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Surface engineering and chemical characterization in ion-nitrided titanium and titanium alloys

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The chemical and physical characteristics of ion-nitrided surface layers, obtained on α–β titanium alloys, are examined and correlated both with the working conditions adopted in the ion-nitriding process and with the alloy chemical composition. Besides the influence of the working parameters on the morphology and on the microstructures of the ion-nitrided surface layers, mainly the alloy element distributions both in surface coatings and in the substrate are analysed for five α–β titanium alloys of industrial use, and for titanium c.p. as reference, ion-nitrided at various treatment temperatures. The nitriding process forms, on titanium alloy parts, high-hardness surface layers consisting of TiN (δ phase) and Ti_2N (ε phase) nitrides and an interstitial solid solution of nitrogen in the close-packed hexagonal lattice of titanium (α phase). The presence and the extent of these phases as well as the ion-nitrided layer morphology are essentially determined by the alloy chemical composition and the working parameters. In particular a low-temperature treatment produces an extended nitrogen diffusion in the matrix beneath a thin continuous nitrided layer, while a high-temperature treatment produces prevalently a continuous nitrided surface layer. The alloy element distribution appears differentiated in the various phases and may be correlated with the different affinity of these elements with nitrogen.

1. Introduction

High-hardness wear-resistant surface layers are easily obtained on titanium alloys by nitriding. The most up-to-date thermochemical treatment, for this purpose, is by glow discharge ion-nitriding. This method allows for a wide temperature range, although temperatures between 900 and 1000° C are usually adopted.

According to the Ti–N phase diagram, reported in Fig. 1 from Murray [1], the outermost parts of the nitrided layers are composed of TiN (δ phase) and Ti_2N (ε phase) [2].

Below these phases there is a solid solution of nitrogen in the close-packed hexagonal lattice of titanium (α phase). ε phase does not exist above 1100° C [1], and therefore, does not form when titanium alloys are nitrided at high temperatures [3]. Most nitriding studies report data for the treatment of commercially pure titanium or of the widely used alloy Ti–6Al–4V [4–7], and there is a general consensus that the morphology of nitrided layers on unalloyed titanium is different from that found on Ti–6Al–4V alloy. In particular, it is pointed out that nitrided layers on pure titanium have a planar interface between the solid nitrogen solution and the matrix, while nitrided Ti–6Al–4V has, at the innermost part of the surface layer, some α phase (rich in nitrogen) platelets embedded in an $\alpha + \beta$ matrix.

Rie and Lampe [5] observe that, when the Ti–6Al–4V alloy is nitrided at 700 and 800° C, its diffusion layer microstructure shows a preferred formation of alpha phase crystals in the $\alpha + \beta$ matrix but no continuous layer of α crystals. In addition, when the ion-nitriding is performed between 900 and 1000° C the Ti–6Al–4V diffusion layer consists of two regions: an outermost homogeneous layer of α phase and a zone of coarse columnar α phase crystals which are embedded in the $\alpha + \beta$ matrix. These same authors state that this morphology is caused by nitrogen which acts as a stabilizer of the α phase in the $\alpha + \beta$ matrix.

It should be recalled that this particular diffusion layer morphology, characteristic in Ti–6Al–4V, is also found in other titanium alloys containing chromium [8] or aluminium, molybdenum iron and chromium [9].

Michel and Gantois [10], however, do not entirely agree with Rie and Lampe; in fact, they have observed that large platelets of α phase (rich in nitrogen) are present in the matrix beneath the surface layer when

