Influence of the Nature of Alloying Elements on the Adherence of Oxide Films Formed on Titanium Alloys

A. M. Chaze* and C. Coddet*

In order to study the influence of aluminum, chromium, and silicon on the adherence of oxide layers to the metallic substrate for binary alloys of titanium, adhesion measurements were carried out and the results were correlated with the oxidation behavior of these materials. Ti–Al, Ti–Cr, and Ti–Si alloys were prepared and oxidized at temperatures of 550–700°C in air and in oxygen, for oxidation times from a few hundred to several thousand hours. The reaction kinetics were followed using continuous thermogravity or daily weighing of samples. For Ti–Al and Ti–Si alloys, a slight decrease in the adherence of oxide layers to the substrate was observed for the lowest aluminum contents (1.65 and 3%) and silicon content (0.25%) as compared with the behavior of unalloyed titanium; at higher levels, the adherence increased with the alloying element content. For Ti–Cr alloys, the addition of chromium increased the adhesion of oxide layers to the substrate for all cases; however, the change in adhesion with chromium content was not monotonic.

INTRODUCTION

In a previous study,[1] the adhesion of oxide films formed on titanium was determined and related to the oxidation behavior of this material. In order to do this, a test was developed in which a tensile force was gradually applied to a stud bonded to the surface of the oxide layer. The adherence of oxide layers to the metal substrate was shown to decrease as the layer thickness increased. In order to study the adhesion as a function of different

*Laboratoire de Métallurgie et Physico-chimie des Matériaux, UA CNRS 849; Université de Technologie de Compiègne BP 233-60206 Compiegne Cédex, France.

parameters such as the temperature or the nature of the oxidizing atmosphere, it is therefore necessary to refer to identical oxide layer thicknesses. This enabled us to conclude, for example, that the adhesion of oxide layers formed on unalloyed titanium, at 550-700°C, decreased when the oxidation temperature increased and that it was greater for oxidation in air than in pure oxygen, which was attributed to the role of nitrogen in the reaction. For titanium and titanium alloys, oxide layers often show a layered structure, the origin of which is attributed, by different investigators,[2-8] to the development of stresses during oxidation. Thus, the development of alloys with better oxidation resistance than that of unalloyed titanium must involve an improvement in the mechanical behavior of the oxide layer and therefore requires a study of the adherence of this layer to the substrate. In this study, alloying elements have been considered that might be expected to form protective surface layers. In effect, the most protective oxides, as far as ionic mobilities are concerned, are alumina, chromia, and silica.[9-11] This work therefore involves the evaluation of the adherence of oxide layers formed on binary alloys of titanium with aluminum, chromium, and silicon.

MATERIALS AND EXPERIMENTAL PROCEDURE

The materials considered in this study—titanium–aluminum alloys with 1.65, 3, 5, and 10% by weight of aluminum; titanium–chromium alloys with 1, 4, 11, and 19% by weight of chromium; and titanium–silicon alloys with 0.25, 0.5, and 1% by weight of silicon (Table I)—were prepared in either nonconsumable electrode or levitation furnaces, from titanium Ti35. The different techniques employed include alloy production, sample preparation, kinetic study of the oxidation reaction, analysis methods, and adherence tests on oxide layers, all of which have been previously described in detail.[1,12-14] The present discussion notes that oxidation reactions were performed in pure oxygen (100 torr) and in air (atmospheric pressure) for temperatures of 550-700°C and for times of a few hundred to several thousand hours.

Table I. Composition and Structures of the Alloys

Alloys	wt.%	Structures
Ti–Al	1.65, 3, 5, 10	α
Ti–Cr	1, 4, 11	$\alpha + \beta$
	19	$\alpha + \beta + \text{TiCr}_2$
Ti–Si	0.25, 0.5, 1	$\alpha + \text{Ti}_5\text{Si}_3$

EXPERIMENTAL RESULTS

The primary aim of the experimental measurements was to establish the role of the oxidation time (oxide layer thickness), of the nature of the oxidizing atmosphere (air or oxygen), and of temperature on the adherence of oxide layers to the metal substrate. A second objective was to determine correlations between the results obtained and the kinetics behavior and/or the morphological characteristics of the oxide layers.

