Measurements of the adhesion of thermal oxide films: application to the oxidation of titanium

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The residual adhesion of titanium oxide films to the metal substrate has been measured, by tensile tests, after cooling of samples of titanium Ti35, oxidized in air and in oxygen at temperatures between 550 and 700° C. Adhesion measurements were then correlated with the oxidation behaviour. These results reveal the important roles of oxidation temperature and thickness of the oxide layer, as well as the significant influence of nitrogen on oxidation in air, on the adhesion of the oxide layers to the metallic substrate.

1. Introduction

The behaviour in corrosive environments of materials used at high temperatures may not be understood by simply considering transport phenomena in the corrosion layer or in the metal immediately below it: it is also necessary to take into account the mechanical properties of the metal–oxide system, properties which play an important role in the performance of these materials. In effect, the corrosion layers can only form a diffusion barrier, and thus act as protective layers, if they are continuous and remain on the substrate. The role of the behaviour of these layers is particularly important for titanium and titanium alloys, for which the oxide layers show a characteristic stratification phenomenon. Thus, when oxidation takes place in oxygen and at temperatures above 700° C, a sucession of sublayers of regular thickness (between 2 and 5 μm) [1–4] is observed; this thickness depending on the temperature and the oxidation atmosphere [5]. This stratification phenomenon is generally attributed to a sudden relaxation of the stresses caused by the oxide growth [2–7]. In effect, during the growth of oxide films under isothermal conditions, several factors may induce stresses in the films or in the adjacent metal [8–14]. Among the more important parameters the ratio of Pilling and Bedworth, the epitaxial relationship between the oxide and the metal, and the variations in the oxide or metal composition during oxidation may be noted [14]; this last phenomenon is particularly revelant for titanium and more generally for all metals of the periods IVA and VA which can accommodate the dissolution of large quantities of oxygen as interstitial solid solution.

The possible modes of stress relaxation are numerous and depend on several factors, particularly the temperature. Thus the stresses may be released by plastic deformation of the oxide and/or of the adjacent metal or by structural modifications such as recrystallization [14]. However, the stresses, if they are large, are likely to cause a macroscopic disturbance of the oxide film such as debonding or cracking; the latter resulting if the adhesion of the film to the substrate is relatively strong. This influence of the stresses may be revealed by a detailed study of the structure of the metal–oxide interface and of its evolution with oxidation conditions (time, temperature, atmosphere) [15, 16]. In general, according to Hindam and Whittle [16], it is essential, in order to clarify the mechanism by which oxide films adhere to the substrate, to understand how the stress distribution and stress relaxation are influenced by the morphology of the metal–oxide interface and the mechanical properties of the oxide layers. For example, it has been shown recently that the magnitude of the compressive stresses developed in the oxide layer formed on nickel depends on the initial sample surface preparation and therefore on the geometry of the metal–oxide interface [17].

In this work, the mechanical properties of the metal–oxide interface have been studied by an evaluation of the adhesion of the oxide films to the substrate using a tensile test consisting of the application of an increasing tensile load to a stud bonded to a surface of the oxide layer. However, the fracture observed may be adhesive, cohesive or a mixture of these; only in the first case may an estimate of the failure stress of the metal–oxide interface be made. The tensile tests must therefore be accompanied by metallographic observations.

2. Materials and experimental procedure

The composition of the unalloyed titanium Ti35 (tensile strength 350 MPa) considered in this study is given in Table I. The technique used to prepare samples, the oxidation procedure and the different methods used to examine and analyse the oxide layers have already been described in detail elsewhere [18–20]. It will simply be noted here that the samples were prepared in the form of parallelepiped plates and polished on wet silicon carbide paper to grade 1000 (18 μm). The oxidation reactions were performed at temperatures between 550 and 700° C and followed either by continuous thermogravimetry for maximum oxidation times of about 500 h in oxygen, or by daily weighing

