

Oxidation phenomena in a Ti_3Al base-alloy[☆]

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Abstract

In this study we present some results regarding phase and surface thermal stability, with particular reference to the oxidation of an intermetallic alloy with the composition Ti–23Al–10.3Nb–4.5V–0.9Cr (at.%).

The isothermal oxidation kinetics were studied by thermogravimetric analysis. From the experimental results we evaluated the parameters of the process. The weight gain curves showed a parabolic trend for time up to 25 h. For longer than 50 h treatments, the kinetics tend to follow a linear trend with the formation of a non-protective surface oxide layer. The microstructure of the oxide scale was investigated with scanning electron microscopy and energy dispersive X-ray analysis and mapping. The identification of the crystalline phases was carried out with X-ray diffraction analysis.

Keywords: Alloy; Energy dispersive X-ray spectroscopy; Oxidation kinetics; Phase stability; SEM; TGA; Thermal stability; Ti_3Al alloy; Weight gain; X-ray diffraction

1. Introduction

Titanium alloys are nowadays widely employed in many technological fields, owing to their exceptional characteristics such as low density, good corrosion resistance and excellent mechanical properties. The main incentive to the development of different classes of titanium alloy comes from the aerospace industry, in which materials with a high strength-to-weight ratio are needed. However, excellent mechanical properties are not sufficient to ensure the success of materials that will have not only to stand

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mechanical stresses but also be exposed to aggressive atmospheres. The alloys based on the intermetallic phases TiAl and Ti₃Al are attracting considerable interest as they might improve the performance of conventional Ti alloys and possibly extend their range of temperature application. With particular reference to gas turbines for aircraft propulsion, Ti-base alloys are already widely used for the blading of the early compressor stages of commercial and military jet engines. For the hottest parts, where the temperature is in excess of 500°C, stainless steels or Ni-base superalloys must be used instead [1, 2]. The temperature limit to the application of Ti alloys is basically determined by the lack of creep strength. In principle both TiAl and Ti₃Al have better mechanical properties [3] so that they may be used above 500°C. As matter of fact, only a limited number of aerospace applications have been reported so far, involving military test engines [4]. This is mainly due to some aspects of these materials, such as poor ductility and oxidation resistance, affecting their fabricability, handling and reliability. Subsequent studies have indicated that multiphase systems are likely to overcome these problems. Titanium aluminides are considered as matrix materials for composites with ceramic reinforcements [5] or as constituent phases of multiphase alloys [6]. In the development of these alloys, the oxidation behaviour has been given very high consideration as it plays a fundamental role in determining the life of the Ti–Al base materials. In this respect concentrations of aluminium much higher than in conventional Ti alloys can have beneficial effects by promoting the formation of α -Al₂O₃. Of course this is not sufficient to ensure the formation of a protective oxide scale on the alloy, as the actual oxidation kinetics are affected by other factors, such as composition, temperature, time, etc., in a very complex way. In the case of Ti-base alloys, one has to consider also the peculiar affinity of this element for oxygen. Indeed extremely high concentrations of this element can dissolve in the alloy, which becomes extremely brittle.

This study presents some results on the oxidation behaviour of a Ti₃Al base alloy, with reference to the microstructural changes brought about by the oxidation reactions in the surface regions. Moreover attention has been devoted to the effect of alloy elements.

2. Experimental

The starting samples of composition Ti–23Al–10.3Nb–4.5V–0.9Cr (at. %) were heat-treated to optimise grain morphology and mechanical properties. According to X-ray diffraction (XRD) analysis the phases present in the alloy are α_2 (ordered hexagonal, DO₁₉) and β (body centered cubic). The oxidation studies were carried out with samples polished down to 800 grit paper, washed in acetone and kept under an inert (N₂) atmosphere before the oxidation tests. The isothermal oxidation kinetics were followed with a thermobalance (sensitivity 10 μ g, shunt: \pm 0.01 mg). For tests longer than 25 h, the samples were put in a furnace and their weight changes measured at fixed time intervals. The tests were carried out in high purity dry air at temperatures ranging from 700°C to 900°C for up to 500 h. Over this temperature range oxidation is one of main surface degradation process [7]. The morphology and the chemical

composition of the oxide scales were, studied, respectively, by scanning electrons microscopy (SEM) and energy dispersive X-ray spectroscopy (EDXS), both on surfaces and on polished cross-sections, whereas X-ray diffraction was used to identify the oxide phases on sample surface (radiation used: Cu-K α). Microhardness tests were carried out to investigate the degradation of the alloying determined by the oxidation process.

