic oxidation was carried out in static air at 1000 and 1100° C. The temperature–time cycle was 1 h at high temperature and 20 min at room temperature, for cooling. The coated as well as oxidized samples were examined using X-ray diffraction, metallography, SEM and electron probe microanalyser.

3. Results and discussion

3.1. Aluminizing

As in the case of pure titanium [5], Ti–14Al–24Nb alloy also forms a thick $TiAl_3$ phase on the surface after aluminizing. This is revealed by the X-ray diffraction of the coated surface. Fig. 1 shows the micrograph of a cross-section of aluminized alloy. Thin inner layers may be lower aluminides such as TiAl. Thin transverse cracks can be seen in the aluminide layer, similar to those found in aluminized titanium [5]. Fig. 2 presents the electron probe microanalysis of a cross-section of the coated sample. From the line analysis it is clear that the niobium content in the aluminide layer is considerably less than that in the matrix.

TABLE I Comparison of properties of titanium aluminides with conventional Ti and Ni-base superalloys [2]

	Ti base	Ti_3Al	TiAl	Superalloys
Density ($g cm^{-3}$)	4.5	4.15–4.7	3.76	8.3
Young's Modulus ($GN m^{-2}$)	110–96	145–110	176	206
Maximum temperature creep (° C)	538	815	1038	1093
Maximum temperature oxidation (° C)	593	649	1038	1093
Ductility, R.T.(%)	20	2–5	1–2	3–5
Ductility, operating (%)	High	5–8	7–12	10–20

0022-2461/88 $03.00 + .12

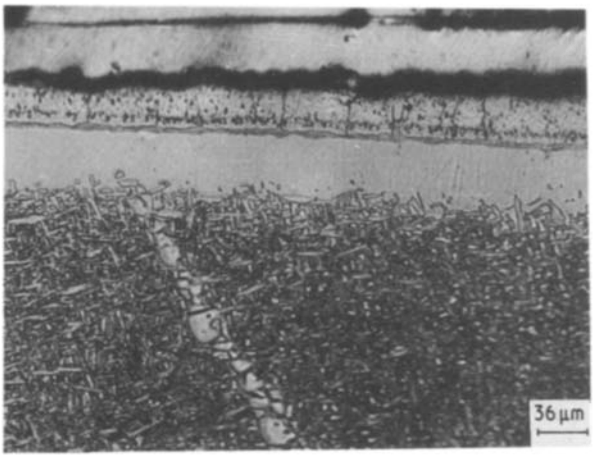

Figure 1 Metallographic cross-section of aluminized Ti–14Al–24Nb alloy.

3.2. Cyclic oxidation

Fig. 3 shows the weight gain against time plot for both aluminized and uncoated samples at 1000° C. The aluminized alloy shows negligible weight gain as compared to uncoated samples. There was no spalling of oxide in either sample at 1000° C. Fig. 4 shows a similar plot at 1100° C. The uncoated sample shows continuous spalling, whereas the coated sample showed no spalling up to 30 h. Figs 3 and 4 clearly illustrate the improvement in the oxidation resistance of the alloy with the coating, even at a temperature of 1100° C.

Barrett and Lowell [7] explained spalling during cyclic oxidation. Initially the sample gains weight due to oxide formation of the surface. Subsequently, the weight gain per unit time decreases, stress develops in the oxide as the thickness of the oxide increases and spalling begins. As the oxide spalls, fresh surface is exposed, the phenomenon is repeated and the spalling continues. For uncoated alloy at 1100° C, the sample undergoes this process (Fig. 4). Initially the weight per unit area increases and with the initiation of spalling a negative slope is established. It can be seen in the curve that after each spalling the sample gains weight before further spalling. It can be considered that in Figs 3 and 4, wherever there is no spalling, the curves are in the initial stages of weight gain and ultimately spalling starts once sufficient oxide thickness has built-up. It is noteworthy that in the case of coated samples, the gains in weight are considerably lower indicating that spalling will be delayed and the surfaces will be protected for longer times. This must be due to the inherently high oxidation resistance of the $TiAl_3$ phase present on the surface.

