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Influence of alloying elements on the dissolution of oxygen in the metallic phase during the oxidation of titanium alloys

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In order to study the influence of aluminium, chromium and silicon on the dissolution of oxygen in the metallic phase during the oxidation of titanium-based alloys, unalloyed titanium Ti35 and the alloys Ti–Al (1.65, 3, 5 and 10% by weight of aluminium), Ti–Cr (1, 4, 11 and 19% by weight of chromium) and Ti–Si (0.25, 0.5 and 1% by weight of silicon) were oxidized in air and in oxygen for durations of up to several thousand hours, between 550 and 700° C. The influence of the alloying elements was studied using microhardness measurements in the metallic zone just beneath the oxide. It was observed that aluminium and silicon cause a significant reduction in the amount of oxygen dissolved in the metallic phase whereas the effect of chromium is negligible. A comparison of the oxidation behaviour of unalloyed titanium in air and in oxygen reveals the marked influence of nitrogen on the dissolution of oxygen into the substrate, causing a reduction in the amount of dissolved oxygen. In addition, for oxidation of the alloys in air, a synergistic effect is observed, particularly between nitrogen and silicon.

1. Introduction

During the oxidation of titanium and its alloys, in addition to the formation of an oxide layer on the metal surface, a considerable amount of oxygen is dissolved into the metal lattice. The diffusion of oxygen in the titanium–oxygen solid solution thus formed plays an important but controversial role in the overall oxidation mechanism of this metal [1–17]. It is well known that the presence of oxygen within the metal lattice leads to a significant modification of the mechanical properties of titanium. For example, Dubertret [18] showed that interstitial oxygen results in the total suppression of the plastic deformation modes in the metal at room temperature, and leads to brittle fracture. Microhardness measurements performed on the diffusion zone formed during oxidation thus reveal the variations in mechanical characteristics and enable the penetration of oxygen into the metal to be visualized. The diffusion coefficient of the oxygen in the metal may be estimated by this method, but care must be taken in the interpretation of microhardness profiles as a one-to-one relation between microhardness and oxygen concentration does not exist; in particular, the relation is dependent on the oxidation temperature of the metal [1, 4, 12, 13, 17]. The values of the diffusion coefficient obtained by this method are presented in Table I.

Other methods have also been used to quantify the oxygen concentration profiles and to calculate the corresponding diffusion coefficients: displacement kinetics of the alpha/beta interface [2], determination of the oxygen amount by nuclear reaction [5, 9, 17, 19], determination of the weight of oxygen in the oxide by thickness measurements [10, 14–16] or weighing of the oxide layer [3], strain ageing [20, 21], internal friction measurements [22], etc. The values of the diffusion coefficient thus determined differ considerably from one another (Table II).

Nevertheless, according to David *et al.* [19] some values of the diffusion coefficient of oxygen in alpha-titanium determined in the temperature range 250 to 950° C fall on the same Arrhenius plot according to the equation: $D(\mathrm{cm^2\,sec^{-1}}) = 0.45 \exp -[(200 \pm 30)\,\mathrm{kJ\,mol^{-1}}]/RT$. This is the case for values calculated by de Paula *et al.* [20, 21] from strain ageing experiments in the temperature range 250 to 400° C, for those found by Bertin [22] at 420 and 490° C and by David *et al.* [19] using direct analysis of oxygen by observation of the 016 (d,p) 017 nuclear reaction at increasing depths in the metal, just below the oxide, in the temperature range 460 to 700° C. It is also the case for values found by Garcia *et al.* [9] in the temperature range 700 to 950° C and for those of Dechamps *et al.* [10] in the range 650 to 875° C.

TABLE I Diffusion coefficients of oxygen in alpha-titanium derived from microhardness measurements

Temperature (° C)	D_0 ($\mathrm{cm^2\,sec^{-1}}$)	Activation energy ($\mathrm{kJ\,mol^{-1}}$)	Reference
800–900	0.5	213	[1]
700–850	5.08×10^{-3}	140	[4]
750–850	16	217	[12]
700–800	1.6	201	[13]

TABLE II Diffusion coefficients of oxygen in alpha-titanium determined by different techniques

Temperature (° C)	D_0 ($cm^2 sec^{-1}$)	D($cm^2 sec^{-1}$)	Activation energy ($kJ mol^{-1}$)	Reference
932–1142	0.778		203	[2]
750–1050	9.4×10^{-4}		286	[3]
750–850	1.32×10^{-4}		130	[5]
650–875	0.408		197	[10]
700–850	0.408		196	[14–16]
700–950	0.45		200.6	[17]
460–700	0.45		200	[19]
290		2.5×10^{-19}		[20, 21]
357		1.0×10^{-17}		[20, 21]
420		4.6×10^{-20}		[22]
490		7.7×10^{-19}		[22]

Previous studies also have shown clearly that the addition to titanium of elements such as aluminium, chromium and silicon modifies the thermodynamic, kinetic, morphological, analytical and mechanical aspects of the oxidation of this metal [23–25]. In this work, it is the role of these elements on the dissolution of oxygen in the metal phase which is examined.