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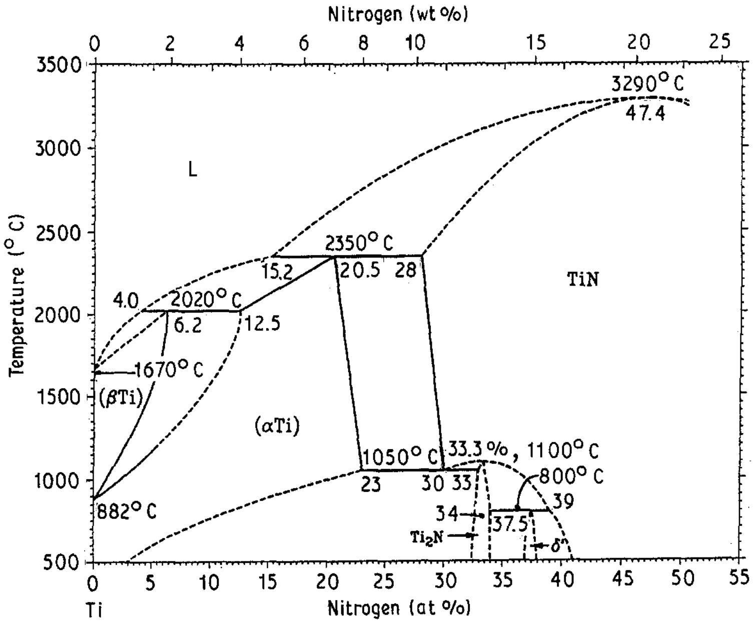

Figure 1 Ti–N phase diagram [1].

the ion-nitriding of titanium alloys is carried out at temperatures either higher or lower than the β transus.

This study aims to define the characteristics of ion-nitrided layers, and in particular, to evaluate the influence of the alloy chemical composition and treatment temperature on the morphology and microstructures of the obtained ion-nitrided layers. It must be noted that the treatment temperature determines the matrix structure of the alloys during the ion-nitriding process. Moreover, this study also considers alloy element distributions in nitrided layers for the different alloys used.

2. Experimental procedures

Five $\alpha + \beta$ titanium alloys and an unalloyed titanium; for comparison, were surface treated by ion-nitriding. Commercially pure titanium grade 4 and two-phase alloys were used for the experimental tests: their compositions are shown in Table I. All the alloys and the pure titanium presented typical annealed microstructures.

In pure titanium the α phase is stable up to 882° C, where it transforms to the β phase; in the five studied alloys both α and β phases are contemporaneously present at room temperature. By using the Ti–Al–V, Ti–Al–Mn, Ti–Al–Mo–Sn and Ti–Al–Fe phase diagrams [11] it is possible to determine the phase constitution of these alloys at high temperatures.

Figs 2a and b, shows the isothermal sections (at 900 and 1000° C) respectively of the Ti–Al–V, Ti–Al–Mn systems; the diagrams demonstrate that the Ti–6Al–4V, Ti–4Al–2Mn alloys are constituted of α and β phases at 900° C, while at 1000° C they are totally made up of β phase. In order to predict which phases are present at different temperatures for the Ti–4Al–4Mo–2Sn alloys, it is necessary to consider the quaternary Ti–Al–Mo–Sn system; unfortunately, to date, this remains unknown: however, as the isothermal section at 1000° C of the Ti–Al–Mo system has been studied [11], it is possible to state that tin only slightly affects the stability of α and β phases. Further, on the basis of these ternary phase diagrams it can be inferred that β transus of the alloys is lower than 1000° C.

Fig. 3 shows the isothermal sections at 1000 and 1100° C of the Ti–Al–Fe system. At 1000° C the alloy Ti–5Al–2Fe has a two-phase $\alpha + \beta$ structure, while at 1100° C it shows *b* structure. In fact, the stability range of β lattice rapidly widens out at a temperature higher than 1000° C siting the β transus of this alloy close to a temperature of 1000° C.

The phase diagram information for β transus temperature was also confirmed by thermal differential analysis and by metallographic analysis. This last analysis was carried out on samples heated at several different temperatures between 900 and 1100° C and then water quenched.

Prismatic samples (24 × 12 × 4 mm) of titanium and titanium alloys were treated in a plasma nitriding equipment similar to the industrial ones used for steel ion-nitriding.