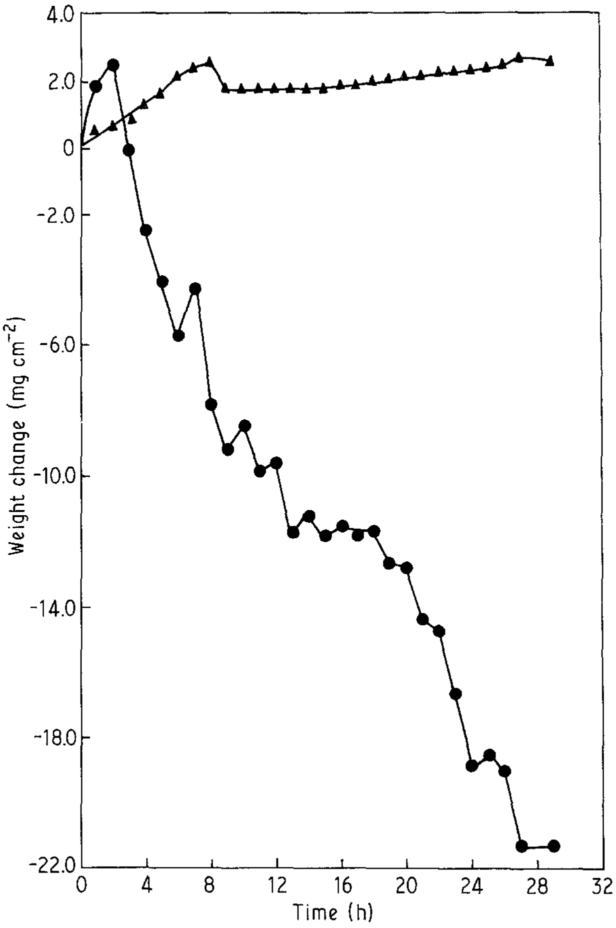

Figure 3 Weight gain against time plot for (▲) the coated and (●) uncoated Ti–14Al–24Nb alloy at 1000° C.

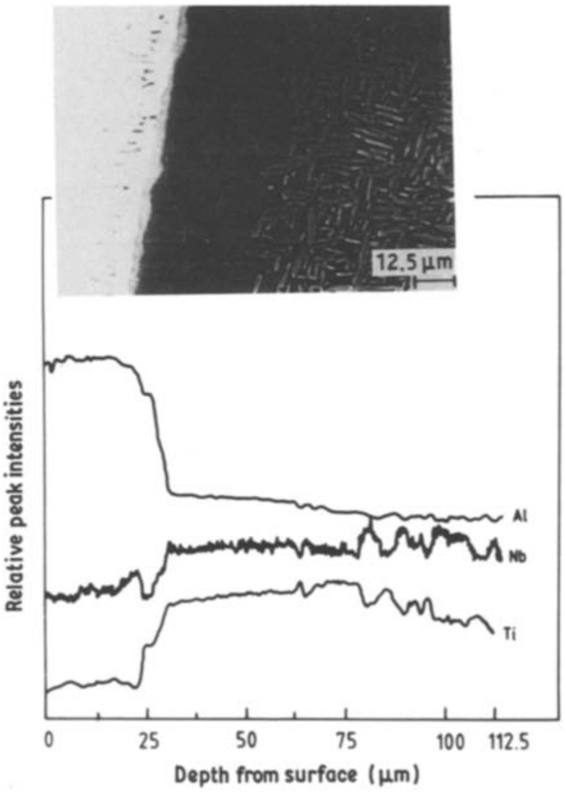

Figure 2 Electron probe microanalysis across the aluminized Ti–14Al–24Nb alloy.

3.3. Phase analysis and microstructure of oxidized samples

Table II presents the results of the X-ray diffraction carried out on the oxidized samples. It can be observed that the uncoated alloy gave predominantly TiO_2 peaks whereas coated sample surfaces contained titanium aluminides ($TiAl_3$ or TiAl). For the uncoated samples, the major difference between 1000 and 1100° C is the presence of Nb_2O_5 at 1100° C. This may be one of the factors contributing to the oxide spalling in the case of oxidation at 1100° C.