Data in the literature are contradictory concerning the influence of aluminium on the dissolution of oxygen in titanium. According to Rosa [26], aluminium reduces the amount of oxygen dissolved in the alloy whereas Menzies and Strafford [27] and Jenkins [28] suggest that aluminium increases the dissolution of oxygen when compared to the unalloyed titanium. As chromium additions improve the mechanical properties of titanium, the influence of small amounts of oxygen has been investigated in several studies. It may be noted that Menzies and Strafford [29] deduced, from morphological observations on TiCr5 and TiCr15 oxidized in carbon dioxide at 1000° C, that the addition of chromium to titanium increased the amount of oxygen dissolved in the metal phase and thus to a greater extent at the higher level of chromium addition. According to Rosa [30], silicon also plays a role in the dissolution of oxygen in titanium but little is known about this influence which was not investigated further.

2. Materials and experimental methods

The reference material in this study was unalloyed titanium Ti35. The choice of alloys (Table III), was made taking into account the phase diagrams, forming considerations and, when available, by reference to data in the literature on the oxidation resistance of this type of alloy. The compositions of the Ti–Al alloys were thus chosen such that only the alpha-phase was present and precipitation of Ti3Al was avoided. It is the formation of this compound which embrittles Ti–Al alloys containing more than 10 to 12 wt % aluminium. For chromium the alloys selected included the eutectoid composition, which was obtained for 14 at % chromium (15 wt %). For silicon, it was not considered appropriate to include the eutectoid composition, given the excessive precipitation of Ti5Si3. In addition, rolling problems were encountered for alloys beyond 1 wt % Si. The alloy compositions are presented in Tables IV to VII.

TABLE III Composition and structures of the alloys

Alloys	wt %	Structures
Ti–Al	1.65, 3, 5, 10	alpha
Ti–Cr	1. 4, 11,	alpha + beta
	19	alpha + beta + TiCr2
Ti–Si	0.25, 0.5, 1	alpha + Ti5Si3

The preparation of samples was as follows:

1. Preparation by several successive melts of buttons (25 g) or ingots (100 g) in an electric arc furnace with a non-consumable electrode or a levitation furnace, respectively [31].
2. Forging, at temperatures of 950, 1050 and 1150° C for Ti–Cr, Ti–Si and Ti–Al, respectively.
3. Cold or hot (650° C) rolling according to the alloy composition, to obtain sheets of 0.5 to 2 mm thickness.
4. Heat treatment of sheets under vacuum at 650° C for 24 h.

The metallographic structures of these sheets have been described in detail by Champin *et al.* [32]. Identification of the phases present in the alloys and the analysis of precipitates were performed by X-ray diffractometry and spectrometry, respectively. The results presented in Table III, can be summarized as follows: (a) Ti–Al alloys: only the alpha-phase of titanium was observed, for all alloy compositions; (b) Ti–Cr alloys: for 1, 4 and 11 wt % chromium, the alpha- and beta-phases were obtained. TiCr2 was observed for 19 wt % chromium only; yet TiCr2 is definitely present at lower chromium contents but in amounts too small to be detected; (c) Ti–Si alloys: for all compositions, 0.25, 0.5 and 1 wt %, both the alpha-phase and the compound Ti5Si3 were observed.

The samples used for oxidation tests were in the form of parallelepiped coupons taken from the sheets described above. The reproducibility of kinetic results being determined to some extent by the surface condition of the material, a standard preparation before oxidation was adopted: the samples were polished under water using silicon carbide paper to a particle size of 18 μm.

The overall weight increases, due to the formation of the oxide film and to the dissolution of oxygen in the metal below the film, were measured by thermogravimetry, for temperatures between 550 and 700° C, following two different experimental procedures due to the long durations of tests (several hundred to

TABLE IV Titanium Ti35 composition

	O2	H2	N2	C	Al	Cr	Si	Fe	Mn
wt%	0.073	0.0009	0.014	0.016	0.007	0.05	0.038	0.052	0.007
at%	0.209	0.043	0.047	0.063	0.012	0.046	0.06	0.045	0.006

TABLE V Composition of the titanium–aluminium binary alloys

	TiAl1.65	TiAl3	TiAl5	TiAl10
wt%	1.65	3.05	5	10
at%	2.89	5.28	8.53	16.47

TABLE VI Composition of the titanium–chromium binary alloys

		TiCr1	TiCr4	TiCr11	TiCr19
Cr	(wt%)	1.00	3.88	11.00	18.80
	(at %)	0.92	3.58	10.22	17.56
Al	(wt%)	0.007	0.035	0.070	0.167
	(at %)	0.012	0.062	0.125	0.300
Fe	(wt%)	0.056	0.074	0.075	0.102
	(at %)	0.048	0.064	0.065	0.089
Mn	(wt%)	0.007	0.01	0.028	0.052

TABLE VII Composition of the titanium–silicon binary alloys

	TiSi0.25	TiSi0.5	TiSi1
wt%	0.23	0.43	0.87
at%	0.39	0.73	1.47

TABLE VIII Comparison of amounts of oxygen dissolved in the metallic substrate O(S.S.) and fixed in the aggregate O(Tot.) during the oxidation reaction in air and in oxygen (700° C, 435 h) for unalloyed titanium ($\pm 0.05\,\mathrm{mg\,cm^{-2}}$)