The adherence measurements were carried out after cooling of the samples and for samples that had generally undergone cooling cycles imposed by the gravimetric method used to determine the oxidation kinetics. However, some measurements taken on samples oxidized under isothermal conditions showed that, for the range of experimental conditions studied here, the thermal cycling imposed by the gravimetric method had no marked effect on the values of the failure stress.

In general, it may be stated that, for all the alloys as well as for pure titanium, the adherence of oxide layers (1) decreased as the oxidation time (hence the oxide layer thickness) increased (Figs. 1 and 2); (2) was dependent on the nature of the oxidizing atmosphere, so that the adhesion was greater for oxide layers formed in air than for those formed in pure oxygen (Table II); and (3) was a function of oxidation temperature; however, in order to evaluate this dependence, the behavior of the different alloys must be compared for identical oxide thickness, which is particularly difficult, as temperature plays an important role in the oxidation rate of the alloy. Thus, for practical reasons, the comparisons were made only for samples oxidized at two different temperatures (Table III). It is thus apparent that the change in adhesion with temperature is quite dependent on the nature of the alloying element: for Ti–Cr alloys, the adhesion increased when the temperature increased, in contrast to the case of unalloyed titanium.[1] For Ti–Al and Ti–Si alloys, however, over the range examined, there was virtually no change in the adherence of oxide layers with temperature. Thus, each of the three alloying elements studied has a particular influence specific to the amount of the element added.

Role of Aluminum and Silicon

For identical oxidation times and a given temperature, aluminum and silicon improve the adhesion of the oxide layers, this improvement being greater as the alloying element content is increased (Fig. 3a,b). However, given the important influence of the amount of the alloying element content on the oxidation rate, the change in the oxide-layer adherence is presented as a function of the layer thickness (Fig. 4a,b), which permits a clearer assessment of the influence of these alloying elements on the adherence.
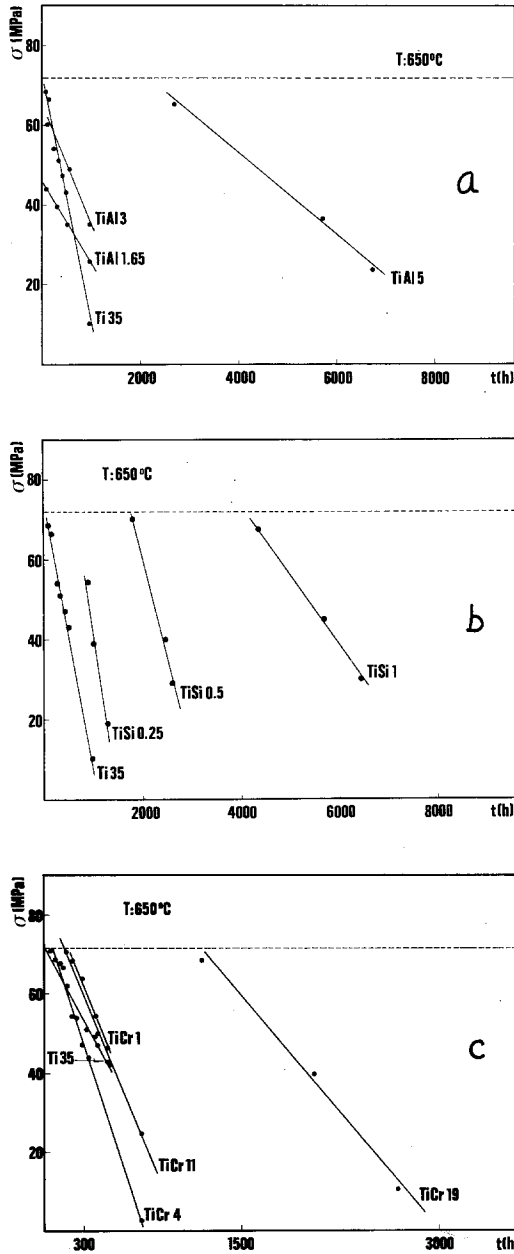
Fig. 1. Dependence of fracture stress of the metal–oxide assembly as a function of oxidation time in air. (a) Ti–Al alloys. (b) Ti–Si alloys. (c) Ti–Cr alloys.
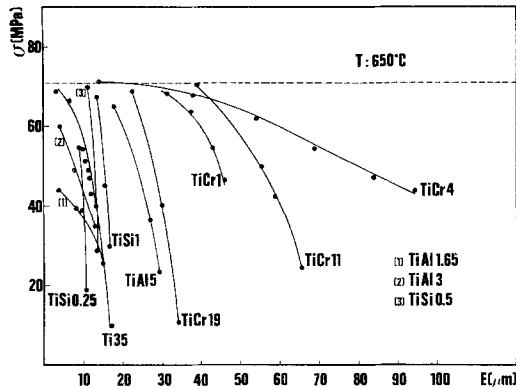
Fig. 2. Dependence of fracture stress of the metal–oxide assembly as a function of oxide-layer thickness for unalloyed titanium and different alloys oxidized in air.

