High-temperature oxidation resistance improvement of titanium using laser surface alloying

M. LI, A. KAR*, V. DESAI
*Mechanical and Aerospace Engineering Department, *and also Center for Research and Education in Optics and Lasers, University of Central Florida, Orlando, FL, USA*

A. KHANNA
Corrosion Science and Engineering, Indian Institute of Technology, Bombay, India

Commercially pure titanium substrate was coated with aluminium by flame spraying or arc spraying techniques and was irradiated with a laser to form a laser-alloyed zone (LAZ). The microstructure of the LAZ was investigated. High-temperature oxidation tests were carried out in air at different high temperatures and the characteristics of the oxide layer were investigated using Auger electron spectroscopy. The aqueous corrosion tests were carried out in 3.5% NaCl solution at room temperature. The laser-processed material showed considerable improvement in the high-temperature oxidation-resistant property while the aqueous corrosion-resistant property of the LAZ was found to remain almost unaffected.

1. Introduction

In the realm of materials processing, surface treatment or surface modification is carried out extensively to improve the oxidation, corrosion and wear-resistant properties of a material by altering the metallurgical structure and chemistry of the surface. There are many available techniques for surface modification, namely electroplating, diffusion, plasma spraying, chemical vapour deposition (CVD), physical vapour deposition (PVD), laser and electron-beam irradiation and ion implantation. The surface properties of materials, which control processes such as corrosion, high-temperature oxidation, wear and even fatigue, can be modified by these techniques. However, the laser surface treatment has several advantages because of its ability to produce a fine-grained structure, amorphous and metastable phases, low porosity, relatively smooth surface, lower heat-affected zone in the substrate, and good bonding between the LAZ and the substrate. Laser surface alloying (LSA) is one of the laser materials processing techniques. In LSA, the desired alloying elements are pre-coated, pre-placed or continuously fed to a substrate material while a laser beam scans the surface. At the irradiated region, the alloying elements and a small portion of the substrate melt almost instantaneously and mix together. The molten material solidifies rapidly behind the scanning laser beam to produce non-equilibrium alloys. The cooling rate is usually about 10^3 K s^{-1}. This high cooling rate inhibits the segregation of the supersaturated elements from the matrix during cooling. Thus a highly non-equilibrium alloy composition can be achieved at the substrate surface for a low

solid-solubility system using the LSA technique. The non-equilibrium structure thus produced has several unique and often useful properties, not found when the alloys are in a regular crystalline state [1]. A desired surface composition and microstructure can be prepared by LSA from relatively inexpensive elemental components, which have good mechanical properties, required for bulk materials.

Titanium, a potential base for refractory alloys, is particularly suitable for aerospace applications, mainly due to its low density and high strength. It easily forms a protective oxide film in a water or moisture environment, thereby making it an important metal for oil, chemical and marine applications. However, above 623 K, more oxygen is absorbed and the oxide layer becomes brittle. Alloying improves the strength as well as increasing the operating temperature limit to about 823 K, beyond which the oxidation rate increases rapidly [2]. In order to increase the operating temperature even further, an alternate approach would be to produce a casing impermeable to oxygen.

Intermetallic titanium aluminides are being considered for high-temperature applications, because of their good strength-to-weight ratio even at elevated temperatures. The intermetallic compounds Ti_3Al, TiAl, and $TiAl_3$ are the most typical titanium aluminides. At high temperatures, these compounds are oxidized to form TiO_2, Al_2O_3, or $TiAlO_5$ [3–5]. Among these three oxides, Al_2O_3 forms a dense scale and can withstand very high temperatures. TiO_2 formed on the surface is stable at very high temperatures but the scale is much more porous than the Al_2O_3 scale. Oxygen can penetrate into the internal layer through

