

## Oxidation of titanium aluminides produced by laser surface alloying

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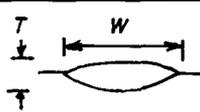
One of the limitations of current high-temperature titanium alloys of the near- $\alpha$  type is the poor oxidation resistance at temperatures above about 600 °C. However, titanium–aluminium alloys in the composition range where the aluminides  $Ti_3Al$  ( $\alpha_2$ ) and  $TiAl$  ( $\gamma$ ) form show better oxidation resistance, particularly in the case of  $TiAl$ . The results reported here form part of an investigation of the formation of titanium aluminide layers on a titanium substrate, as an approach to improving oxidation resistance and erosion resistance. Laser alloying, involving feeding aluminium powder into a laser-generated melt pool at various rates, has been used to produce layers with aluminium contents ranging from about 20 to 80 at% [1]. Details of the constitution and fine-scale microstructural features of the layers resulting from their rapid solidification have been reported elsewhere [2–4]. In the present work exploratory oxidation tests were made of three alloyed layers, namely Ti–30 at% Al, Ti–43 at% Al and Ti–55 at% Al, including compositional and microstructural analysis.

A 2 kW c.w.  $CO_2$  laser was used to produce the aluminide-containing regions as single tracks on commercial purity titanium (IMI-125 Grade 2). Table I shows schematic shapes, dimensions and the structures of these alloyed zones, which were obtained by varying the powder flow rates while maintaining other parameters constant (i.e. power, beam diameter and speed). Compositional analysis at several locations in the alloyed zone showed reasonable homogeneity with scatter within  $\pm 1$  at% Al. The oxygen content of two of the alloyed zones was measured and an average value of approximately 0.6 at% was found. The surfaces of these layers showed a rippling effect of the type previously reported [5], the ripple spacing being about 10  $\mu m$ . More details of the experimental arrangements and laser processing parameters can be found elsewhere [1].

The sample, which contained the three alloyed layers, was heated in an electric furnace in air at a temperature of 1050 °C for periods of 24 and 96 h, respectively, and was air-cooled to room temperature. A transverse section of the laser-alloyed zones was cut and standard methods of metallography were used, which include grinding, polishing and etching for examination of the oxide layers. Scanning electron microscopy–energy-dispersive X-ray analysis (SEM–EDX) was used to determine the titanium and aluminium contents; the program used was LINK software designed for elemental analysis with a ZAF correction. The oxygen content was not analysed but was calculated by subtracting the total of Ti and Al from 100%. The oxide layer, which formed on the commercial purity Ti substrate exposed for 24 h at 1050 °C, was thick (about 100  $\mu m$ ), porous and tended to flake off or spall from the substrate. In contrast, the oxide layers on the alloyed zones were thin and had a good adherence; some slight loss of oxide may occur during sample preparation. X-ray diffraction analysis of the oxide on the commercial purity Ti showed several peaks indexed as  $TiO_2$ .

Fig. 1a shows an SEM micrograph of the surface of the Ti–30 at% Al alloy exposed for 24 h at 1050 °C. Two distinct layers were observed: an external porous layer 50  $\mu m$  thick and an intermediate layer between the external oxide layer and the alloyed zone (Fig. 1a). SEM examination showed that the external layer contained porosity (Fig. 1b). EDX analysis showed that this layer consisted predominantly of oxygen (61 at%), and the aluminium and titanium contents were 19 and 20 at%, respectively; the composition of this layer was nearly constant at different locations, with scatter within  $\pm 1$  at%. The intermediate oxide layer, as observed by SEM using backscattered electron imaging (BSI), showed a duplex lamellar-type structure with average spacing of about 2  $\mu m$ , formed to a depth of

TABLE I The alloyed layers used in the present work (1.8 kW, 3 mm and 7 mm  $s^{-1}$ )

Alloy (at%)	Powder flow rate ( $g s^{-1}$ )	Shape	Microstructure	
			$W \times T$ (mm)	At room temperature      At 1050 °C
Ti–30Al	0.06		$1.93 \times 0.4$	$\alpha_2$ $\alpha_2$
Ti–43Al	0.07		$2.0 \times 0.40$	$\alpha_2 + \gamma$ $\alpha_2 + \gamma$
Ti–55Al	0.08		$2.13 \times 0.5$	$\alpha_2 + \gamma$ $\gamma$