Thus, it may be seen that for oxide layers formed at 650°C (1) the addition of aluminum for low aluminum contents (1.65 and 3%) tends to reduce slightly the adherence of the layer compared with unalloyed titanium, and to increase it for 5% aluminum; and (2) the addition of silicon initially increased the adherence, but this improvement disappeared when the oxide-layer thickness reached 10 μm; however, this limit tends to increase as the silicon content increases.

Table II. Comparison of Fracture Stress (±5 MPa) of the Metal–Oxide Assembly Obtained for Oxide Layers Formed in Air and in Pure Oxygen up to the Same Weight Gain

	Fracture stress (MPa)		Oxidation conditions	
Alloys	Air	O_2	°C	Δm (mg · cm^{-2})
TiCr1	68	40	650	5
TiCr4	70	45	650	2.4
TiCr11	50	30	650	1.2
TiCr19	>75	52	700	7.2
TiAl1.65	40	22	650	1.9
TiAl3	60	48	650	1.15
TiSi0.25	>75	60	650	1.6
TiSi0.5	25	0	700	3
TiSi1	74	50	700	2

Table III. Comparison of Fracture Stresses (± 5 MPa) of the Metal-Oxide Assembly Obtained
for Oxide Layers Formed in Air

Alloys	Oxidation conditions					
	600°C		650°C		650°C	700°C
	Δm_1 (mg·cm^{-2})	(MPa)	(MPa)	Δm_2 (mg·cm^{-2})	(MPa)	(MPa)
TiCr1	4.3	38	>75	9	46	69
TiCr4	4.4	41	70	7.5	60	>75
TiCr11	1.75	70	>75	7	50	>75
TiCr19	3.88	25	40	8	0	>75
TiAl1.65	3	27	30	6.5	0	0
TiAl3	2	53	49	6.1	0	6
TiAl5	6	30	36.5	3.2	70	65
TiSi0.25	2.3	20	19	2.95	0	5
TiSi0.5	3	73	70	2.9	32	25
TiSi1	4	50	45	2	80	74
Ti35	—	—	—	1.65	58	4

Role of Chromium

The influence of chromium content cannot be represented by a monotonic relationship with adhesion (Fig. 3c). In fact, compared with titanium, a low-chromium addition led to a slight increase in adhesion (for a given temperature and oxidation time), which decreased from around 4% and then increased again strongly beyond 11%. However, if the considerable influence of the chromium content on the oxidation rate is again taken into account, it may be seen that, for identical oxide thicknesses, the chromium addition increased the layer adhesion for all cases (Fig. 4c), the maximum improvement being observed for 4% chromium.