the TiO_2 scale and therefore oxidation would continue at a relatively high rate if the surface is covered only with TiO_2. Among the different intermetallic compounds, Ti_3Al, which has higher titanium composition, has higher hardness and good wear resistance. At high temperatures, the TiO_2 scale forms first and then the Al_2O_3. Because there is insufficient aluminium to form a dense protective oxide scale, the porous Al_2O_3 allows titanium to diffuse outward through the Al_2O_3 scale, and as a result, TiO_2 scale forms at the external oxide layer. However, the TiO_2 scale is not a good barrier to oxygen diffusion, and therefore the oxidation process would continue at a relatively high rate. On the other hand, the aluminium-rich compound $TiAl_3$ can form a protective Al_2O_3 scale, due to the presence of a sufficient amount of aluminium. After the Al_2O_3 scale forms, the diffusion of oxygen drops rapidly and the oxidation rate would be very small. For this reason, $TiAl_3$ has better oxidation resistance than Ti_3Al. However, the wear resistance of $TiAl_3$ is lower than that of Ti_3Al due to the lower titanium content in $TiAl_3$. On the other hand, TiAl has higher wear resistance but lower oxidation resistance than $TiAl_3$. $TiAl_3$ is considered to be the best choice for high-temperature applications among these three compounds.

By using the laser surface alloying technique, an alloy of $TiAl_3$ can be produced on the substrate surface by controlling the laser processing parameters. To carry out laser surface alloying at the aluminium-coated titanium substrate surface, the aluminium coating on the substrate can be furnished by flame spraying aluminium powder. The coating thickness is chosen to be proportional to the thickness of the layer that needs to be alloyed. In order to reduce the aluminium evaporation during the laser irradiation, one could reduce the laser intensity or coat the substrate with multiple layers of titanium and aluminium alternately, especially with a titanium layer on the top, because titanium has a higher evaporation temperature. Because the laser surface alloying is a very rapid process, the frequency of the laser pulse should be sufficiently high to maintain the continuity of laser irradiation. Compared with a pulsed laser, the continuous wave (CW) CO_2 laser is usually preferred for surface alloying.

2. Background

Reducing the consumption of scarce and expensive elements such as chromium, nickel and molybdenum by surface alloying rather than bulk alloying in the steel and superalloy industries is attracting much attention. The cost consideration demands reduction in precious-metal usage in the electronics, decorative, photographic, and chemical-processing industries. The earliest attempt to use the LSA technique dates back to 1964 [6]. With improvement in the quality of different laser systems, more work has been done on LSA to improve the corrosion, oxidation, and wear resistance of materials.

Abboud and West [7-10], produced a series of Ti-Al alloyed layers containing from 17-80 at % Al

using a 2 kW CW CO_2 laser and a powder feed technique. After examining the effects of the laser parameters on the alloyed layers, they selected 1.8 kW laser power, 3 mm beam diameter, and 7 mm s^{-1} relative beam scanning speed as the laser processing parameters. The compositional analysis by energy dispersive spectroscopy EDX of some alloyed layers showed a reasonable degree of homogeneity. Diffusion of aluminium into the unmelted substrate was not observed. The microstructural study of the laser-alloyed Ti-Al layer showed that the microstructure of the alloyed layer containing up to 36 at % Al was basically martensite such as the disordered lath martensite, α', in 17 at % Al alloy, ordered massive and acicular martensite in 23 at % Al alloy; and ordered massive, acicular, and lath martensite in both 30 and 36 at % Al alloys. It was found that the increase in the proportion of massive martensite with increasing aluminium content is consistent with an increase in the martensite transformation starting temperature, M_s. For the aluminium content above 43 at %, no martensite was observed. The phases for the compositions of 43-80 at % Al were dendrites of $\alpha_2 + \gamma$ in the Ti-43 at % Al alloy, dendrites of either α_2 or $\alpha_2 + \gamma$ and interdendritic regions of γ in the Ti-50 at % Al alloy, dendrites of $\alpha_2 + \gamma$ and interdendritic γ in the Ti-55 at % Al alloy, single-phase γ in the Ti-60 at % Al alloy, and $TiAl_3$ dendrites and aluminium solid solution in the interdendritic regions in the Ti-80 at % Al alloy. The microstructures of the Ti-50 at % Al and Ti-55 at % Al alloys are consistent with the occurrence of the peritectic reaction $L + \beta \rightarrow \alpha$ and $L + \alpha \rightarrow \gamma$ and not the reaction $L + \beta \rightarrow \gamma$ Owing to large undercooling during LSA, the solid-state transformations were completely suppressed and the crystal growth was found to be limited by the collisional frequency of the atoms at the growing interface.