Atmosphere	Oxygen	Air
O(S.S.)($\mathrm{mg\,cm^{-2}}$)	3.00	1.99
O(Tot.)($\mathrm{mg\,cm^{-2}}$)	6.33	4.67
O(S.S.)/O(Tot.)	0.48	0.43

several thousand hours): (1) continuous thermogravimetry under a partial pressure of oxygen of 100 torr; (2) semi-continuous thermogravimetry in air (at atmospheric pressure), by daily weighing of samples. These two procedures, as well as the methods employed to examine and analyse the oxide layers, have been described in detail elsewhere [23–25, 33]. Microhardness measurements were performed on polished transverse sections using a Leitz microhardness tester with a Vickers indenter. The penetration of the diamond is controlled automatically by a hydraulic system which ensures a constant pressure. The distance from the metal–oxide interface to the centre of the indentation is determined using a micrometer linked to the microhardness tester. The applied load was 25 g. Results are presented as the average of several measurements.

3. Experimental results

3.1. Unalloyed titanium

The microhardness profiles measured on samples oxidized in air and in oxygen at 700° C for 435 h are presented in Fig. 1. A significant difference in the penetration of oxygen in the metal between atmospheres of pure oxygen and ambient air may be noted. These profiles approach those of oxygen concentration as a function of depth obtained by Garcia, using nuclear microanalysis (Fig. III.5a in [6–8]) for similar experimental conditions: both types of profile show three distinct zones (Fig. III.6e in [6–8]). This similarity allows confirmation that this method effectively reveals the oxygen concentration profile. Thus, microhardness measurements were employed to obtain a simple estimate of the amounts of oxygen dissolved in the metal. In order to do this, the data of Garcia [6–8] and Dubertret [18] were available, relating microhardness to oxygen content in the titanium–oxygen solid solution; the data of Dubertret were used, assuming an oxygen concentration at the metal–oxide interface of 25 at % [6–8]. The results obtained are presented in Table VIII. The decrease in the amount of oxygen which enters the solid solution on oxidation in air is thus clearly demonstrated.

3.2. The role of aluminium

Microhardness measurements in the metal zone just beneath the oxide for the different alloys oxidized in air at 700° C for the same length of time reveal a reduction in the penetration of oxygen for the alloys containing 3 and 5 wt% aluminium, this reduction being more marked when the aluminium content in the alloy is higher (Fig. 2). These aluminium additions also promote an increase in the hardness of the alloy; however, for 1.65 wt% aluminium content a decrease in the hardness, compared with that of pure titanium, is noted and there also appears to be a very slight increase in the depth of oxygen penetration. In order to clarify the influence of aluminium on the dissolution of oxygen in the metal, an estimate of the amounts of oxygen dissolved was attempted, as for the

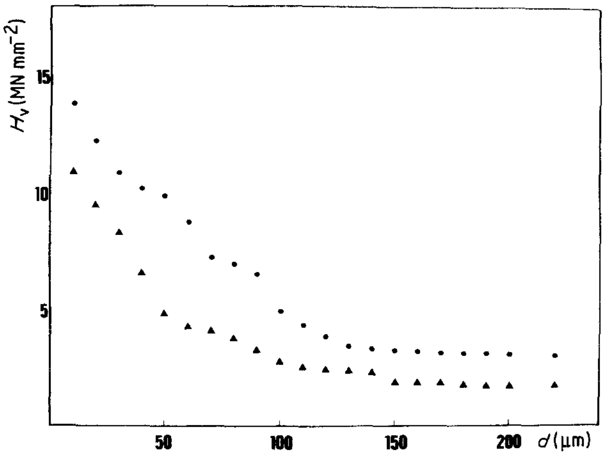

Figure 1 Microhardness of the metallic core plotted against depth, for titanium (Ti35) oxidized in (●) oxygen and in (▲) air (700° C, 435 h).

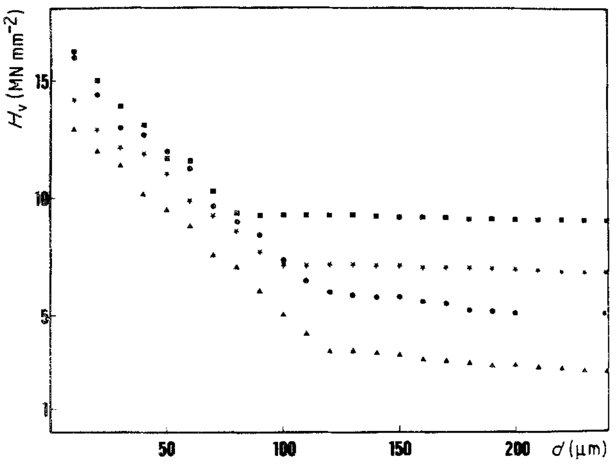

Figure 2 Microhardness of the metallic core plotted against depth, for pure titanium and Ti–Al alloys oxidized in air (700° C, 950 h). (●) Ti35, (▲) TiAl1.65, (★) TiAl3, (■) TiAl5.