3. Results and discussion

Fig. 1 shows the thermogravimetric curves. There are three basic models to describe the oxidation rate, following the equation: $W^n = k_p t + C$, where W = weight change per unit surface area; n = oxidation exponent; k_p = rate constant; t = time; C = constant; and $n = 1$, $n = 2$ and $n = 3$ correspond to linear, parabolic and cubic relationships, respectively. The k_p has an Arrhenius-like temperature-dependence: $k_p = k_o \exp(E_a/RT)$, where k_o = rate constant, E_a = activation energy, R = gas constant and T = absolute temperature. For all the temperatures considered in this study, the kinetic curves showed good parabolic time-dependence. According to the Wagner's theory [8], this corresponds with rate control by solid state diffusion of the reactants through a growing compact scale, with possible simultaneous diffusion of the gaseous reactant into the metal matrix. Fig. 2 shows the k_p vs. $1/T$ plot obtained with our results as compared with literature data for other titanium alloys. The observed oxidation kinetics are even faster than in TiO₂-forming alloys which, as is known, do not produce a highly protective oxide scale.

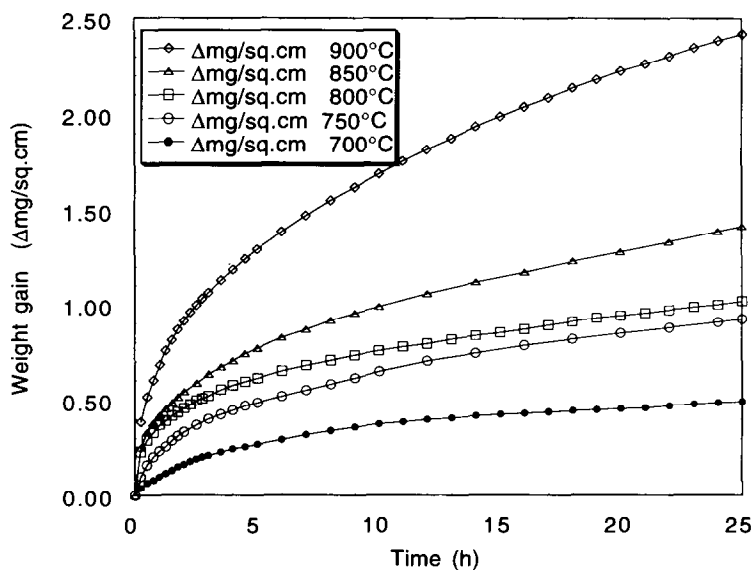


Fig. 1. Thermogravimetric curves for the alloy oxidised for 25 h in air at 700–900°C.

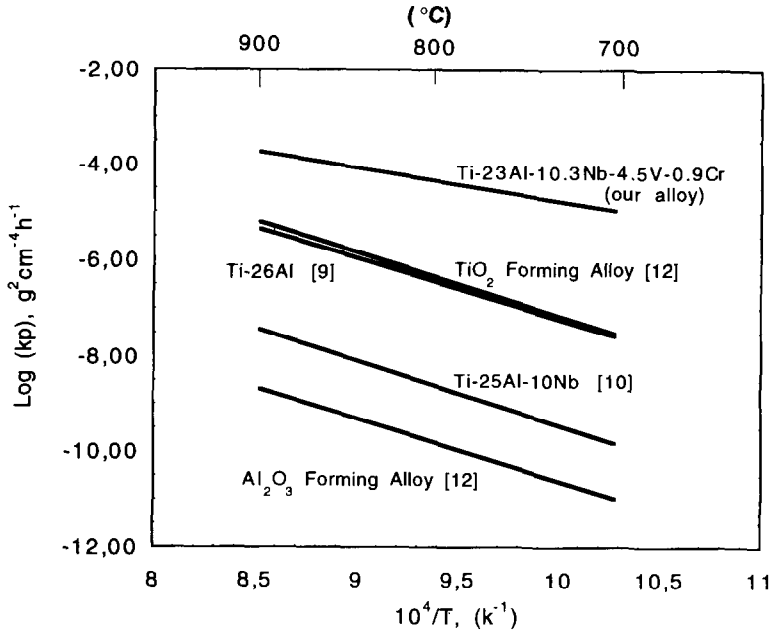


Fig. 2. Arrhenius plot of $K_{p,s}$ reported in the literature, for several Ti-Al-base alloys.