Hirose et al. [4] studied the wear and oxidation properties of titanium aluminides formed on a titanium surface by laser alloying. The titanium aluminides were formed on a commercially pure titanium substrate by laser alloying using a precoated aluminium layer for various laser operating parameters. The phases formed in the alloyed layers were found to change as the penetration ratio, P, was increased in the following manner

$$Al + TiAl_3 \rightarrow (Al) + TiAl_3 \rightarrow (TiAl_3) + TiAl \rightarrow (TiAl)$$

$$+ TiAl_3 \rightarrow TiAl_3 \tag{1}$$
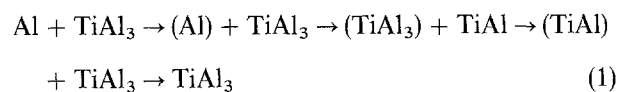
where the phases within the parentheses are the minor phases and $P = S_s/(S_s + S_d) \times 100$, where P is the penetration ratio (%), S_s the cross-sectional area of the melted substrate and S_d the cross-sectional area of the deposited layer. The average hardness of the alloyed layers increased with the titanium content up to about 40%, after which it saturated to a value of 500-600 H_v in Ti_3Al-dominant layers. The alloyed layers had a higher adhesive wear resistance than that of the commercially pure titanium. The oxidation tests, carried out at 1273 K in dry air flow, showed that the alloyed layers had a significantly higher oxidation resistance than that of the commercially pure

titanium. The $(TiAl_3)$ + TiAl layer had the highest oxidation resistance among the alloyed layers.

A recent study [5] concerning the oxidation behaviour of two-phase (Ti_3Al and TiAl) intermetallic compound, Ti–42 at % Al, in air at 1073 and 1273 K has shown that the oxidation at 1273 K is much faster than that at 1073 K. However, the oxidation kinetics are similar, and follow the parabolic law. During heating, TiO_2 scale forms initially on the surface at about 973 K, and then Al_2O_3 scale forms at 1273 K. For isothermal heating, TiO_2 scale grows slowly and Al_2O_3 does not appear up to about 1073 K, while at 1273 K both TiO_2 and Al_2O_3 scales grow rapidly. The outer scale consists of TiO_2 and the inner one consists of a mixture of TiO_2 and Al_2O_3. It was also observed that the amount of Al_2O_3 increased at an area adjacent to the oxide–compound interface.

Figure 1 Optical micrograph of a cross-section of the alloyed layer produced at a power of 11 J/pulse.

3. Experimental procedure

For the present study, commercially pure titanium metal (having trace amounts of iron, chromium and aluminium) was coated with aluminium (99.95% pure) using oxy-acetylene flame and arc spraying techniques. For convenience, specimens are designated as FT1, FT2, AT2, LT1, and LT3, where "F" refers to the flame-sprayed specimens, "A" the arc-sprayed specimens and "L" the laser-treated specimens that were coated using the flame spraying technique prior to laser treatment. Numbers 1, 2 and 3 refer, respectively, to 100, 200, and 300 μm thick aluminium coating deposited on the specimens. An Nd: YAG pulsed laser with 300 W power was used to carry out the laser treatment. The pulse width of 15 ms, beam diameter of 2 mm and scanning speed of $1.5\ mm\,s^{-1}$ were kept constant in all the laser treatments of this study. Laser surface alloying was carried out in a specially designed chamber where a constant flow of argon gas provided as a protective atmosphere.