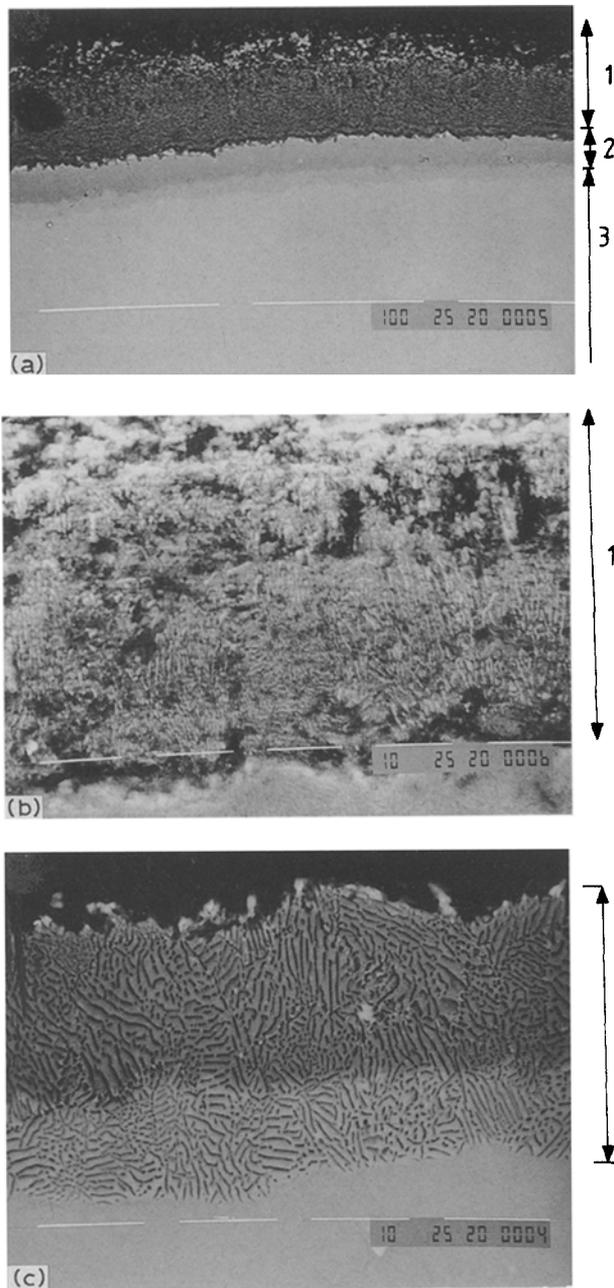


Figure 1 Ti-30 at% Al alloyed zone. SEM-BSI micrographs showing: (a) external oxide layer (1), intermediate oxide layer (2) and alloyed zone (3), (b) external layer (1) at high magnification and (c) intermediate oxide layer (2) at high magnification.

30  $\mu\text{m}$  (Fig. 1c), and there was a change in contrast in the lower part of the intermediate layer. SEM-EDX analysis across the intermediate layer showed a progressive decrease in the oxygen content from about 60 at% to zero; correspondingly the titanium increased from a value characteristic of the external layer to the value in the substrate; the aluminium content increased from 14 at% in the top of the intermediate layer to a value of 27 at% in the lower part of the intermediate layer (Fig. 2). Further work is needed to elucidate the nature of this layer, but it is possible that it consists of a mixture of  $\text{Ti}_3\text{Al}$  with a dispersion of titanium-rich oxide. Data from the literature [7] for a similar atmosphere indicate that an aluminium-rich oxide is not favoured at this range of aluminium content and temperature.

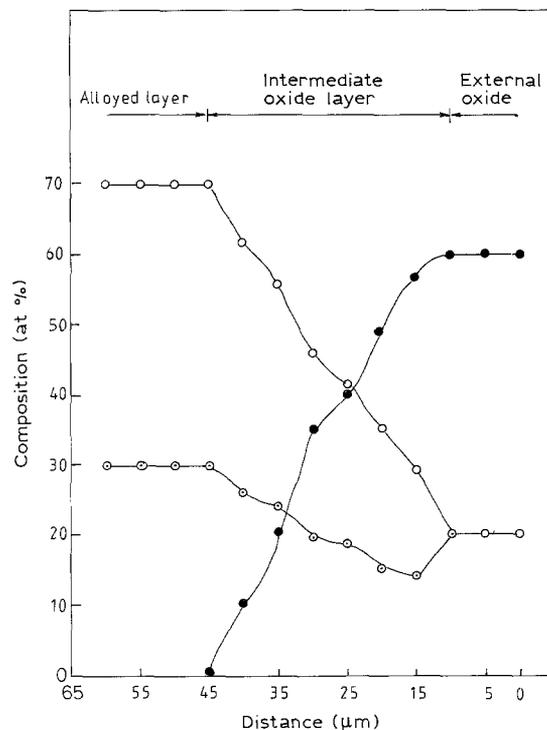


Figure 2 Variation of the (○) Ti, (⊙) Al and (●) O across the external oxide, the intermediate oxide layer and the alloyed zone.