previous case of unalloyed titanium, assuming that the hardness–concentration relationship is unaffected by the presence of aluminium. In order to do this, the microhardness profiles of the various alloys were put in line with that of unalloyed titanium by a shift of ordinates. The results obtained are presented in Table IX. It may be noted that the presence of aluminium promotes a decrease in the amount of oxygen dissolved in the metal phase, compared with the case of unalloyed titanium, in relation to the amount of aluminium in the alloy. This result confirms the data found by Rosa [26] who related the oxidation resistance of Ti–Al alloys to the reduction in the amount of oxygen dissolved in the alloy just beneath the oxide layer. However, the values of solubility limits for oxygen in the metal phase reported by Rosa appear surprising [30]. The addition of aluminium to titanium would reduce the solubility of oxygen in titanium from 35 at % to 0.3 at % at 700° C! On the other hand, it appears that the work of Menzies and Strafford [27] on the oxidation behaviour of the TiAl5 alloy in carbon dioxide does not confirm these results. According to these authors the alloy containing 5 wt % aluminium oxidizes more quickly than pure titanium at 1000° C; this behaviour was attributed to the more extensive dissolution of oxygen in the alloy than in the unalloyed titanium, which appears to be in agreement with the observations of Jenkins [28] for the TiAl3 alloy oxidized in oxygen. Recently, in our laboratory, Quach-Kamimura *et al.* [35], using oxygen nuclear microanalysis, compared quantitatively the diffusion profiles of oxygen in pure titanium and in TiAl6 after a diffusion treatment at 750° C for 160 h. Their results clearly showed a decrease in the amount of oxygen dissolved into the metal when aluminium is added.

3.3. The role of chromium

The dissolution of oxygen in the metal zone beneath the oxide is accompanied by phase changes which can be seen in Fig. 3: a progressive transformation of the beta-phase into alpha + TiCr2 is observed in the zone contaminated by oxygen. The microhardness measurements in the metal phase for the different alloys oxidized for the same length of time, 435 h, appear to show a slight reduction in the depth of oxygen penetration as chromium content is increased (Fig. 4). As for the Ti–Al alloys, an attempt was made to determine the amounts of oxygen dissolved in the metal from the microhardness profiles. The results obtained are shown in Table X. It may be seen that the amounts of dissolved oxygen decrease slightly as the chromium content in the alloy increases. Given the atomic size of chromium and its affinity for oxygen, which are similar to those of titanium, and also its beta-forming nature, one might suppose a priori that the dissolution of oxygen in the alloy is not fundamentally changed but that it might be slightly reduced, however, with respect to the pure metal (the oxygen solubility being lower in the beta-phase); this is indeed what is observed. However, this result does not agree with that found by Menzies and Strafford [29]:

TABLE IX Comparison of amounts of oxygen dissolved in the metallic substrate O(S.S.) and fixed in the aggregate O(Tot.) during the oxidation reaction in air and in oxygen (700° C, 435 h) for Ti–Al alloys (±0.05 mg cm^{-2})

Metallic substrate	O(S.S.)(mg cm^{-2})		O(Tot.)(mg cm^{-2})		O(S.S.)/O(Tot.)	
	air	oxygen	air	oxygen	air	oxygen
Ti35	1.99	3.00	4.67	6.33	0.43	0.48
TiAl1.65	2.02		4.63		0.44	
TiAl3	1.91		4.23		0.45	
TiAl5	1.06	1.69	2.18	4.36	0.49	0.39

TABLE X Comparison of amounts of oxygen dissolved in the metallic substrate O(S.S.) and fixed in the aggregate O(Tot.) during the oxidation reaction in air and in oxygen (700° C, 435 h) for Ti–Cr alloys (±0.05 mg cm^{-2})

Metallic substrate	O(S.S.)(mg cm^{-2})		O(Tot.)(mg cm^{-2})		O(S.S.)/O(Tot.)	
	air	oxygen	air	oxygen	air	oxygen
Ti35	1.99	3.00	4.67	6.3	0.43	0.48
TiCr1	1.92		27.16		0.07	
TiCr4	1.89		*		–	
TiCr11	1.86	2.88	*	19.65	–	0.15
TiCr19	1.81		8.02		0.23	

*Unavailable values because the oxide layers scale off at this temperature.