The alloyed layers were sectioned transversely and prepared by grinding, polishing with alumina, and etching for metallographic studies, compositional analysis, and hardness measurement. Pure titanium, aluminium-coated titanium and the laser-treated specimens were subjected to high-temperature oxidation by exposing the specimens in dry air at 873 and 973 K for about 250 h. Anodic potentiodynamic polarization tests were carried out in 3.5% NaCl solution to compare the aqueous corrosion resistance of pure titanium, pure aluminium, and surface-alloyed specimens. After the oxidation tests, the phases in the oxide layers were determined by X-ray diffraction, and the compositions were analysed using Auger electron spectroscopy.

4. Results and discussion
4.1. Characterization of laser-treated specimens

Fig. 1 shows an optical micrograph of a cross-section of the alloyed layer produced at a power of 11 J per pulse. The microstructure within the alloyed layer is very fine and there is hardly any evidence of porosity
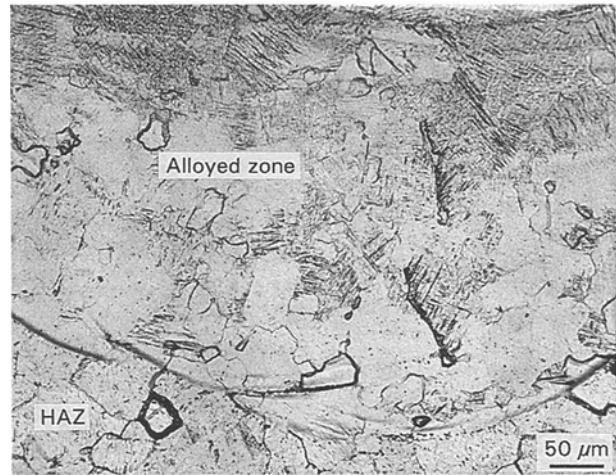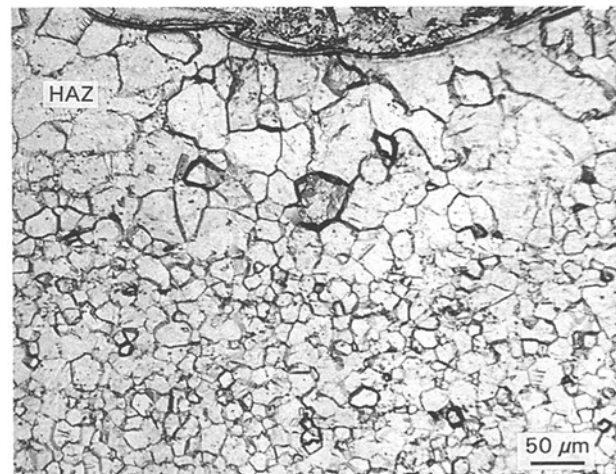

Figure 2 Microstructures of the laser-alloyed layers and the heat-affected zones.

within the alloyed layer. Because the strength of a material increases as the grain size decreases, the strength of the laser-alloyed layer is expected to be enhanced due to the fine microstructure. Fig. 2 shows that the microstructure is changed within the alloyed layer as well as in the heat-affected zone (HAZ) due to laser processing, which implies that the strength of the HAZ can be affected considerably although a narrow HAZ is produced during LSA.