DISCUSSION

As for the case of unalloyed titanium,[1] for the three alloys Ti–Al, Ti–Cr, and Ti–Si oxidized in air or in oxygen, the adherence was observed to decrease rapidly as the layer thickness increased, which could result from a buildup of stresses with thickness. It was shown previously that oxide layers always exhibit a duplex structure (Fig. 5) with an inner layer (thick and microcrystalline) and an outer layer (with columnar grains) and also that the relative thicknesses of these inner and outer sublayers change with time, temperature, and the nature of the alloying element.[12-14] In the case
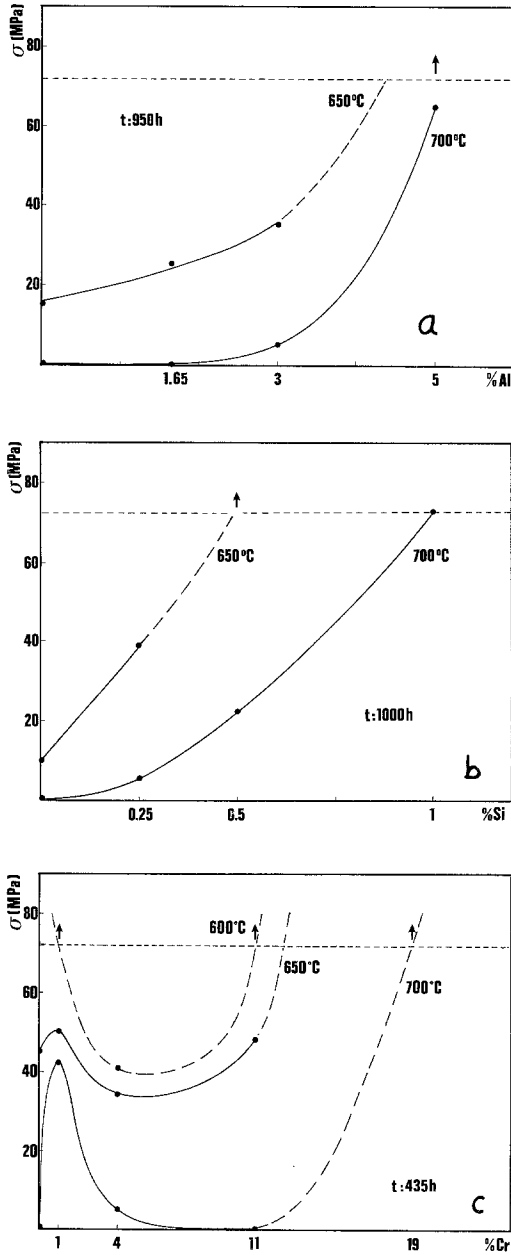
Fig. 3. Dependence of fracture stress of the metal–oxide assembly as a function of alloying-element content. (a) Ti–Al alloys. (b) Ti–Si alloys. (c) Ti–Cr alloys.
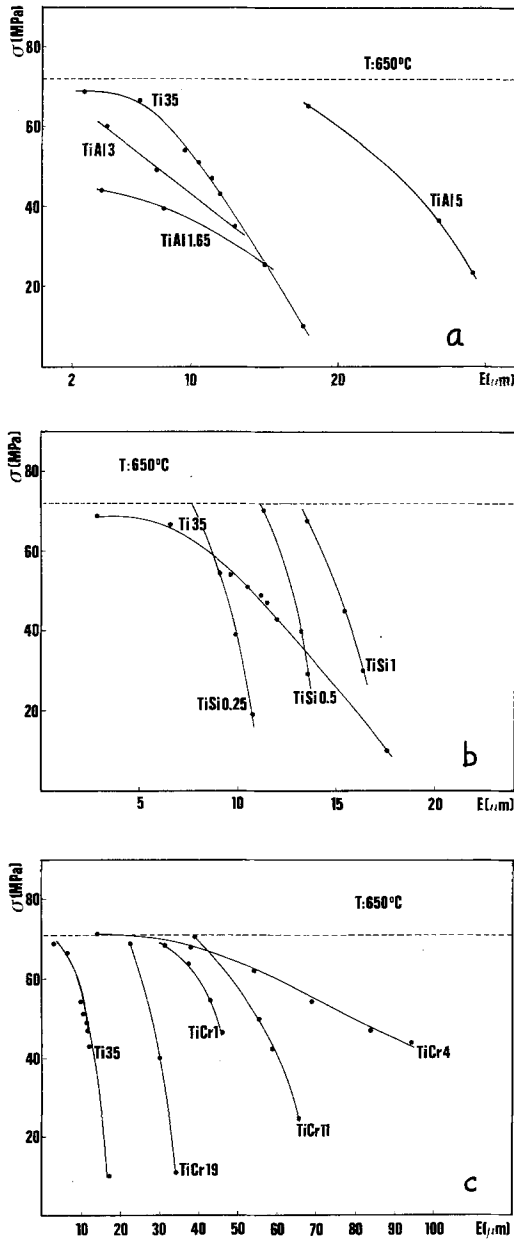
Fig. 4. Dependence of fracture stress of the metal–oxide assembly as a function of oxide-layer thickness for unalloyed titanium and alloys oxidized in air. (a) Ti–Al alloys. (b) Ti–Si alloys. (c) Ti–Cr alloys.
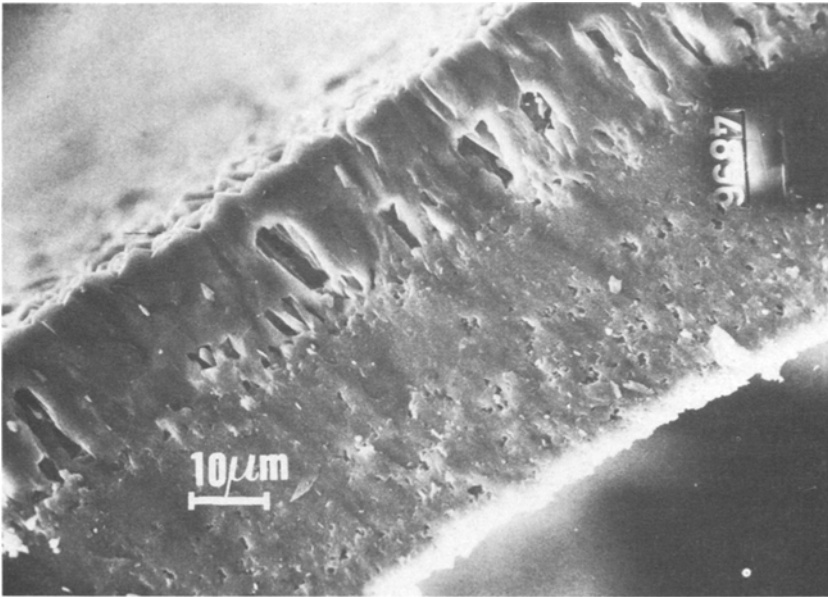
Fig. 5. Transverse section of an oxide layer formed on a TiCr4 alloy at 700°C.