The working conditions during ion-nitriding treatment were selected as follows

(i) treatment temperature 900 and 1000° C;
(ii) gas composition N_2 80%–H_2 20%;

TABLE I Chemical composition of materials

Materials	Composition (wt %)								
	Al	Fe	V	Mo	Sn	Mn	Si	O	N
Ti c.p.	–	0.05	–	–	–	–	–	0.123	0.006
Ti–6Al–4V	5.98	0.09	3.25	–	–	–	–	0.16	0.03
Ti–4Al–2Mn	4.5	0.05	–	–	–	1.96	–	0.067	0.003
Ti–4Al–4Mo–2Sn	4.09	0.04	–	4.1	2.09	–	0.48	0.16	0.006
Ti–6Al–6V–2Sn	5.87	0.04	5.9	–	2.11	–	–	< 0.2	< 0.04
Ti–5Al–2Fe	4.73	1.91	–	–	–	–	–	< 0.2	< 0.04

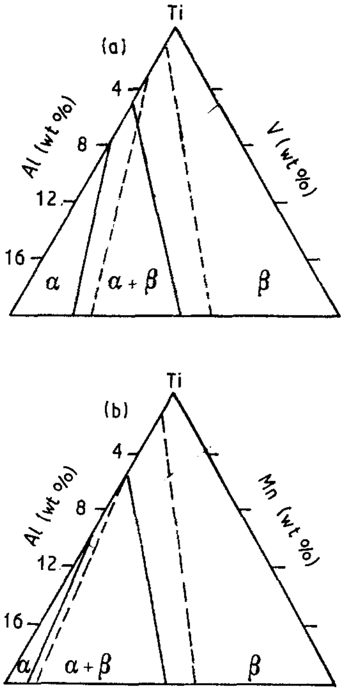

Figure 2 (a) Ti–Al–V system; (b) Ti–Al–Mn system; (---- isothermal section at 900° C, —— isothermal section at 1000° C).

(iii) treatment pressure 10 Torr (1.3 kPa);

(iv) treatment periods 12 and 32 h;

(v) current density between 0.15 and 0.25 mA mm^{-2};

(vi) voltage 450 V.

After the treatment, the samples were sectioned perpendicularly to the external surface and their microstructures were examined by optical metallographic techniques and scanning electron microscopy. X-ray diffractometry (Cu$K\alpha$) was performed to identify the phases constituting the surface layers while alloy elements distributions in the different phases were determined by microanalysis through energy dispersive X-ray analysis (EDAX). Microhardness measurements (Knoop indenter, 10 g load) were carried out on the phases constituting both the nitrided layer and the matrix.

3. Results and discussion

The nitrided layers are constituted of a sequence of phases δ, ε, α, which decrease in nitrogen content from the surface to the innermost part of the samples. Table II illustrates surface layer phases in the nitrided samples and lists the used treating conditions. As the Ti–N phase diagram shows, the ε phase was always present in the layers when unalloyed titanium was nitrided at 900 and 1000° C. On the contrary, this phase did not form in appreciable amounts when $\alpha + \beta$ titanium alloys were nitrided at 1000° C, possibly because the presence of alloy elements narrows the temperature range of ε phase stability.

TABLE II Surface layer phase composition against nitriding conditions (gas composition: 80% N_2, 20% H_2; pressure 10 Torr)

Materials	Time (h)	Temperature (° C)	
		900	1000
Ti c.p.	12	$\delta + \varepsilon + \alpha$	$\delta + \varepsilon + \alpha$
Ti c.p.	32	$\delta + \varepsilon + \alpha$	$\delta + \varepsilon + \alpha$
Ti–6Al–4V	12	$\delta + \varepsilon + \alpha$	$\delta + \alpha$
Ti–6Al–4V	32	$\delta + \varepsilon + \alpha$	$\delta + \alpha$
Ti–4Al–2Mn	12	$\delta + \varepsilon + \alpha$	$\delta + \alpha + (\varepsilon)$
Ti–4Al–2Mn	32	$\delta + \varepsilon + \alpha$	$\delta + \alpha + (\varepsilon)$
Ti–4Al–4Mo–2Sn	12	$\delta + \varepsilon + \alpha$	$\delta + \alpha$
Ti–4Al–4Mo–2Sn	32	$\delta + \varepsilon + \alpha$	$\delta + \alpha$
Ti–6Al–6V–2Sn	12		$\delta + \alpha$
Ti–5Al–2Fe	12		$\delta + \alpha$

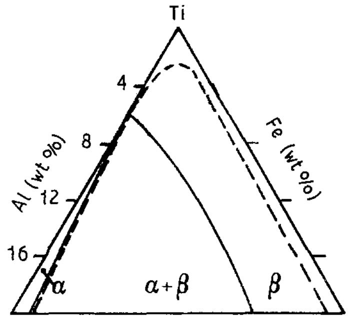

Figure 3 Ti–Al–Fe system. (---- isothermal section at 1000° C, —— isothermal section at 1100° C).