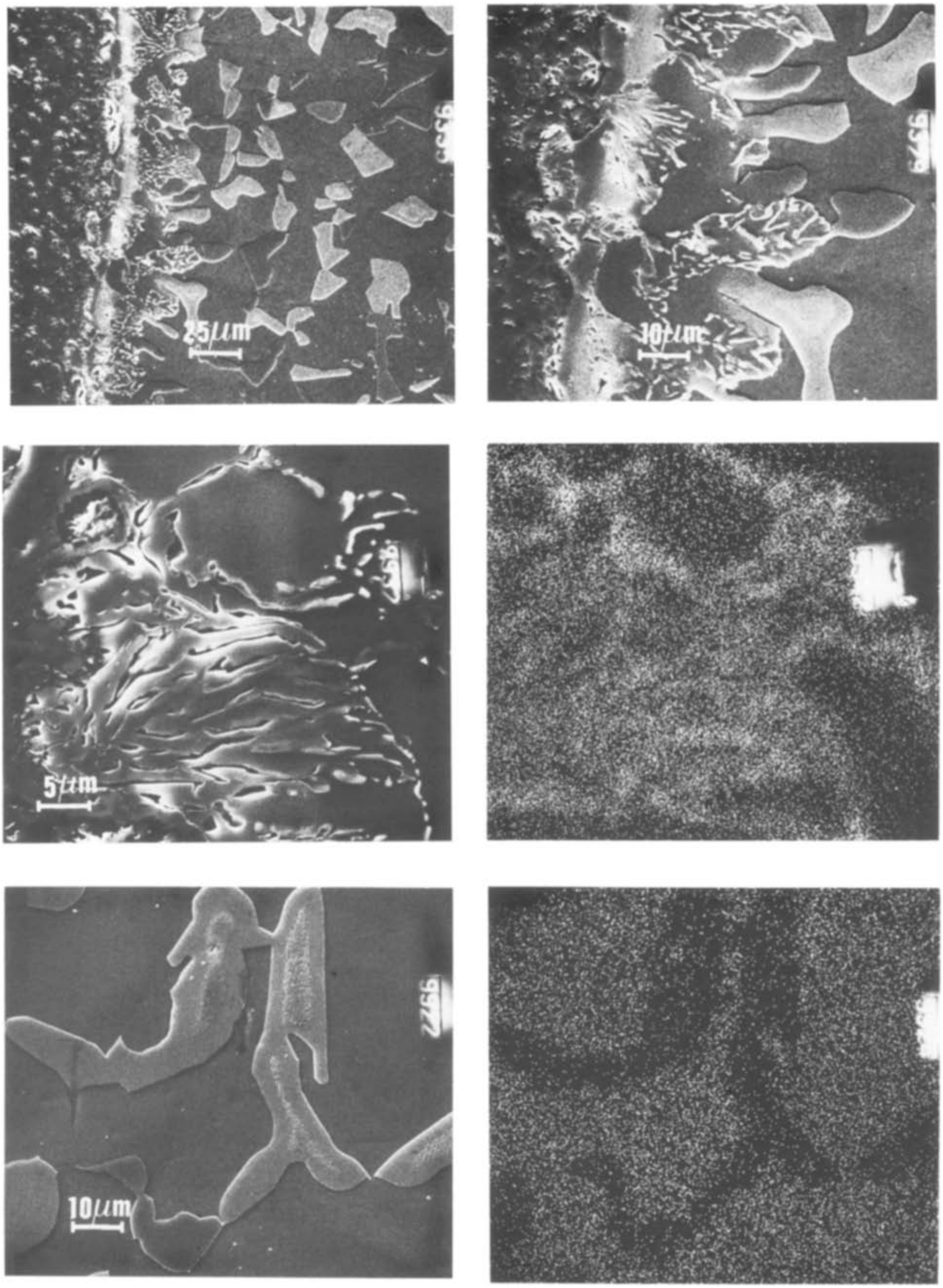

Figure 3 Structure of the metallic zone beneath the oxide for a TiCr11 alloy, oxidized at 700° C, showing the transformation of the beta-phase in alpha + TiCr2 following the oxygen dissolution into the alloy. Cr*Kα* radiation.

according to these authors, the presence of chromium would increase the amount and depth of penetration of the oxygen in the metal phase when compared with unalloyed titanium, the increase being greater as the chromium content in the alloy is increased; the diffusion of oxygen in the substrate being the phenomenon which would control the oxidation rate of the alloys. It should be remembered, however, that the alloys studied by Menzies and Strafford (TiCr5 and TiCr15) were oxidized at 1000° C in carbon dioxide and that their conclusions were based solely on morphological observations. It could appear, therefore,

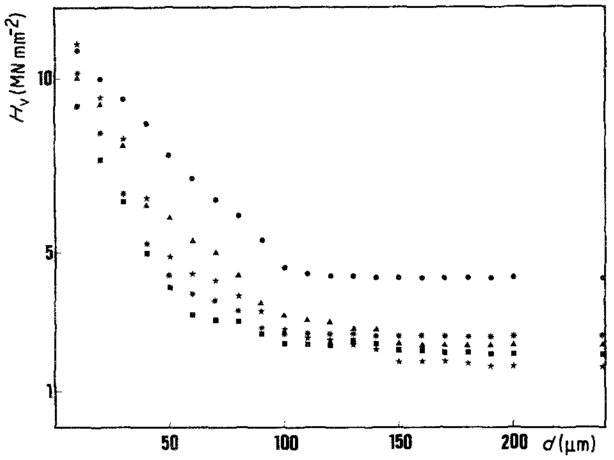

Figure 4 Microhardness of the metallic core plotted against depth, for unalloyed titanium and Ti–Cr alloys oxidized in air (700° C, 435 h). (★) Ti35, (▲) TiCr1, (●) TiCr4, (*) TiCr11, (■) TiCr19.

that they did not take into consideration the presence of carbon which may play a role in the oxidation process of these alloys.