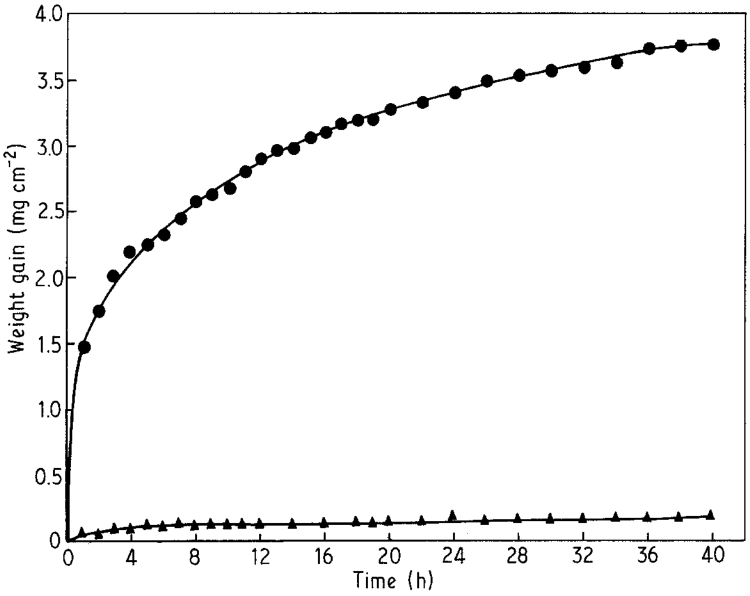

Figure 4 Weight change against time plot for (▲) the coated and (●) uncoated Ti–14Al–24Nb alloy at 1100° C.

Figs 5 and 6 show micrographs (optical and SEM) of the sections of coated and uncoated samples after cyclic oxidation at 1000 and 1100° C, respectively. The optical micrographs show the overall coating or oxide/metal interface, whereas SEM images bring out surface oxide layers clearly. For the coated samples, oxidized at both temperatures, the aluminized layer is clearly seen to be present on the surface from the optical images. This was also confirmed by electron probe microanalysis across the interface, which showed high amounts of aluminium at the surface. As mentioned already, the remaining aluminide layer continues to protect the samples if the cyclic oxidation continues. From the SEM picture, it is evident that in all cases oxide layers are present on the surface. At 1100° C for the uncoated sample the oxide layer contains a network of cracks, which must contribute to spalling. From the coated sample at 1100° C (Fig. 6), even though certain cracks are present, the oxide layer looks compact and adherent. At 1000° C,