TABLE I Titanium Ti35 composition

	O_2	H_2	N_2	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	0.060	0.045	0.006

of samples oxidized in air for durations of a few hundred to a several thousand hours; the latter conditions are near to those which the material or its alloys might encounter in service in turbine engines. The residual adhesion of the oxide layers to the substrate was measured, after cooling of oxidized samples, by debonding of these layers using the tensile test described above [21]. The method used was as follows: small studs of 3 mm diameter covered with an epoxy resin were fixed using a clip (Fig. 1) to the surface of the oxide layer. This assembly was placed in an oven at 150°C for 1 h to polymerize the adhesive. The clip was then removed and the assembly (oxidized sample-bonded stud) tested in a tensile microtesting machine. These assemblies allow a maximum fracture stress of around 75 MPa to be measured. Given that the adhesion thus determined may depend on the quality of the bond, each test was repeated several times for each sample in order to allow a satisfactory acceptable value to be obtained. Given the size of the specimen, ten measurements were taken for each case.

3. Results and discussion
3.1. Influence of measuring conditions
The majority of the results were obtained for titanium samples oxidized discontinuously in air. Because the samples were removed from the oven to be weighed after cooling, their true oxidation time was thus reduced in comparison with the isothermal conditions; however, this reduction was determined to be about 2% which is negligible given the long oxidation periods studied (several thousand hours). The periodic cooling of samples due to the discontinuous gravimetric measurements may, in fact, affect the mechanical strength of the oxide layers due to the stresses caused by the thermal cycling. In effect, it has been shown that during repeated cooling of a specimen there is a considerable acoustic activity suggesting that irreversible modifications of the layer take place [22, 23]. In order to evaluate the influence of this thermal cycling on the adhesion of the oxide films to the metal substrate, comparative measurements were made after an oxidation in air under isothermal conditions. The different tensile tests performed showed that the thermal cycling caused by the discontinuous gravimetric method had no significant effect on the values measured, at least for the times studied here (Table II). Thus, this result justifies the use of the

methodology of carrying out tests on samples which have undergone some thermal cycling.

3.2. Effect of temperature
The evolution of the metal–oxide adhesion strength, as a function of oxidation temperature, was studied for samples of titanium oxidized discontinuously in air, for a given weight increase. It may first be noted that, for temperatures below 650°C, the adhesion strengths of oxide layers are relatively high while they tend towards zero from 700°C (Fig. 2). In parallel, the structure of the oxide layers also evolves with temperature. In effect, over the temperature range considered, the oxide layer is generally observed to consist of two distinct sub-layers having different appearances: an external sub-layer consisting of large columnar crystals, and an internal sub-layer in contact with the metal, thick and microcrystalline, and layered when the temperature exceeds 700°C; this layer often includes numerous aligned voids. These two sub-layers are separated from each other by a large amount of aligned pores, the size of which appears to increase with temperature (Fig. 3). The relative thicknesses of these sub-layers also evolves with temperature; thus the relative size of the external sub-layer increases from 550 to 650°C and then decreases, becoming very small over 700°C, when the internal sub-layer is stratified (Fig. 4).

3.3. Effect of oxidation time
The study of the evolution of the adhesion strength of the oxide layers formed on titanium as a function of time shows that the adhesion decreases significantly as the oxidation duration increases (Fig. 5). This evolution may be linked to that of the structure of the layer as a function of oxidation duration. In effect, as may be seen in Fig. 6a, the total thickness of the layer and the thickness of the internal sub-layer formed in air at 650°C increase with time according to an approximately parabolic law, whereas the external sub-layer thickness grows rather linearly; thus, at the start of the reaction, the oxide layer consists largely of the internal sub-layer and then the relative importance of the external sub-layer increases with time (Fig. 6b) suggesting a growth process by recrystallization which is in agreement with previous results [24–27]. It should, however, be noted that, from a mechanical
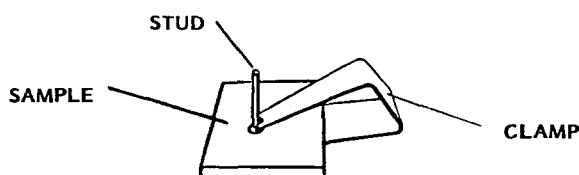

Figure 1 Principle of sample-stud assembly.