Since the samples were cooled rapidly in the plasma nitriding equipment after ion-nitriding, their matrix microstructure was defined by the heat treatment temperature, thus, in agreement with their β transus temperature, most of the titanium alloy samples nitrided at 1000° C displayed acicular α crystals, β phase and prior β grain boundaries in the matrix. On the contrary, when nitrided at 900° C, the titanium alloy samples presented polygonal crystals of primary α in an acicular $\alpha + \beta$ two-phase structure.

Pure titanium samples cooled in the equipment

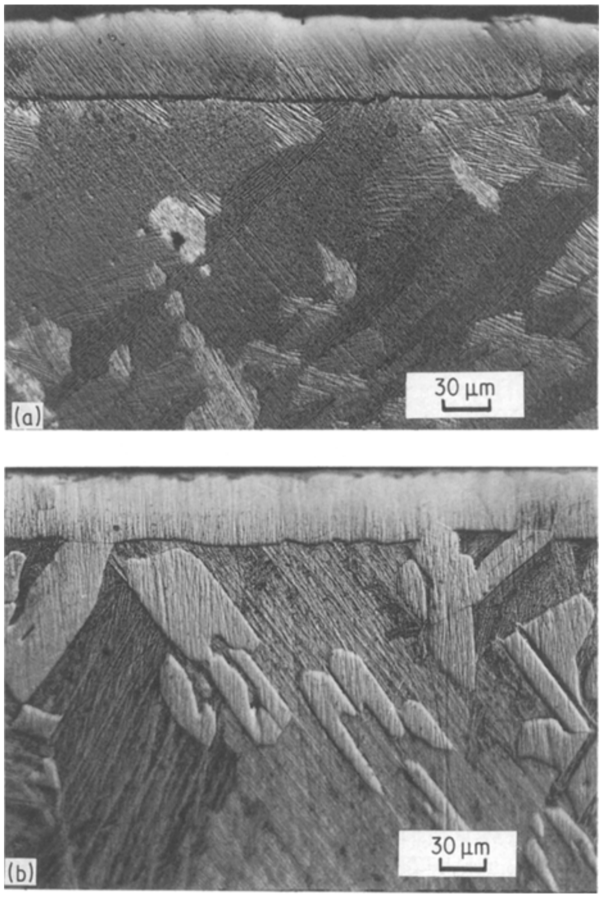

Figure 4 (a) Ti–4Al–2Mn alloy and (b) Ti–6Al–4V alloy nitrided for 12 h at 1000° C.