Fig. 3 shows an SEM-BSI micrograph of the laser surface alloyed Ti-43 at% Al layer exposed for 24 h at 1050  $^{\circ}\text{C}$ . An external porous oxide layer and an intermediate oxide layer were observed. EDX analysis of the external oxide layer showed that it consisted of titanium, aluminium and oxygen at a nearly uniform composition of about 35, 25 and 40 at%, respectively. The intermediate oxide layer had a thickness of 20  $\mu\text{m}$  consisting of grains

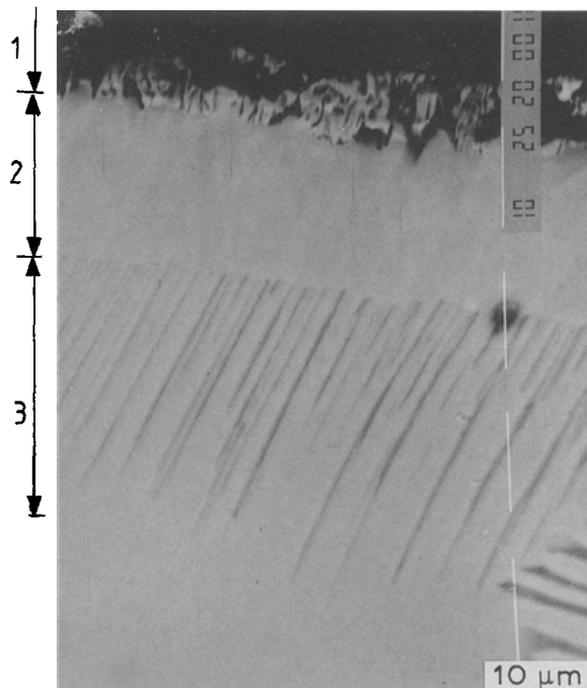


Figure 3 Ti-43 at% Al alloyed zone. SEM-BSI micrograph showing (1) external oxide, (2) intermediate layer and (3) aluminium-depleted region of alloyed zone.

oriented perpendicular to the surface of the alloyed zone. This layer showed a composition of about 32 at% Ti, 48 at% Al and 20 at% O. Also, there was a region of the alloyed layer below the intermediate oxide layer which showed a lamellar structure. EDX analysis showed that the dark plates had a composition of about 45 at% Ti, 20 at% Al and 35 at% O, whereas the composition of the light plates was about 63.5 at% Ti and 36.5 at% Al. The average Al content of this zone was less than the nominal composition of the alloyed layer (i.e. 43 at% Al). The Ti-55 at% Al alloy after exposure for 24 h at 1050 °C showed a thin porous external oxide layer about 15  $\mu\text{m}$  thick and an intermediate oxide layer of the same thickness which appeared by SEM using BSI as a grey region located between the external scale and the alloyed zone (Fig. 4). EDX analysis showed that the composition of the intermediate layer was nearly constant with a composition of about 32 at% Ti, 58 at% Al and 10 at% O, whereas the composition of the base alloyed layer below the intermediate layer was about 51 at% Al, i.e. less than the nominal composition of the alloyed layer (55 at% Al).

The sample held for 96 h at 1050 °C showed an increase in the extent of the external oxide layer with increasing exposure time (Table II). The external scale thickness of the Ti-55 at% Al alloyed layer was smaller by a factor of about 10 than in the Ti-30 at% Al alloyed layer, and smaller by a factor of 2 than in the Ti-43 at% alloyed layer (Table II).

The literature shows that the oxidation behaviour of titanium-aluminium alloys is complex; the oxidation rates and the nature of the oxidation products are sensitive to a number of parameters, including temperature, time and substrate composition. The present results are concerned only with composition

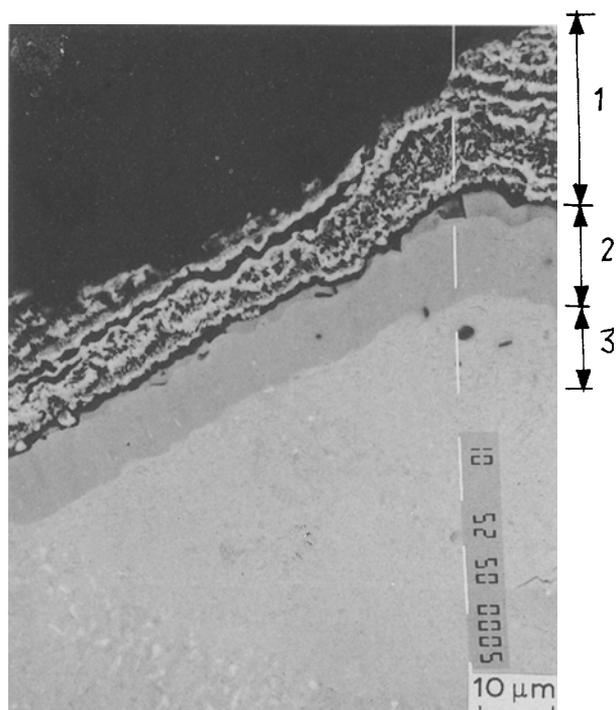


Figure 4 Ti-55 at% Al alloyed zone. SEM-BSI micrograph showing (1) the external oxide, (2) intermediate oxide layer and (3) aluminium-depleted region of alloyed zone.