The composition of the alloy formed at the substrate surface and the depth of the alloyed zone are related to the material properties in a complex manner. Because the thermo-physical properties, such as the low melting and boiling temperatures and high vapour pressure of aluminium are not favourable for laser irradiation, it was also difficult to obtain the desired composition of the alloy by using a pure aluminium coating. Many trial runs were carried out for various coating thicknesses and laser pulse energies. Fig. 3 shows the distribution of aluminium in the titanium matrix starting from the free surface for 100 μm thick coated specimens at 7 and 14 J per pulse energies. The aluminium distribution is very uniform
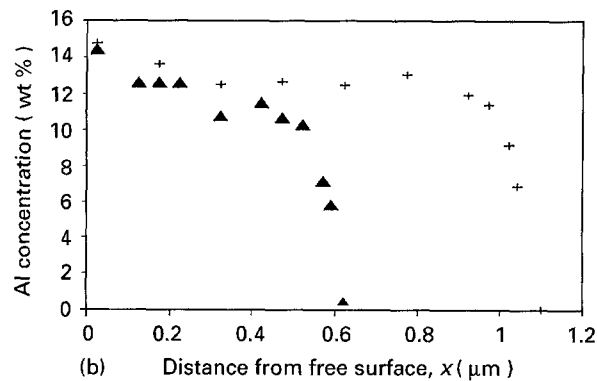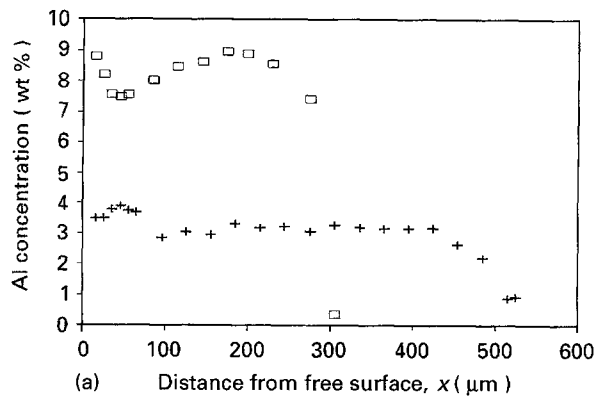
Figure 3 EDX depth profile of aluminium content within the laser-alloyed layer with (a) 100 μm Al pre-coat, (+) 14 J/pulse, (□) 7 J/pulse, and (b) (▲) 200 and (+) 450 μm Al pre-coat, at 16 and 15 J/pulse, respectively.

Figure 4 Microhardness measurements within and outside the laser surface alloyed layer (A,H_v368; B,H_v392; C,H_v380; D,H_v412; E,H_v184; F,H_v161; G,H_v143).

Figure 5 Weight gain versus oxidation time for pure titanium, aluminium-coated titanium, and laser surface alloyed layers in air at 873 K. (✗) LT3, (▲) LT1, (✕) LT2, (□) FT3, (×) FT1, (∇) FT2, (■) Ti.

throughout the entire alloyed layer. Because only a small portion of the substrate was melted and mixed with aluminium coating at low pulse energy, the aluminium concentration within the alloyed layers is much higher than that at the high pulse energy. At the high pulse energies, more of the substrate is melted and some aluminium is vapourized. The locations of Vickers microhardness measurements (load = 98 mN) in the laser-melted zone (A, B, C, D) and the substrate (E, F, G) are shown in Fig. 4. The results indicate that the laser-melted zone is much harder (Vickers microhardness H_v = 390) compared to the titanium substrate (H_v = 160).

4.2. Oxidation resistance of the alloyed layers

Weight gain versus time plots for the oxidation of bare titanium substrate, aluminium-coated titanium and laser-treated Al/Ti specimens are shown in Figs 5 and 6. The oxidation tests were run in air at 873 and 973 K for about 250 h. It can be seen from these two figures that the oxidation rate of titanium metal decreases as a result of aluminium coating alone without any laser treatment and that the rate of oxidation does not vary significantly with the coating thickness. A slight increase in oxidation rate at a coating thickness in excess of 100 μm could be due to higher porosity. Figs 5 and 6 show that laser treatment further reduces the oxidation rate which ensures better oxidation-

resistant property of the laser-treated surface alloy. The enhancement of the oxidation resistance could be due to better substrate–coating bonding, fine microstructure of the alloyed zone and the formation of TiAl or Ti₃Al intermetallics.