3.4. The role of silicon

In the metal beneath the oxide (and nitride) layer, after an oxidation in air, there is no obvious modification of the initial structure of the alloy (Fig. 5). However, microhardness profiles in the zone contaminated by oxygen (Fig. 6) reveal a significant reduction in the penetration of oxygen for the alloys, this reduction being larger for higher silicon contents. As for the previous cases, an estimate of the amount of oxygen dissolved in the metal was made. Table XI shows the results. It may be noted that silicon, like nitrogen, acts considerably to prevent the dissolution of oxygen into the substrate. In addition, a synergistic effect is observed between the silicon and the nitrogen since the reduction in the amount of oxygen dissolved during the oxidation of TiSi1 in air (86%) is considerably higher than the simple addition of the effects of silicon (66%) and nitrogen (34%) taken separately. This phenomenon is perhaps linked to the presence of titanium nitride detected in the oxide layer for the oxidation of the most highly alloyed composition.

4. Discussion

It was observed that the penetration of oxygen into titanium is influenced by the presence of the alloying elements aluminium, chromium and silicon. We have thus shown that:

1. aluminium promotes a reduction in the amount of oxygen dissolved in the substrate: this reduction is larger when the aluminium content is increased;
2. chromium has virtually no effect on oxygen dissolution: however, this dissolution, which is extensive for unalloyed titanium, appears slightly reduced when the chromium content in the alloy is notably increased;

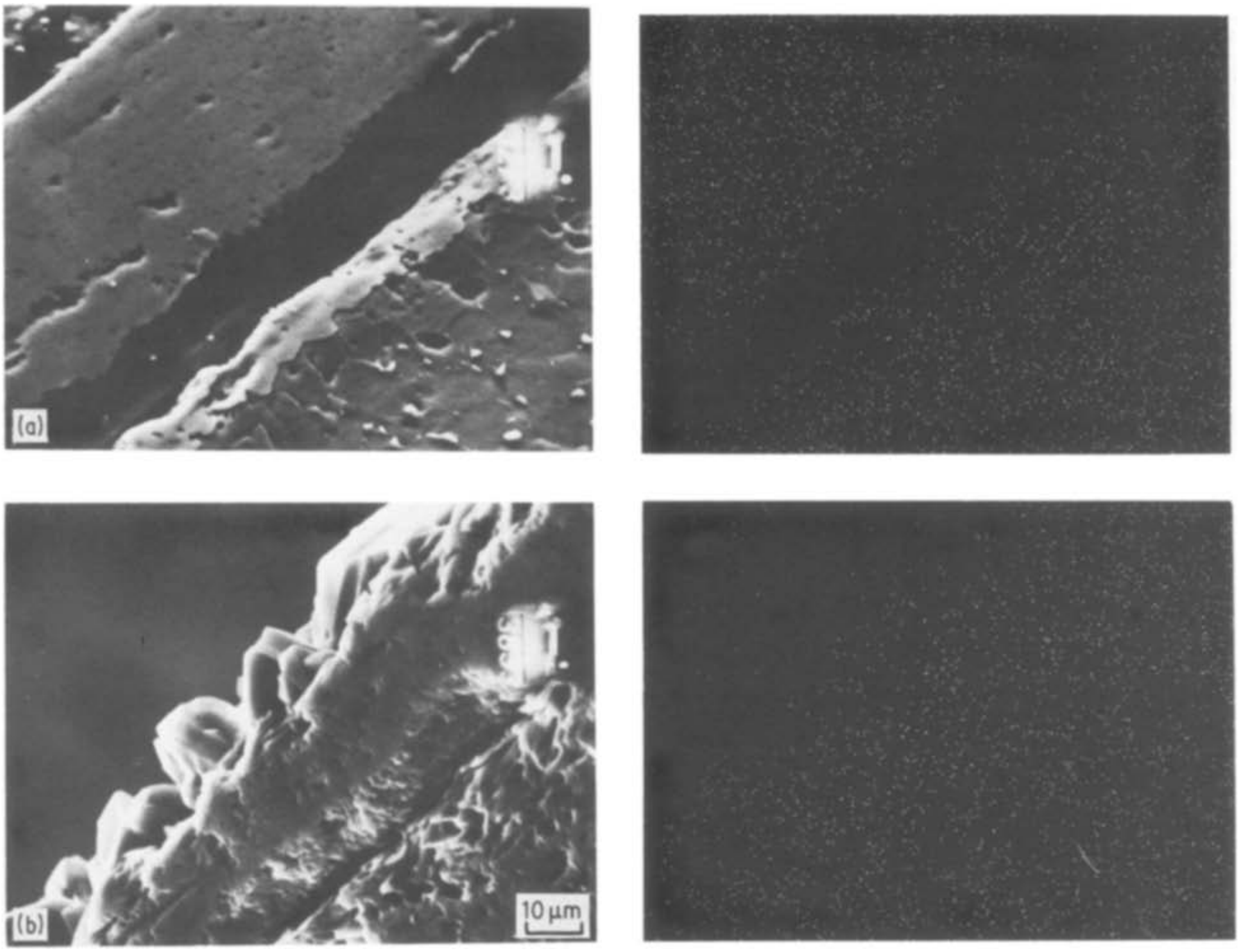

Figure 5 Cross-sections of the oxide layers formed on the TiSi1 alloy oxidized at 850° C: (a) in air, (b) in oxygen; electron micrographs and corresponding X-ray images of the silicon. Si$K\alpha$ radiation.