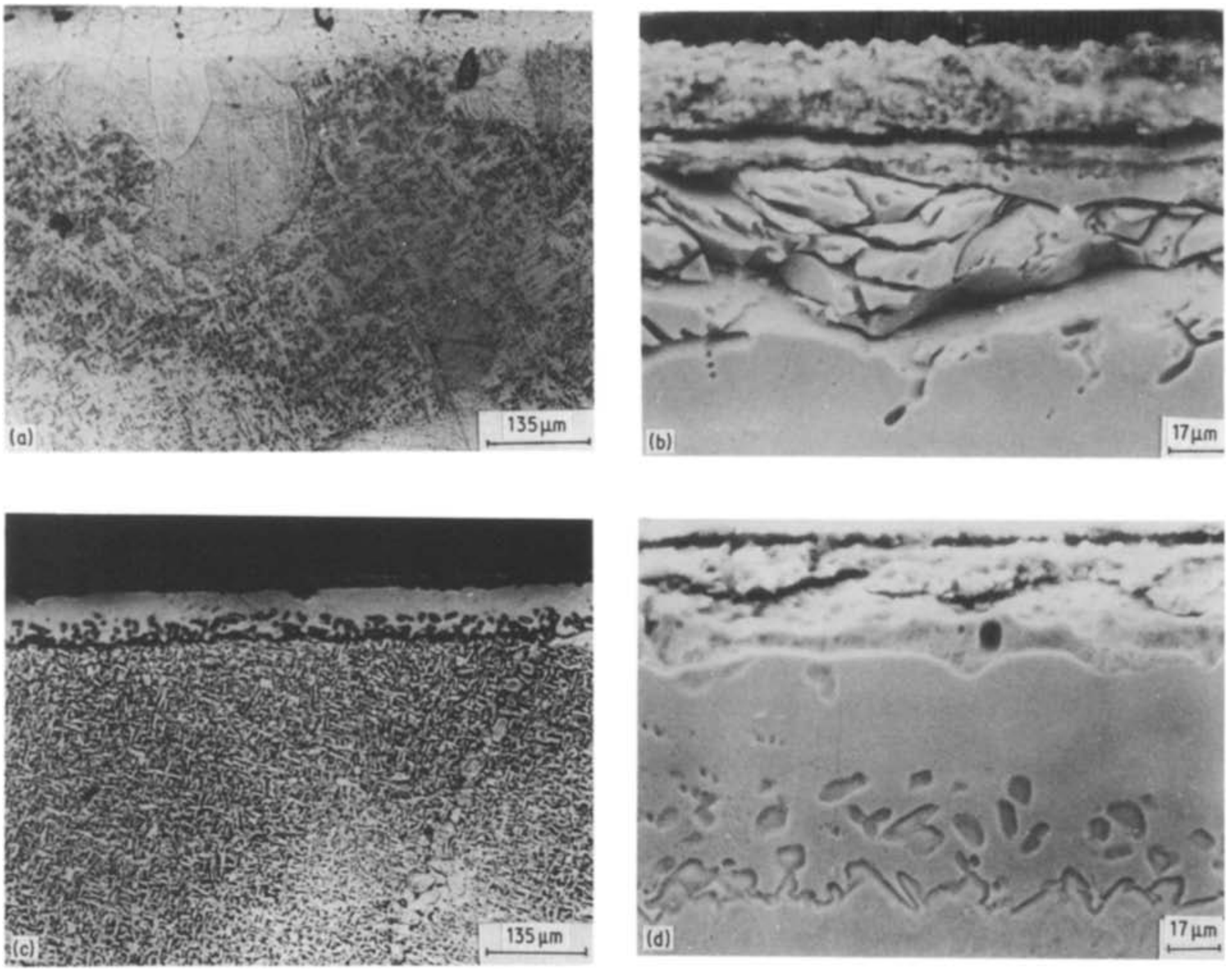

Figure 5 Optical and SEM cross-sections of uncoated (a, b) and coated (c, d) Ti–14Al–24Nb alloy after oxidation at 1000° C.