The oxides formed during the oxidation tests were found to be mainly alumina at 873 K and TiO₂ and alumina at 973 K test temperatures. A list of the products formed in the oxidized and laser-treated unoxidized samples is given in Table I as identified by X-ray diffraction. The Auger electron spectroscopy depth profile is shown in Fig. 7 to indicate that the oxygen diffusion through the alloyed layer is about 0.5 μm.
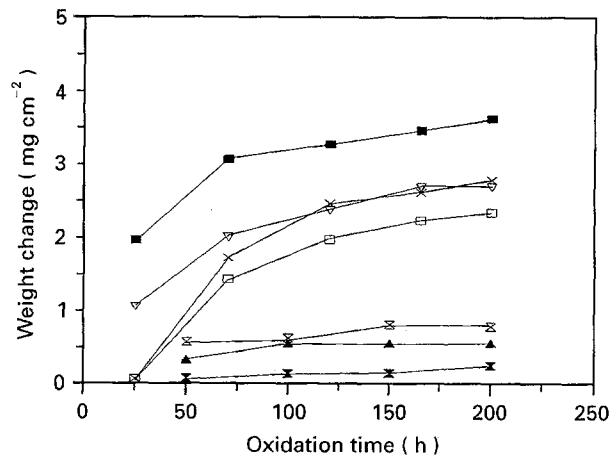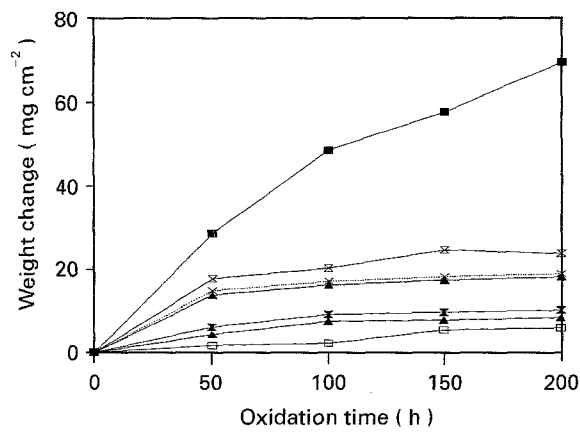
Figure 6 Weight gain versus oxidation time for pure titanium, aluminium-coated titanium, and laser surface alloyed layers in air at 973 K. (□) LT2, (▲) LT3, (⊠) LT1, (▲) AT1, (×) FT3, (⊠) FT2, (■) Ti.

TABLE I Types of phases detected on the surface of the various samples after oxidation tests

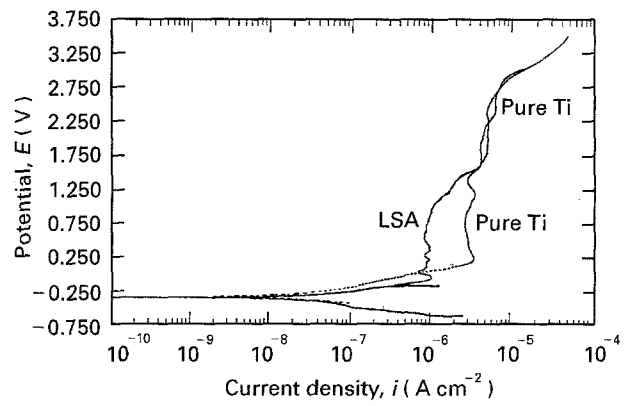| Samples	Oxidation condition	Types of phases observed
LT1	Unoxidized	Ti, TiAl
LT3		Al
Pure Ti	Oxidation at 873 K	TiO_2
FT1		$TiAl_3$, α-Al_2O_3
FT3		TiAl, α-Al_2O_3
LT1		TiAl, $TiAl_3$, α-Al_2O_3
LT3		Al, α-Al_2O_3
Pure Ti	Oxidation at 973 K	TiO_2
FT4		TiAl, αAl_2O_3
AT1		TiAl, α-Al_2O_3
LT1		TiO_2, α-Al_2O_3
LT3		TiAl, α-Al_2O_3

Figure 8 Anodic potentiodynamic polarization curves of pure titanium and the laser-alloyed layer.