TABLE II Comparison in isothermal and thermal cycling conditions of the fracture stress ($\pm$ 5 MPa) of the oxide layers formed in air on titanium

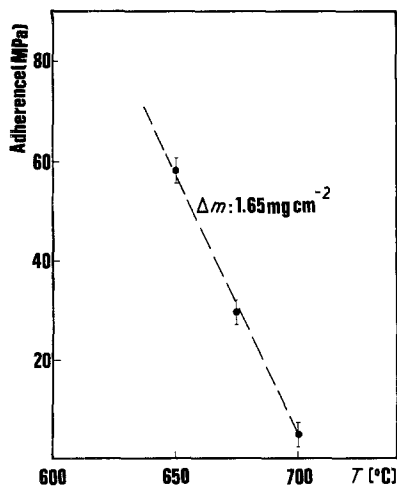|	Isothermal conditions	Thermal cycling
650°C, 150 h	66	70
650°C, 240 h	54	50
700°C, 72 h	4	0

Figure 2 Evolution of the oxide scale adherence (fracture stress) as a function of the oxidation temperature in air for unalloyed titanium, for a weight gain of $1.65\,\mathrm{mg\,cm^{-2}}$.

TABLE III Comparison of the fracture stress ($\pm 5\,\mathrm{MPa}$) of the oxide layers formed on unalloyed titanium in air and in oxygen at different temperatures

Oxidation conditions	Air	O$_2$
$600°\,C$, $\Delta m = 0.9\,\mathrm{mg\,cm^{-2}}$	75	56
$650°\,C$, $\Delta m = 1.7\,\mathrm{mg\,cm^{-2}}$	54	37
$650°\,C$, $\Delta m = 2.5\,\mathrm{mg\,cm^{-2}}$	43	28
$700°\,C$, $\Delta m = 0.9\,\mathrm{mg\,cm^{-2}}$	64	49
$700°\,C$, $\Delta m = 1.4\,\mathrm{mg\,cm^{-2}}$	39	20

whereas it is virtually instantaneous at a temperature of 700° C, thus showing the role of the structure of the scale. Moreover, it is interesting to note that this effect is probably only related to the relative organization of the oxide crystals because the temperature does not seem to affect the crystal size if one considers similar weight gains (Fig. 8).