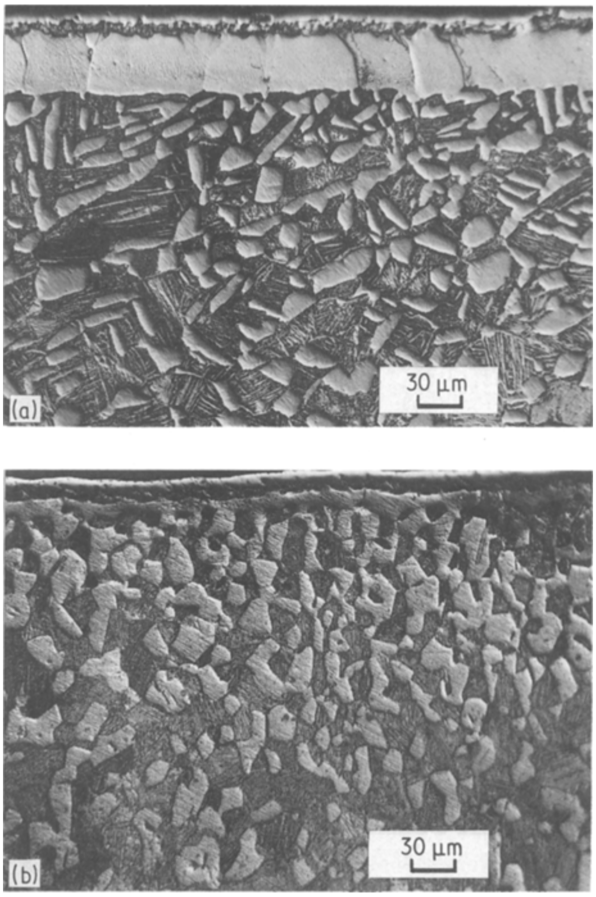

Figure 5 (a) Ti–4Al–2Mn alloy and (b) Ti–6Al–4V alloy nitrided for 12 h at 900° C.

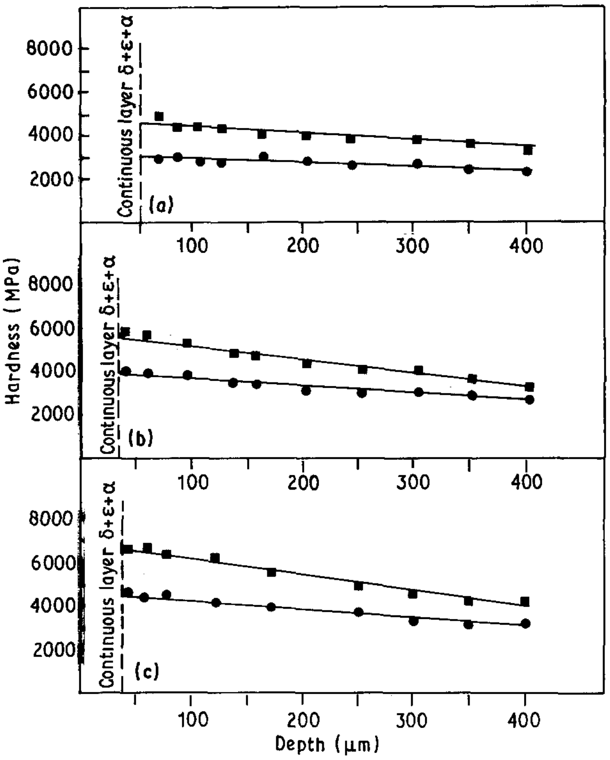

Figure 6 Microhardness profiles for two-phase matrix and α phase (rich in nitrogen) in the alloys nitrided for 12 h at 900° C. ■ α crystals rich in nitrogen, ● two phases $\alpha + \beta$ metal matrix. (a) Ti–4Al–2Mn, (b) Ti–6Al–4V, (c) Ti–4Al–4Mo–2Sn alloy.

from both 900 and 1000° C had the same matrix structure because these two temperatures are higher than the titanium β transus.

It was observed that in the nitrided samples of unalloyed titanium the interfaces α phase–metal matrix were always planar; in titanium alloy samples nitrided at 1000° C, the interface was planar for Ti–6Al–6V–2Sn and Ti–4Al–2Mn (Fig. 4a); in other titanium alloys the interface was not completely planar. In fact, the latter alloys presented a few elongated α crystals: these started at the continuous layer and penetrated into the $\alpha + \beta$ metal matrix (Fig. 4b).

The diffusion layer of the $\alpha + \beta$ alloys displayed a very different morphology when treated below the β transus temperature (at 900° C). In these alloys many α phase crystals were observed to be embedded in the matrix beneath the surface layer; the number of these crystals decreased in relation to the distance from the external surface; few primary α crystals were found to be present in the core of the sample. This particular morphology was especially associated with long ion-nitriding times (Figs 5a and b).