4.3. Aqueous corrosion resistance of the alloyed layers

The oxidation-resistant property is considered to be the most important quality for high-temperature applications. However, the poor aqueous corrosion resistance of some of the components may cause the whole system to fail, and therefore the aqueous corrosion resistance should also be considered as one of the important properties. Fig. 8 shows that the corrosion behaviour of the laser-alloyed layers is similar to that of pure titanium in this study, which means that laser surface alloying of pure titanium with aluminium does not induce considerable degradation of the corrosion-resistant property of the surface.
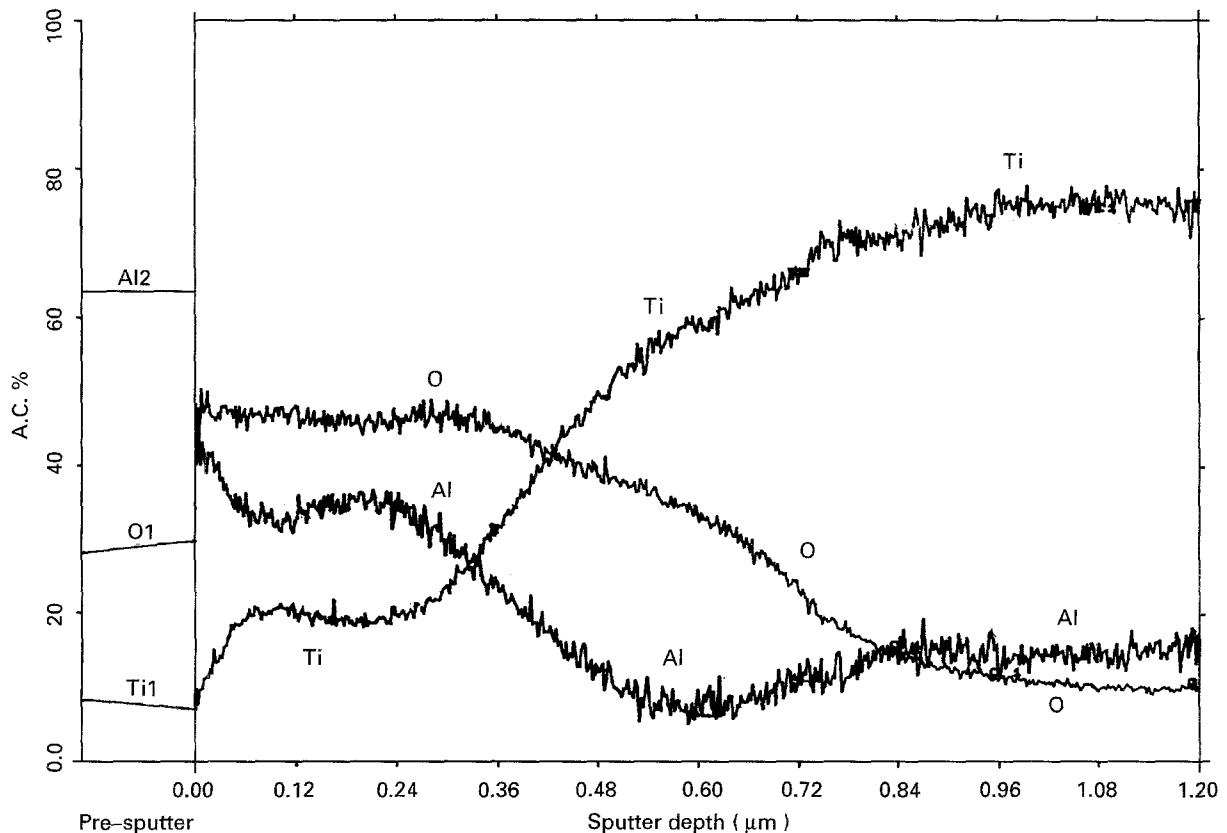

Figure 7 Auger depth profile of aluminium, titanium and oxygen within the laser-alloyed layer after 15 h oxidation test at 1023 K.

5. Conclusion

This paper presents a systematic study concerning the high-temperature oxidation-resistant property of Ti–Al alloys produced at the titanium substrate surface by using the flame spraying, arc spraying and laser-treatment techniques. The aqueous corrosion resistance of the alloyed layers has also been investigated.

Fine microstructures have been observed in the alloyed and heat-affected zones. The hardness of the laser-melted region is found to be higher than that of the titanium substrate. The oxidation resistance of the laser-alloyed layer is shown to be higher than that of the flame- and arc-sprayed coatings of aluminium on titanium substrate. The aqueous corrosion resistance of the laser-alloyed layer is similar to that of the pure titanium substrate.

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