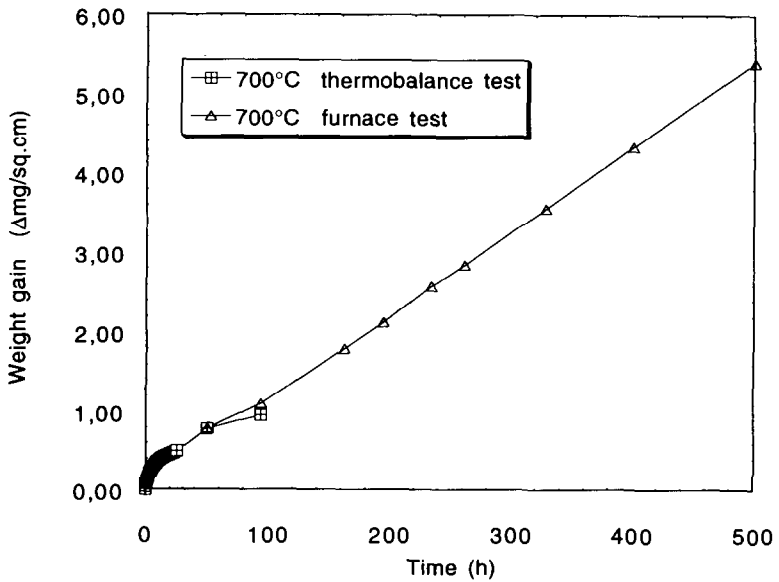


Fig. 3. Thermogravimetric curves for the alloy oxidised at 700°C for up to 500 h in air.

From the parabolic rate constant calculated at different temperatures the activation energy of oxidation has been calculated as: $E_a = 147 \text{ kJ mol}^{-1}$. For comparison the activation energy for oxidation of the stoichiometric Ti–26Al alloy is: $E_a = 255 \text{ kJ mol}^{-1}$ [9]. An activation energy so low and a parabolic rate constant so high compared with literature data are probably a result of the influence of the alloying elements. Niobium promotes the growth of Al_2O_3 -rich protective oxides and makes the scale more compact, reducing the overall oxidation process [10] (see Fig. 2). Vanadium has

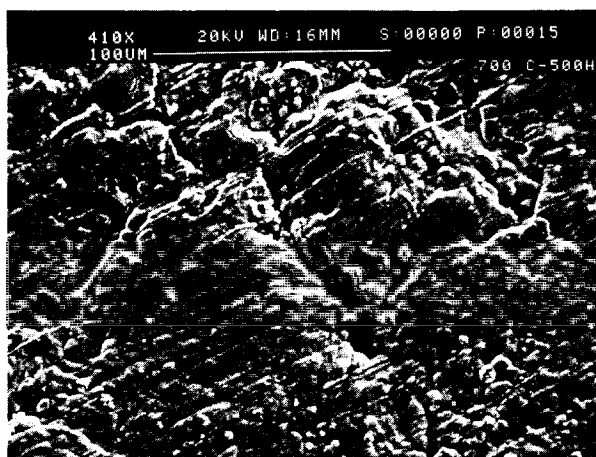


Fig. 4. SEM micrograph showing cracks on the oxide surface of the sample treated at 700°C for 500 h.