3.4. Influence of the oxidizing atmosphere

The measurements of the residual adhesion of the oxide layers to the substrate were also perfomed in a comparative manner in air and in oxygen. The results obtained, for identical weight increases at a given temperature (Table III), show that the adhesion of the layers is in all cases greater for samples oxidized in air than for those oxidized in oxygen. It should be noted that the weight increases measured in air are always lower than those measured in oxygen for identical temperatures and oxidation times. Moreover, the temperature range for which the kinetics are approxi-
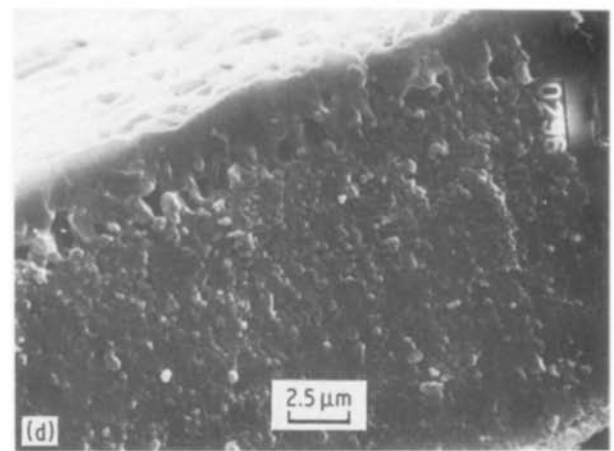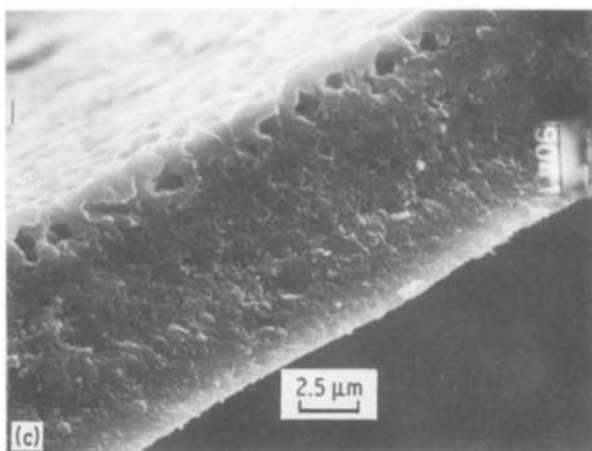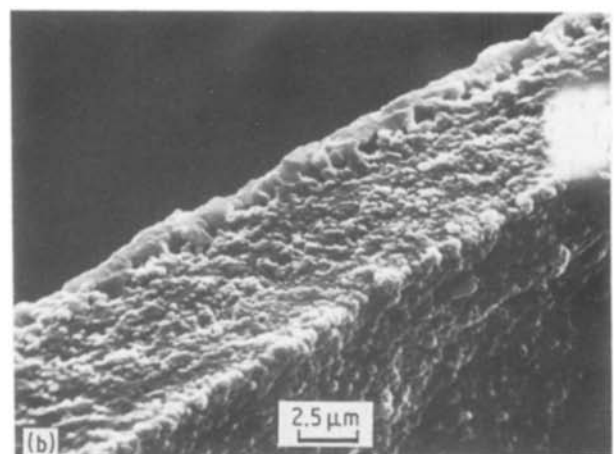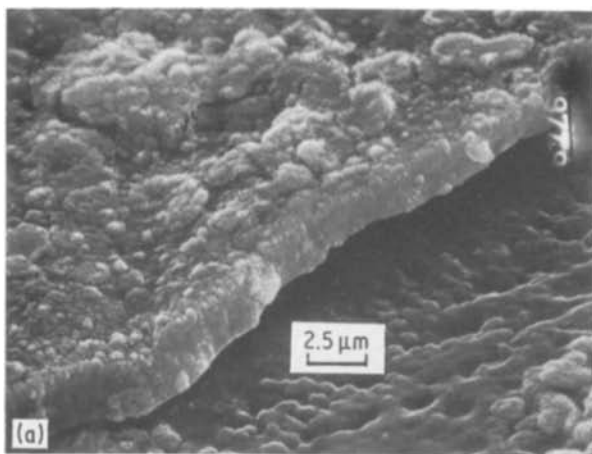
point of view, the comparison of the behaviour of oxide layers of different thicknesses is not valid. For this reason the evolution of the adhesion of the oxide layers has also been presented as a function of their thickness (Fig. 7); the reduction in the adhesion of the layers when their thickness increases is thus clearly quantified. The effect of temperature, independently of its role on the oxidation rate, is still important because the reduction in adhesion only becomes marked beyond a thickness of 5 to 7 μm at 650° C,