TABLE XI Comparison of amounts of oxygen dissolved in the metallic substrate O(S.S.) and fixed in the aggregate O(Tot.) during the oxidation reaction in air and in oxygen (700° C, 435 h) for Ti–Si alloys ($\pm 0.05\,\mathrm{mg\,cm^{-2}}$)

Metallic substrate	O(S.S.)($\mathrm{mg\,cm^{-2}}$)		O(Tot.)($\mathrm{mg\,cm^{-2}}$)		O(S.S.)/O(Tot.)	
	air	oxygen	air	oxygen	air	oxygen
Ti35	1.99	3.00	4.67	6.33	0.43	0.48
TiSi0.25	1.01		2.37		0.43	
TiSi0.5	0.74		2.00		0.37	
TiSi1	0.43	1.03	1.30	2.52	0.33	0.41

3. the role of silicon in preventing oxygen dissolution is important and increases with the silicon content; this effect is even more evident in air, when nitrogen is present.

In addition, for the oxidation of pure titanium in air, nitrogen also influences the dissolution of oxygen in the metal phase. In order to simplify comparisons, values of the amounts of oxygen dissolved in the alloys have been normalized taking the value for pure titanium as a reference (Tables XII and XIII). Thus, it may be observed that these values are all less than, or equal to, that for unalloyed titanium (within experimental error: $\pm 0.05\,\mathrm{mg\,cm^{-2}}$).

Given that titanium is the metal likely to give the most extensive solid solution with oxygen (34 at % according to the equilibrium diagram) it is not surprising to note that the addition of alloying elements results in all cases in a decrease in the amount of dissolved oxygen, for the same length of reaction time.

The alpha-forming or beta-forming nature of the alloying elements could be taken into account, since the amount of oxygen dissolved in alpha-titanium and beta-titanium are very different: 34 at % in alpha-titanium and only 4 at % in beta-titanium. As far as the alloying elements considered here are concerned, aluminium is alpha-forming, chromium is strongly beta-forming and silicon is slightly alpha-forming [36]. According to these data one might expect, therefore, a significant reduction in the solubility of oxygen due to chromium, as this element will form an alpha + beta alloy, and practically no change will result from aluminium and silicon additions as the corresponding alloys remain in the alpha-form at the temperatures considered. It is thus not possible to explain this phenomenon simply in terms of the alpha-forming or beta-forming nature of the alloying elements.

On the other hand, the evolution of the size of the titanium cell with respect to the alloying element additions may play an important role. In effect, the elements aluminium, chromium and silicon are in substitution sites in the lattice, whereas oxygen occupies interstitial positions. Now, aluminium causes a contraction of the lattice of alpha-titanium whereas chromium and silicon leave it virtually unchanged [37–39]. The decrease in the volume of the titanium cell following the introduction of aluminium thus causes a reduction in the volume of interstitial sites available to accept oxygen, which could explain the reduction in the amount of dissolved oxygen observed for this type of alloy; however, this phenomenon cannot be proposed to explain the influence of silicon or chromium additions.

From the point of view of metallurgical structures it is observed that silicon, having a very low solubility, forms very fine precipitates of composition Ti5Si3. These very stable precipitates could play a role in slowing the diffusion of oxygen in the alloy.

A marked difference in the penetration of oxygen into the metal phase was observed between a pure oxygen atmosphere and ambient air. Nitrogen thus appears to play a role in the dissolution of oxygen in the metal substrate. There are a number of relevant facts known: nitrogen is present (in the form of nitrides) at the interface after the oxidation of certain alloys [33]; the thermodynamic stability of oxides is distinctly superior to that of nitrides, for titanium; the diffusion coefficient of nitrogen in titanium is about ten times smaller than that of oxygen [19, 40]. One