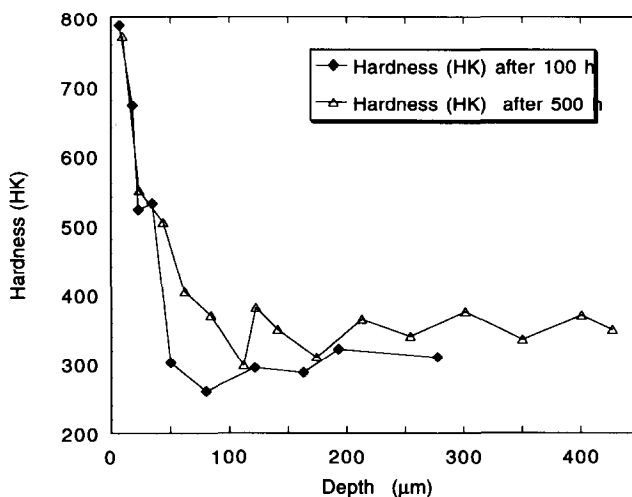


Fig. 5. Hardness profiles for samples treated at 700°C for 100 h and 500 h. The distance is measured starting from the oxide–alloy interface.

a largely detrimental effect on oxidation, as its oxides may dissolve the protective layers and enhance ionic conductivity through the scale [9]. These phenomena can result in consistent acceleration of the oxidation and explain the results of our analysis.

Longer than 25 h tests were also performed. Two alloy sheets were put in a furnace at 700°C for 500 h. The samples were removed at regular intervals to measure the weight changes. The resulting curve is shown by Fig. 3. In the graph we have also plotted the points obtained from the thermogravimetric analysis for times up to 25 h, carried out in the thermobalance. After initial parabolic behaviour of the oxidation kinetics, the

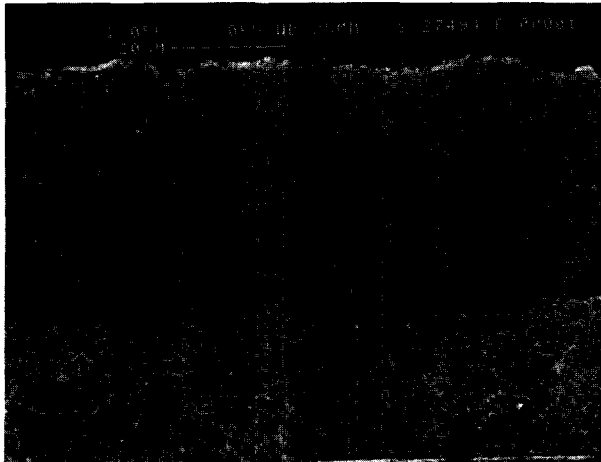
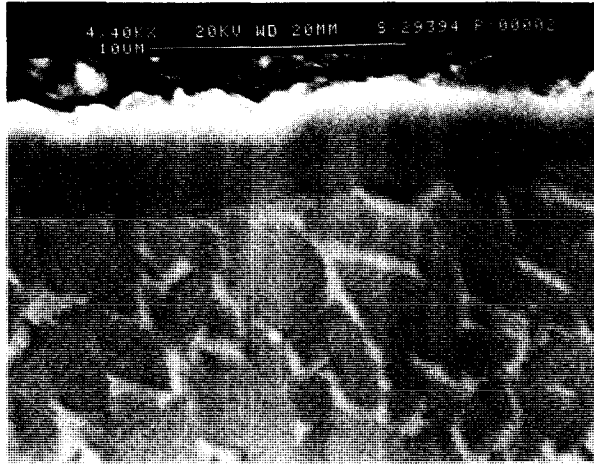


Fig. 6. Cross-section SEM micrograph of samples oxidised for: a) 100 and b) 500 h at 700°C. Note, in the latter, the fracture at the interface between the oxide scale (upper part) and the alloy.

weight curve becomes linear, showing that the oxide scale is not protective in respect of oxidation. A linear trend can be determined by several mechanisms, associated with phase boundary reactions, formation of a porous scale, etc. [11]. The observed kinetics are most likely determined by the formation of cracks on the surface of the oxide scale. Some are shown by the SEM micrograph in Fig. 4. These cracks are generated by the relief of stresses present in the scale, determined by the mismatch at the alloy–oxide interface. This is commonly observed in titanium and its alloys when thermally treated in an oxygen-rich atmosphere. Such an effect is determined by oxygen dissolution, which produces a significant lattice expansion. Surface cracks were probably not produced by thermal cycling of the specimens during the weight check operations, otherwise we would have observed discontinuities in the weight curve after each removal from the furnace. Further proof of the proposed mechanism responsible for the linear curve comes from hardness tests, whose results are summarised in the profiles reported in Fig. 5. The hardness of the alloy just beneath the oxide is more than doubled with respect to the bulk value. The surface hardness of the alloy attains the same value in the sample treated for 100 h as in the sample treated for 500 h at 700°C. The widths of the hardened regions are different, and are larger the longer is the oxidation time. Another effect which might intervene in changing the mechanical properties of the surface region is associated to the active role of oxygen as an α stabiliser, which can therefore transform part of the β phase grains into α -Ti or α_2 -Ti₃Al.