Microhardness measures, carried out on the cross-sections of all the specimens, indicated that the continuous nitrided layer had hardness values greater than 10 000 MPa; a maximum value of about 20 000 MPa was detected on the sample surfaces. In the samples showing planar interfaces between the continuous nitrided layer and the matrix, microhardness decreased with the depth until the metal matrix hardness value was reached. For some specimens of $\alpha + \beta$ alloys nitrided at 900° C, inhomogeneous microhardness values were measured below the outermost continuous layer. In fact the α phase crystals embedded in the matrix showed high microhardness which decreased with the distance from the external surface, while the $\alpha + \beta$ matrix showed lower microhardness values which were not dependent on the depth. Thus, two different microhardness curves were considered suitable to show the characteristics of the zone located below the continuous nitrided layer. The microhardness profiles for the α phase crystals rich in nitrogen and for the metal matrix are shown for three alloys nitrided at 900° C (Fig. 6).

In the analysis of the alloy element influence on the various present phases, an evaluation was made to see if the different tendency of these elements to combine with nitrogen determined different solubility behaviour in surface nitrides as compared with the matrix. Fig. 7 reports the concentration profiles of aluminium, vanadium, manganese, iron, molybdenum and tin obtained on samples of the five alloys treated at 1000° C for 12 h. These diagrams show clearly the behaviour of the different alloy elements.

It may thus be noted that aluminium tends to diffuse from the matrix towards the layer of the nitrogen solid solution in α titanium and then from this towards the nitride (δ or $\delta + \varepsilon$) layer reaching the highest concentration near the external surface. Tin shows no preferred distribution in the different phases. Finally, vanadium, manganese, iron and molybdenum decrease their concentrations to negligible values in the surface nitrided layer and reach maximum concentration in the matrix $\alpha + \beta$ near the interface with the same nitrided layer. This behaviour may be correlated with the different solubility of the alloy elements in the two