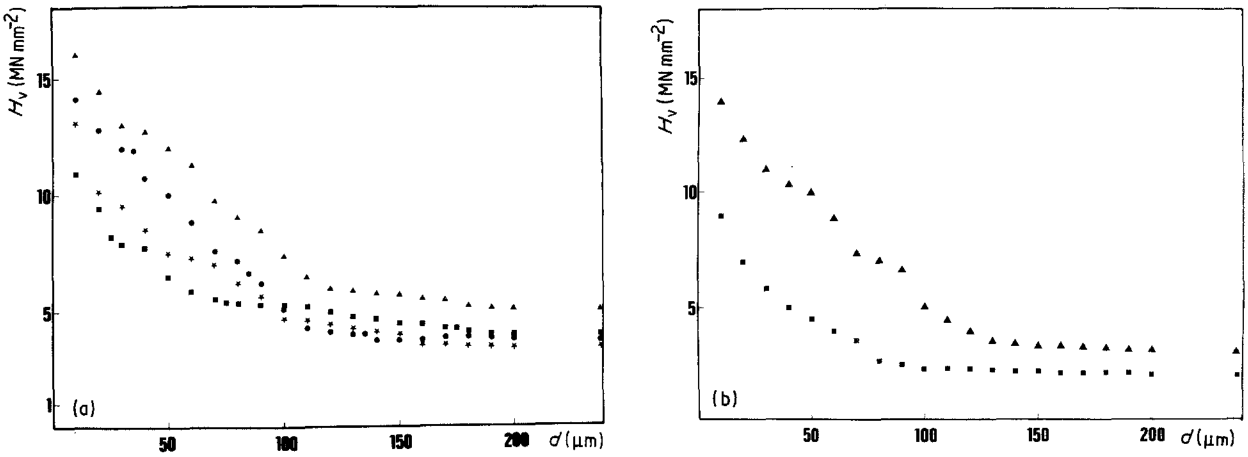

Figure 6 Microhardness of the metallic core plotted against depth, for unalloyed titanium and Ti–Si alloys oxidized: (a) in air (700° C 950 h), (▲) Ti35, (●) TiSi0.25, (★) TiSi0.5, (■) TiSi1. (b) in oxygen (700° C, 435 h), (▲) Ti35, (■) TiSi1.

TABLE XII Comparison of amounts of oxygen dissolved in the metallic substrate O(S.S.), dissolved in the layer O(layer) and fixed in the aggregate O(Tot.) during the oxidation reaction in oxygen at 700° C for the different alloys relatively to the unalloyed titanium

Substrate	O(S.S.)	O(layer)	O(Tot.)	O(S.S)/O(Tot.)
Ti35	1*	1*	1*	0.48†
TiAl5	0.56	0.81	0.69	0.39
TiCr11	0.96	5.08	3.12	0.15
TiSi1	0.34	0.45	0.40	0.41
Ti35 oxidized in air	0.66	0.81	0.74	0.43

*Conventional reference value.

†Ratio obtained from the real values (cf. Tables VIII to XI).

might, therefore, imagine that nitrogen acts to slow the stage of oxygen dissolution at the internal interface by occupying some of the reaction sites.

For alloys, a reduction in the amount of oxygen dissolved in the substrate is also observed for oxidation in air compared with oxidation in oxygen. Table XIV shows clearly that for aluminium and chromium, the effects of the alloying element and of nitrogen are simply additive, while for silicon one observes a marked synergistic effect between the two elements; this fact is probably correlated with the presence of titanium nitride at the internal interface.

5. Conclusion

This study has enabled confirmation to be made of the important role played by the dissolution of oxygen in the metal phase during the oxidation of titanium. The influence of nitrogen and the marked effect of the alloying elements on this phase of the oxidation process has also been revealed. Finally, the "interaction" between nitrogen and one of the alloying elements has been shown. The influence of aluminium on the dissolution of oxygen in the metal phase appears clear and is revealed as a decrease in the amount of oxygen dissolved, this being related to the aluminium content in the alloy. The influence of silicon also results in a significant decrease in the depth of penetration of oxygen into the substrate, accompanied by a synergistic effect between nitrogen and silicon for oxidation in air. On the other hand, the influence of chromium is virtually negligible.

TABLE XIII Comparison of amounts of oxygen dissolved in the metallic substrate O(S.S.), dissolved in the layer O(layer) and fixed in the aggregate O(Tot.) during the oxidation reaction in air at 700° C for the different alloys relatively to the unalloyed titanium

Substrate	O(S.S.)	O(layer)	O(Tot.)	O(S.S)/O(Tot.)
Ti35	1*	1*	1*	0.43†
TiAl1.65	1.02	0.97	0.99	0.44
TiAl3	0.96	0.87	0.91	0.45
TiAl5	0.53	0.42	0.47	0.49
TiCr1	0.96	9.41	5.81	0.07
TiCr4	0.95	?	?	–
TiCr11	0.93	?	?	–
TiCr19	0.91	2.32	1.72	0.23
TiSi0.25	0.51	0.51	0.51	0.43
TiSi0.5	0.37	0.53	0.43	0.37
TiSi1	0.22	0.32	0.28	0.33
Ti35 oxidized in oxygen	1.51	1.23	1.35	0.48

*Conventional reference value.

†Ratio obtained from the real values (cf. Tables XIII to XI).

TABLE XIV Comparison of the simultaneous effects of the nitrogen and of the alloying element on the reduction of the oxygen dissolution in titanium (700° C, 435 h) ($\pm 0.05\,\mathrm{mg\,cm^{-2}}$)

Metallic Substrate	O(S.S.) (oxygen) ($\mathrm{mg\,cm^{-2}}$)	O(S.S.) (air) ($\mathrm{mg\,cm^{-2}}$)	$R1$	$R2$	$R3$	$R4$
Ti	3.00	1.99	0.34	–	–	–
TiAl5	1.69	1.06	–	0.44	0.65	0.63
TiCr11	2.88	1.86	–	0.04	0.38	0.36
TiSi1	1.03	0.43	–	0.66	0.86	0.77

$R1$ = reduction factor observed for the effect of the nitrogen = $(A - B)/A$

$R2$ = reduction factor observed for the effect of the alloying element = $(A - C)/A$

$R3$ = reduction factor observed for the simultaneous effect of nitrogen and alloying element = $(A - D)/A$

$R4$ = reduction factor calculated as a linear combination of $R1$ and $R2 = R1 + R2 - (R1R2)$

where

A = O(S.S.) (Ti/oxygen); B = O(S.S.) (Ti/air);

C = O(S.S.) (alloy/oxygen); D = O(S.S.) (alloy/air)

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