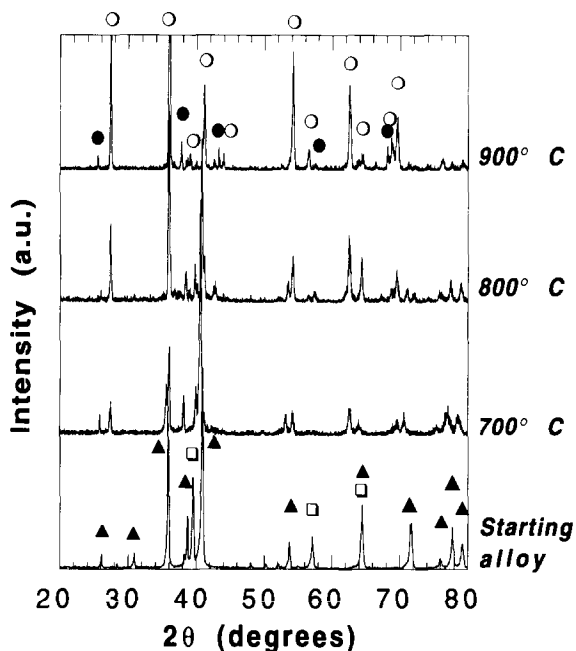


Fig. 7. X-ray diffraction patterns of the starting alloy and of the samples oxidised at 700, 800, and 900°C for 25h. \blacktriangle - α_2 -Ti₃Al; \square - β Ti; \circ -TiO₂, \bullet - α Al₂O₃.

Fig. 6 (a and b) shows the SEM micrographs of the samples treated at 700°C for 100 and 500 h prepared to characterise the morphology of the oxide scale. This seems very compact, free from macroscopic defects and porosity in both cases. The main difference between the two microstructures is in the oxide–alloy interface. After 100 h the interface is only slightly affected by the modifications associated with the oxidation process. The same is not true after 500 h: the specimen shows a fracture which runs