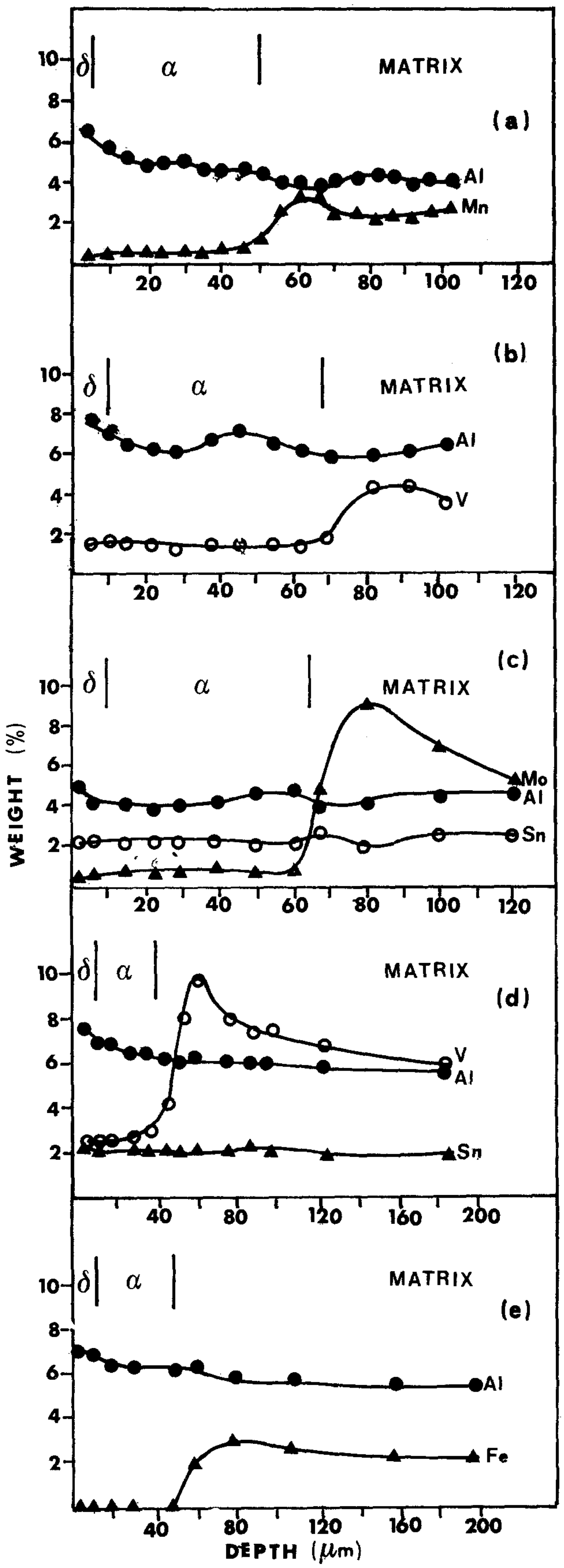

Figure 7 Concentration profiles for alloy elements in the alloys nitrided for 12 h at 1000° C. (a) Ti–4Al–2Mn alloy; (b) Ti–6Al–4V alloy; (c) Ti–4Al–4Mo–2Sn alloy; (d) Ti–6Al–6V–2Sn alloy; (e) Ti–5Al–2Fe alloy.

lattices of titanium (α and β), with their different affinity for nitrogen and, for the transition elements only, with their affinity for hydrogen, boron, carbon and nitrogen, as described by Hagg and Kiessling [12]. In fact nitrogen affinity decreases in the first transition series with the increase of the "d" electrons number of the metals and causes a preferred and differentiated distribution of the metallic atoms in the various phases of the nitrided layers.

Very different surface layer characteristics were obtained by nitriding two-phase $\alpha + \beta$ alloys at specific treatment temperatures. In fact, very thick hardened layers were also obtained when ion-nitriding was carried out at a temperature lower than the β transus. In this case, below a thin (50 to 60 μm), compact and continuous layer composed of δ, ε and α (solid solution of nitrogen in titanium) phases, there formed a large zone (a few hundred micrometres) containing hard α phase crystals rich in nitrogen. It is, therefore, possible to relate this phenomenon to the diffusion process of nitrogen in the titanium alloys. It is well known that the diffusion coefficient for nitrogen in β titanium is at least tenfold greater than that calculated for α titanium at the same temperature [13, 14]. In addition, according to Wasilewski and Kehl [14], nitrogen diffuses more slowly in titanium nitrides than in the titanium lattices (α and β). Further, in titanium nitriding, after the formation of a thin nitrided layer on the sample surface, the layer growth rate is controlled by the nitrogen diffusion through the nitrides. Below the continuous layer (constituted of δ, ε and α phases) nitrogen diffuses quickly in the $\alpha + \beta$ metal matrix; thus, in the nitrided samples it is possible to find nitrogen at a few hundred micrometres from the external surface, while the continuous nitrided layer maintains a thickness of some tens of micrometres, only.

Moreover, nitrogen is more soluble in α titanium (up to 22 at %) [1] than in β titanium (up to 6 at %) [1] and has a tendency to concentrate below the continuous nitrided layer, in the α crystals of the two-phase ($\alpha + \beta$) matrix. This increased nitrogen content causes hardened α crystals to form.

On the contrary, when ion-nitriding is carried out at a temperature below α or above β transus, the metal matrix is one-phase and the nitrogen shows a homogeneous distribution pattern under the continuous nitrided layer.

4. Conclusions

In the titanium alloys ion-nitriding study, particular attention was given to the influence exerted by the matrix microstructure on the surface layer characteristics and to the alloy elements distribution in the present phases. In brief the primary results demonstrate the following.

(i) Ion-nitriding of titanium alloys provides the formation of high hardness surface layers constituted of δ, ε and α (rich in nitrogen) phases.

(ii) Nitriding of titanium alloys at temperatures below the β transus produces an extended nitrogen diffusion in the matrix beneath the continuous nitrided layer and a high nitrogen concentration in α crystals. This results in the formation of a large two-phase diffusion zone as well as of a thin continuous surface layer.

(iii) The number and hardness of the α crystals containing nitrogen decrease with depth; these crystals are harder than the metal matrix for the presence of nitrogen.

(iv) Ion-nitriding of unalloyed titanium and $\alpha + \beta$ titanium alloys, at a temperature higher than their β transus, produces only continuous surface layers; the two-phase diffusion zone is not present.

(v) The differentiated distribution of alloy elements in the various phases may be correlated with the different affinity of these elements with nitrogen. The hardness of the different phases rich in nitrogen may be considered not to be affected by the presence in the matrix of transition elements.

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