TABLE II External oxide scale formed on commercial purity Ti and Ti-Al alloyed layers exposed at 1050 °C for 24 h

Exposure time (h)	External oxide scale thickness ( $\mu\text{m}$ ) <sup>a</sup>			
	Ti	Ti-30 at% Al	Ti-43 at% Al	Ti-55 at% Al
24	100	50	8-10	2-5
96	550	100	20	10

<sup>a</sup>Measurements exclude any oxide lost by spalling.

as a variable for oxidation at 1050 °C in air. They show, in agreement with the literature, that multiple oxide layers form, and the rate of formation of the external layer decreases with increasing aluminium content. For example, Kahveci *et al.* [6] found, during oxidation testing of Ti-25 at% Al, Ti-43 at% Al and Ti-50 at% Al alloys for 24 h at 1100 °C, that the external oxide scales on the Ti-25 at% Al alloy were 4.5 times thicker than on the Ti-50 at% Al alloy, whereas the oxide scales formed on the Ti-43 at% Al alloy were similar to those on the Ti-25 at% Al alloy.

Although external oxide layers and an intermediate layer have been observed by Lee and Waldman [8] and Choudhury *et al.* [9] during oxidation testing of titanium-aluminides, the composition and the nature of the external oxides were different from in the present results. Lee and Waldman [8] found a mixture of  $\text{TiO}_2$  and  $\text{Al}_2\text{O}_3$  in the inner region of the external oxide layer and a mixture of  $\text{TiO}_2$  and  $\text{Al}_2\text{O}_3$  in the outer region, during oxidation testing of the Ti-47 at% Al alloy at temperatures ranging from 400 to 1500 °C for periods of 4-40 h. Choudhury *et al.* [9] found only  $\text{TiO}_2$  in the outer region of the external layer and a mixture of  $\text{TiO}_2$  and  $\text{Al}_2\text{O}_3$  in the inner region. In the present work no division of the external layer into inner and outer regions was clearly detected; possibly some loss of the outer region of the external oxide occurred during handling of the sample. Lee and Waldman [8] found an intermediate oxide layer (designated by them as an "interfacial zone") between the external oxide layer and the substrate; the microstructure was similar to that in the present work on the Ti-43 at% Al alloyed zone but the proportions of titanium and aluminium were different. In the present work on the Ti-43 at% Al alloyed layer a slight depletion of aluminium was observed in the lamellar structure below the intermediate layer (Fig. 3); the structure is interpreted as consisting of  $\alpha_2$  + an oxide-containing aluminium and titanium and was not reported by Lee and Waldman. A similar effect was observed in the Ti-55 at% Al alloy, but the structure in the aluminium-depleted region was not lamellar and is interpreted as single-phase  $\gamma$ . It is proposed that outwards diffusion of aluminium from these regions is the cause of the higher aluminium content in the intermediate layers.

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## References

1. J. H. ABBOUD and D. R. F. WEST, *Mater. Sci. Technol.* **7** (1990) 353.
2. *Idem*, *J. Mater. Sci. Lett.* **9** (1990) 308.
3. *Idem*, *Mater. Sci. Technol.* **7** (1991) 827.
4. *Idem*, *J. Mater. Sci.* in press.
5. T. CHANDE and J. MAZUMDER, *Appl. Phys. Lett.* **41** (1982) 42.
6. A. I. KAHVECI, G. WELSCH and G. E. WASIELEWSKI, in Sixth World Conference on Titanium, edited by P. Lacombe and R. Tricot, Cannes, 6–9 June 1988 (Société Française de Metallurgie) p. 1015.
7. R. A. PERKINS and K. T. CHIAN, *Scripta Metall.* **21** (1987) 1505.
8. E. U. LEE and J. WALDMAN, *ibid.* **22** (1988) 1389.
9. N. S. CHOUDHURY, H. C. GRAHAM and J. W. HINZE, in Proceedings of the Conference on "Properties of High Temperature Alloys", edited by F. S. Pettit, March 1977 (Electrochemical Society Princeton, NJ, 1977).

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