Figure 3 Cross-sections of oxide layers formed on titanium at different temperatures in air. (a) 550° C, (b) 600° C, (c) 650° C, (d) 700° C.
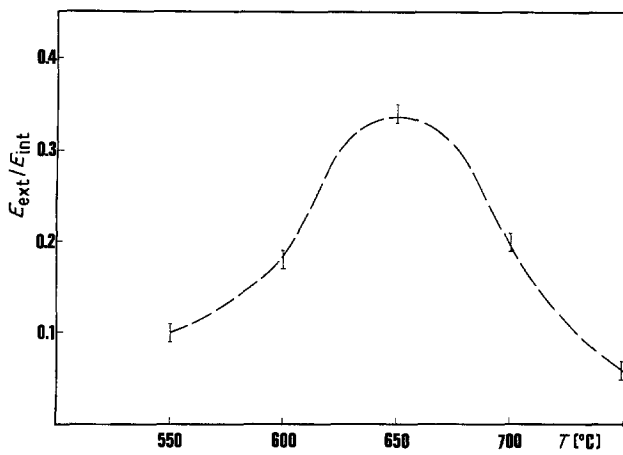
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Figure 4 Ratio of the external to the internal sub-layer thicknesses as a function of temperature for unalloyed titanium oxidized in air, for 1200 h.
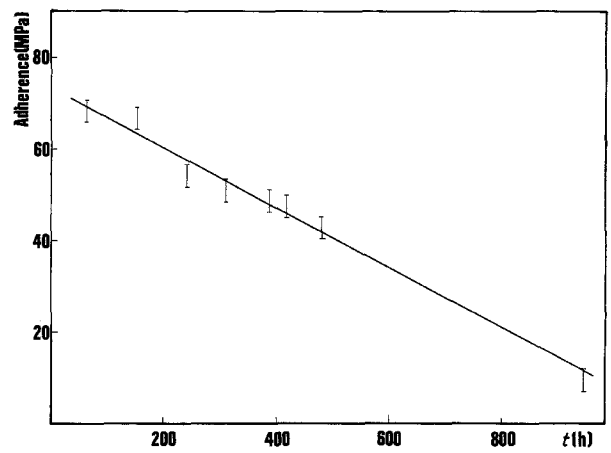

Figure 5 Evolution of the oxide scale adherence (fracture stress) as a function of the oxidation time in air for unalloyed titanium oxidized at 650° C.

mately parabolic is larger for oxidation in air in comparison with oxidation in oxygen: in air, an increase in the value of the activation energy for the reaction is also noted, to a value $(214 \, kJ \, mol^{-1})$ which tends towards that found for the nitriding reaction of titanium [28]. As far as the structure is concerned, the stratification of the oxide layers, which is seen when the oxidation is performed in oxygen, is not observed after oxidation in air. This phenomenon could possibly be related to the presence of some water vapour, which is also known to influence the morphology of these oxide layers [1].

3.5. General behaviour

Overall, the results show that the mechanical behaviour of the oxide layer depends on several factors, and in particular the thickness and the structure of the layer and thus on the temperature and oxidation time as well as on the nature of the oxidizing atmosphere. Our measurements confirm the observations of Feldman et al. [24–26] who noted qualitatively that the oxide layers formed on titanium are very adherent to the substrate up to a given thickness which decreases as temperature increases. The fact that adhesion decreases rapidly with increasing thickness of the

oxide layers appears to be in agreement with the fact that the stresses associated with the oxide growth should increase as the thickness increases. From structural observations, it may be deduced that the release of stresses under isothermal conditions, for the range of temperatures considered, takes place by grain-boundary sliding and recrystallization; and just as for the adhesion, these two mechanisms depend equally on the layer thickness and the temperature. The reduction in adhesion as a function of temperature and in particular the adhesion tending to zero from 700° C is in agreement with the structural observations because the stratification of the layer is observed above 700° C. This result indicates a definite correlation between adhesion and the structure of the oxide layers.