of aluminum[12] and silicon,[14] the growth of the outer sublayer was attributed mainly to a recrystallization process of the inner layer, while in the case of chromium[13] it was attributed to an increase in the rate of cationic diffusion. If one considers the adhesion of oxide layers to be strongly dependent on the stress state in the metal-oxide system (stress growth and stress relaxation), one should observe a certain correlation between the residual adherence of the layers and the ratio of the external E_{ext} to the internal E_{int} sublayer thicknesses. This is indeed the case, as shown in Fig. 6 where, for clarity and ease of calculation, the change of the thickness of the total layer corresponding to a given adherence of 45 MPa is a function of the ratio E_{ext}/E_{tot}. Thus, it seems clear that the adherence is strongly affected by the growth mode of the layer (large difference between Ti-Cr and Ti-Si or Ti-Al alloys). For chromium, the addition of this element promotes an important partial growth of the oxide layer at the oxide-gas interface. This should result, compared with unalloyed titanium, in a reduction of the stress level for a constant layer thickness; therefore, we observe the absence of stratification of the inner layer and improved adhesion of the oxide to the metal substrate.

For aluminum and silicon, the generally accepted growth mode of titanium oxide in the temperature range considered (i.e., by inward oxygen
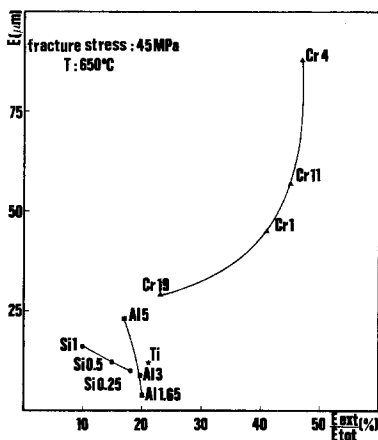
Fig. 6. Dependence of total thickness of the oxide layer, corresponding to a fracture stress of 45 MPa, as a function of the ratio of the external sublayer E_{ext} to the total oxide layer E_{tot} thicknesses.

diffusion) does not seem to be notably affected. From structural observations, it was deduced[12,14] that the relaxation of stresses under isothermal conditions, in the temperature range considered here, occurs mainly by grain-boundary sliding, recrystallization, and eventually fracture. As shown in Fig. 6, the recrystallization process appears to be hindered by the addition of aluminum and silicon to titanium; we therefore believe that the existence of a two-phase system for the higher concentration alloys, i.e., the presence of silica and alumina,[12,14] could promote a relaxation of stresses by grain-boundary sliding. This mechanism would be consistent with the observation of a reduction in either the porosity or (depending on the oxidation temperature) the stratification, of the oxide layer, or both, as well as an increase in the adhesion of the layer to the metal. These effects increase with increasing alloying content. It may be noted as well that the equivalent volume of alumina, lower than that of rutile, results in an overall expansion coefficient for the oxide, which is lower than that for unalloyed titanium. From this viewpoint, an increase in aluminum content in the alloy is favorable.

CONCLUSIONS

In this study the adherence of thermal oxide films formed on titanium-base alloys has been evaluated and related to the oxidation behavior of these alloys. It has been shown that the adhesion of oxide layers to the metal substrate always decreased considerably when the oxidation time or the oxide thickness increased. On the other hand, the change of adherence with oxidation temperature is complex, as it depends on the nature of the alloying element. These alloying elements influenced the oxidation kinetics,

thereby modifying the thickness of oxide layers for a given oxidation time. Thus, it is necessary, in order to compare their influence on the mechanical behavior of the oxide layers, to refer to identical oxide thicknesses. Under these conditions, it has been established, first, that chromium additions, for all concentrations studied here, resulted in improved adherence of the layers, which may be related mainly to a modification of the growth mode of the oxide layer; and second, that aluminum and silicon, with respect to unalloyed titanium, slightly decreased the adherence of the oxide layers to the metal substrate for low contents and increased it for higher contents, this behavior being attributed to the role of second-phase particles on the grain-boundary sliding process.

REFERENCES

1. C. Coddet, A. M. Chaze, and G. Beranger, *J. Mater. Sci.* **22** (1987).
2. E. A. Garcia, *Met. Corros. Ind.* **638**, 329-341 (1978).
3. M. Dechamps, J. Desmaison, and P. Lefort, *J. Less-Common Met.* **71**, 177 (1980).
4. F. Motte, C. Coddet, P. Sarrazin, M. Azzopardi, and J. Besson, *Oxid. Met.* **10**(2), 113 (1976).
5. C. Coddet, P. Sarrazin, and J. Besson, *J. Less-Common Met.* **51**, 1-12 (1977).
6. C. Coddet, J. F. Chrétien, and G. Beranger, *Titanium and Titanium Alloys, Scientific and Technological Aspects*, Vol. 2, Williams and Belov, eds. (Plenum, New York, 1982, pp. 1097-1105).
7. Y. Adda and J. Philibert, *La diffusion dans les solides*, Vol. II (Presses Universitaires de France, Paris, 1966).
8. R. J. Brook, J. Yee, and F. A. Kroger, *J. Am. Ceram. Soc.* **54**(9), 445 (1971).
9. F. A. Kroger, *High Temp. Corros. NACE* **6**, 89-100 (1983).
10. A. M. Chaze, C. Coddet, and G. Beranger, *J. Less-Common Met.* **83**, 49 (1982).
11. A. M. Chaze and C. Coddet, *Oxid. Met.* **21**(3/4), 205 (1984).
12. A. M. Chaze and C. Coddet, *Oxid. Met.* **27**, 1 (1987).
13. G. Beranger and C. Coddet, *J. Microsc. Spectrosc. Electron.* **5**, 793 (1980).