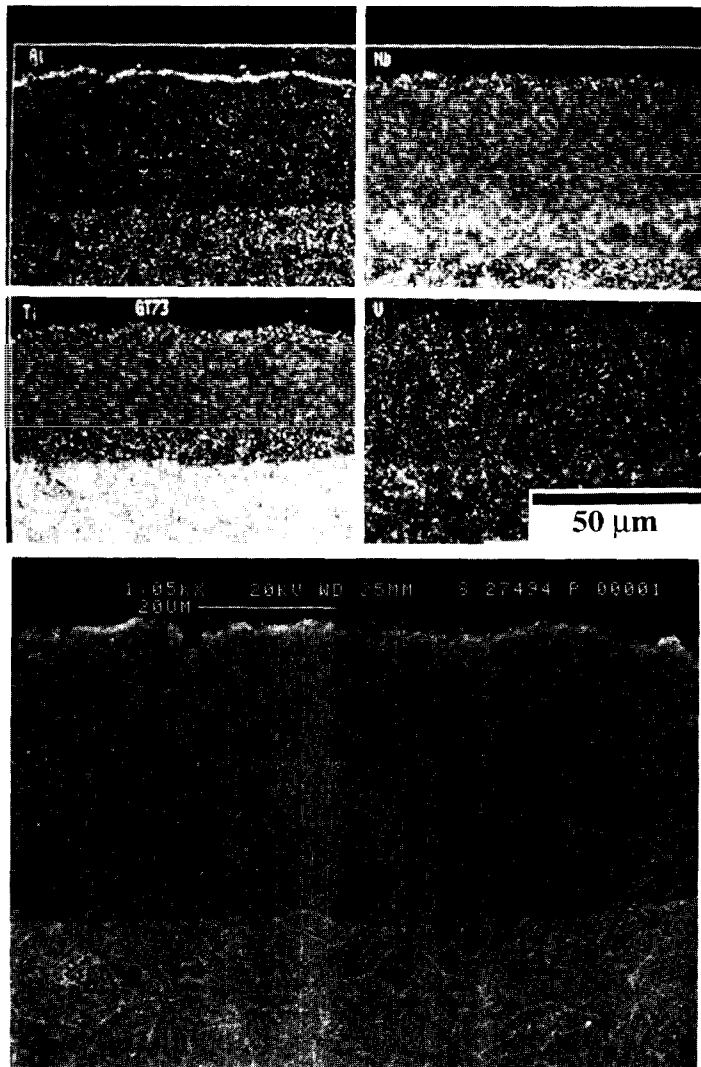
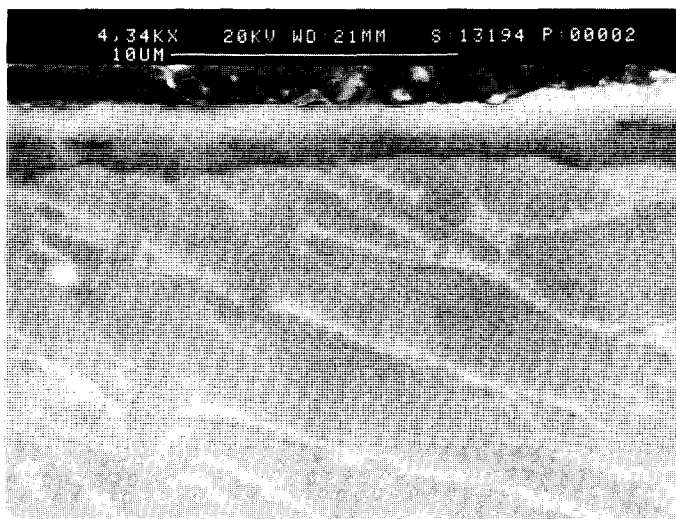
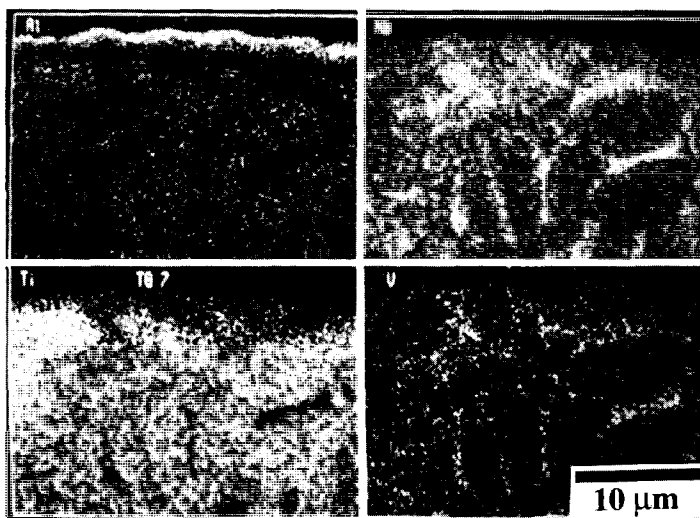


Fig. 8. X-ray maps of the four major elements present in the alloy for the samples: a) 500 h 700°C; b) 25 h 700°C; c) 25 h 900°C. Elements as indicated in the figures and the corresponding SEM micrographs are also reported.

parallel to the oxide–metal interface. Interestingly the crack does not coincide with the interface in all regions, but extended portions of the sample where the crack runs inside the alloy were observed. This latter observation confirms that the oxide scale, at this stage, has not completely lost its adhesion to the substrate. On the other hand the fracture of the alloy and the scale detachment in the sample oxidised for 500 h are further indications of stress building up in the interfacial region, as discussed above. XRD analysis carried out on the surface of the oxidised samples proved the two main



phases present in the oxide scale to be α - Al_2O_3 and TiO_2 (rutile), at all the temperatures considered. This is shown in Fig. 7, the diffraction patterns of the samples oxidised at 700, 800, and 900°C for 25 h with indication of the crystallographic phases. The high temperature phase of aluminium oxide, α - Al_2O_3 , is stabilised down to room temperature by the presence of secondary elements in the scale.