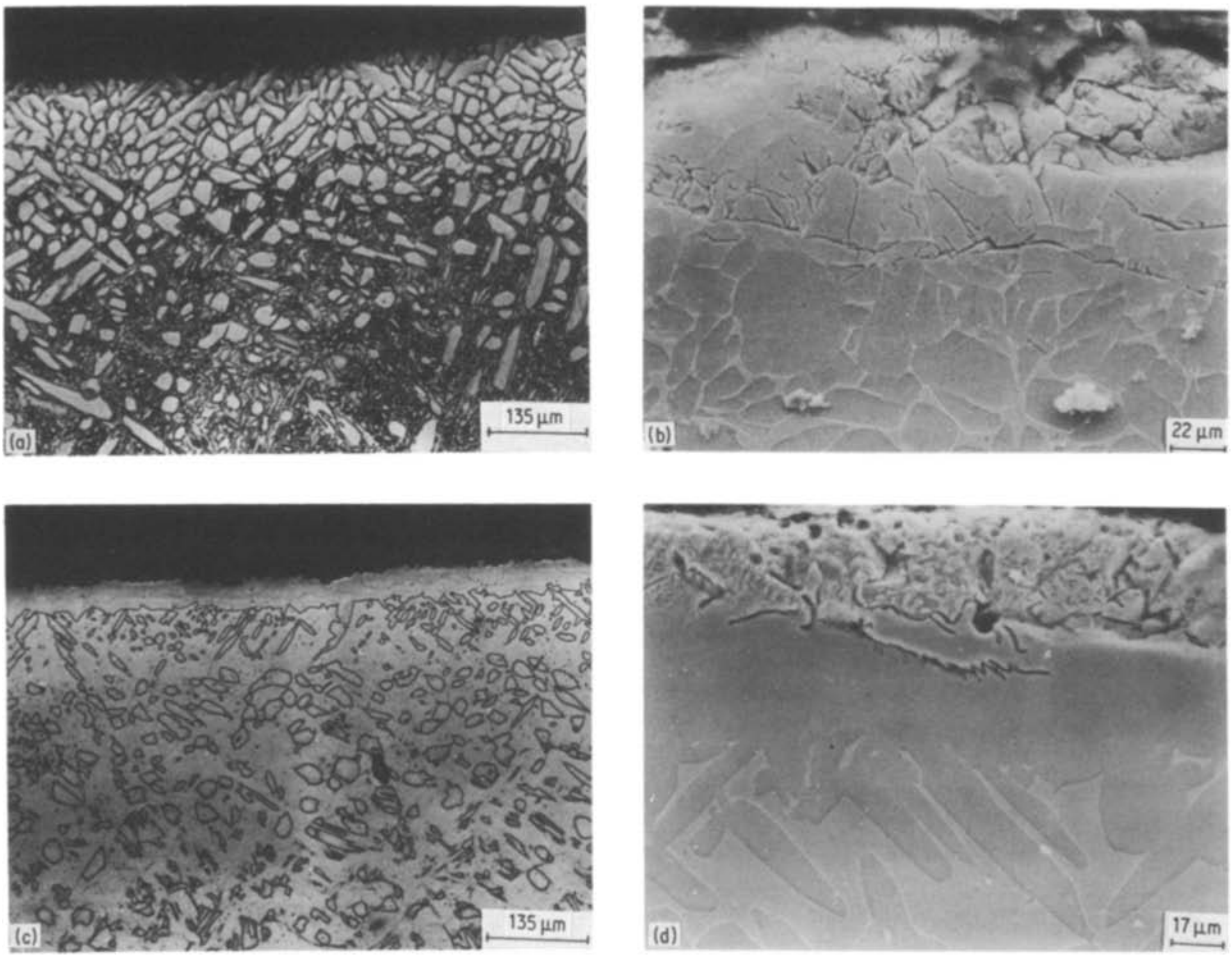

Figure 6 Optical and SEM cross-sections of uncoated (a, b) and coated (c, d) Ti-14Al-24Nb alloy after oxidation at 1100° C.

for the uncoated sample (Fig. 5), the oxide layer exhibits a layered structure. The coated sample is also seen to have an oxide layer with cracking on the top layers. As the X-ray penetrates deeper into the surface, the results of both X-ray and SEM should be viewed together to draw the final conclusions. It should also be kept in mind that a certain amount of cracking in the oxide layers can be produced during metallographic preparation. From the above discussion it can be concluded that (1) the coated samples contain thin oxide layers with minor quantities of Al_2O_3 and TiO_2, and (2) uncoated samples develop thicker oxide layers (or spalling at 1100° C) with major quantities of TiO_2 and minor quantities of Al_2O_3 and Nb_2O_5.

4. Conclusion

Aluminizing of a Ti–14Al–24Nb alloy produces a $TiAl_3$ layer on the surface. This layer contains a reduced amount of niobium compared to the matrix. Cyclic oxidation experiments at 1000 and 1100° C proved that this coating improves the oxidation resistance of the alloy. This conclusion is further supported by the phase content and microstructure of the oxidized sample. This alloy (Ti–14Al–24Nb) with an aluminide coating can withstand much higher temperatures compared to the creep limit of 815° C, for Ti_3Al (Table I).

Acknowledgements

The author thanks Mrs J. Annapurna for her help in the experimental work, Mr A. K. Gogia for supplying the aluminide samples and useful discussions, and the X-ray diffraction, Metallography and SEM groups for their help. He is also grateful to Dr P. Rama Rao, Director, Defence Metallurgical Research Laboratory, Hyderabad for his constant encouragement and permission to publish this work.

TABLE II Phase analysis of the surface after oxidation

Sample designation	Oxidation temp. (° C)	Phases formed	
		Major	Minor
Upcoated alloy sample	1000	TiO_2	Al_2O_3
Uncoated alloy sample	1100	TiO_2	Al_2O_3, Nb_2O_5
Uncoated alloy spall	1100	TiO_2	Nb_2O_5
Aluminized alloy	1000	TiAl, $TiAl_3$	Al_2O_3
Aluminized alloy	1100	TiAl	TiO_2, Al_2O_3 $TiAl_3$

References

1. J. HOLWACH and T. K. REDDEN, "Ti/Al Design/Cost Trade-off analysis", AFAPL-TR-78-74 (General Electric Co., Cincinnati, Ohio, 1978).
2. H. A. LIPSITT, Titanium aluminides – an overview, in "High temperature ordered intermetallic alloys", MRS symposia proceedings, edited by C. C. Koch, C. T. Liu and N. S. Stoloff (Materials Research Society Pittsburgh, 1985) pp. 351–64.
3. N. S. CHOWDARY, H. C. GRAHAM and J. W. HINZE, "Oxidation behaviour of Titanium aluminides", in Proceedings of the Symposium on "Properties of high temperature alloys" (Electrochemical Society Princeton, New Jersey, 1977) pp. 668–80.
4. M. G. MENDIRATTA and N. S. CHOWDARY, "Properties and Microstructure of High Temperature Materials", Technical Report, AFML-TR-78-112 (Systems Research Laboratories Inc., Dayton, Ohio, 1978) pp. 47–59.
5. J. SUBRAHMANYAM and J. ANNAPURNA, *Oxid. Metals* **26** (1986) 275.
6. J. SUBRAHMANYAM, Patent applied.
7. C. A. BARRETT and C. E. LOWELL, *J. Test. Eval.* **10**(6) (1982) 273.

Received 7 July
and accepted 9 October 1987