X-ray mapping shows the element distribution in the scale. Some cases are shown by Fig. 8 (a, b and c), where the X-ray maps for a few selected samples are illustrated

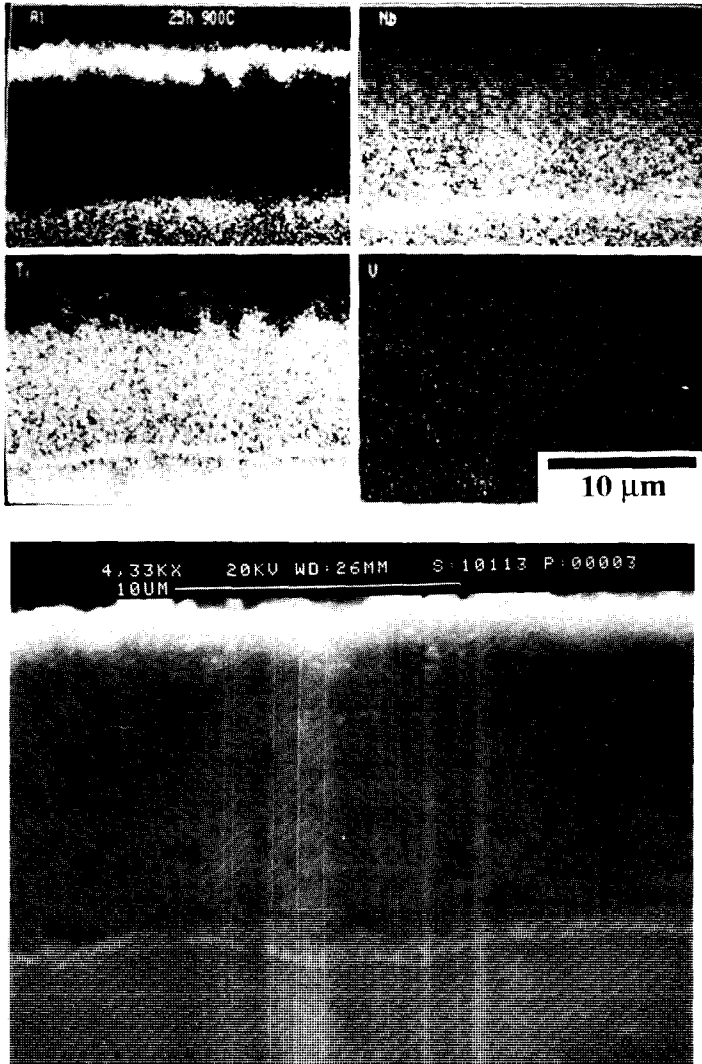


Fig. 8. (Continued)

together with the corresponding SEM pictures. In the sample oxidised for 500 h at 700°C, it is possible to see a thin Al₂O₃ layer on the top of the scale. The distribution of the other major elements, niobium and vanadium, is fairly homogeneous. Indeed niobium and vanadium atoms are soluble in TiO₂. A scale featuring a layered structure, with a surface aluminium enrichment already appears after 25 h oxidation at 750°C and higher temperatures, e.g. 900°C, as shown by maps 8b and 8c.

4. Conclusions

The oxidation behaviour of a Ti₃Al-base alloys has been studied at 700–900°C. The weight gain curves followed the parabolic rate law up to 25 h at 700–900°C, indicating the growth of a compact oxide scale on the surface of the alloy. For times longer than 50 h at 700°C the oxidation rate becomes linear as the growing scale is no longer able to provide protection to the alloy. The resulting kinetics are much faster than for other titanium alloys. This can be tentatively ascribed to the detrimental effect of vanadium. Hardness measurements and the cross section micrographs revealed the formation of an alloy layer beneath the oxide scale, significantly affected by composition changes and inward diffusion of oxygen. The results obtained so far afford some information on the predominant phenomena and give indications on the operating conditions suitable for this alloy.

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