As far as the nature of the oxidizing atmosphere is concerned, the nitrogen plays a role in reducing the oxidation rate. In effect, for oxidation in air, principally in the presence of oxygen and nitrogen, if the water vapour is ignored in a first approximation, the rate of growth of the oxide layer is reduced with respect to that observed in oxygen. The stress level attained in oxide layers of identical thickness seems lower than that reached during oxidation in oxygen, this being revealed by the absence of stratification and
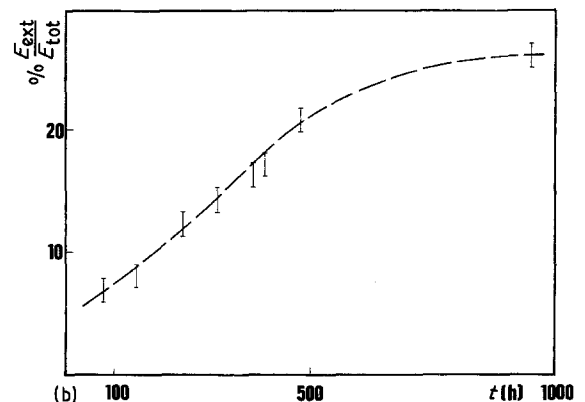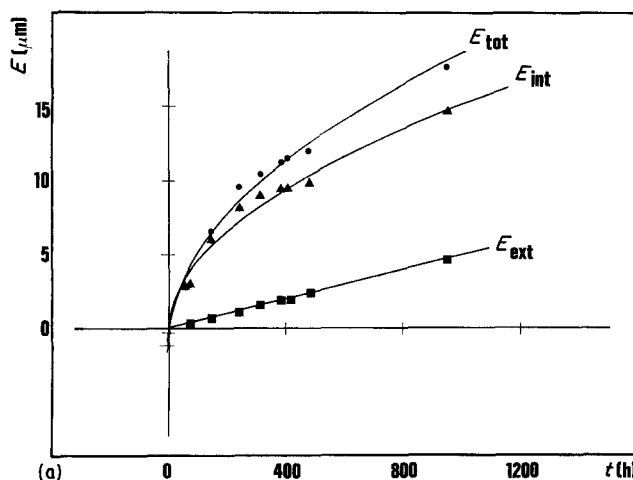

Figure 6 (a) Evolution, as a function of the oxidation time in air at 650° C, of the respective thicknesses of the internal and external sub-layers and of the total thickness of the oxide layers formed on titanium. (b) Ratio of the external sub-layer to the total oxide layer thicknesses as a function of oxidation time, for unalloyed titanium oxidized in air at 650° C.
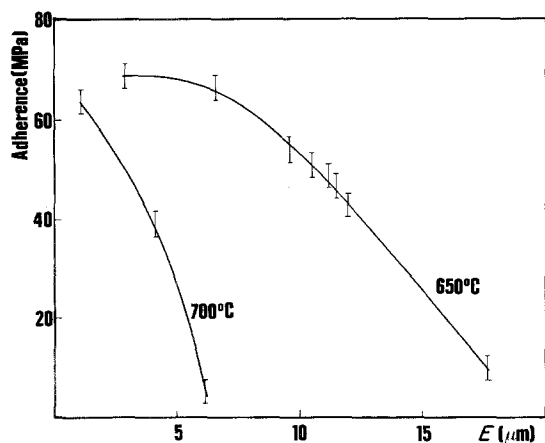
Figure 7 Evolution of the oxide scale adherence (fracture stress) as a function of the oxide scale thickness for unalloyed titanium oxidized at 650° C and 700° C in air.

Figure 8 Evolution of the oxide crystal size plotted against oxidation temperature for a same weight gain of $0.68\,mg\,cm^{-2}$.

by an improved residual adhesion of the oxide to the metal substrate. In addition, for oxidation in air, as noted previously, the temperature range over which a parabolic kinetic law applies is extended towards higher temperatures compared with the range for oxidation in oxygen [29], which indicates the improved protective properties of the oxide layer. This result agrees with the work of Morton and Baldwin [30] who noted that the transition from parabolic to linear kinetics is considerably delayed in air compared with oxygen. The activation energy associated with the oxidation process in air is of the same order of magnitude as that for nitriding of titanium, which suggests a significant influence of nitrogen on the oxidation mechanism, this influence being also confirmed by the fact that a decrease in the proportion of oxygen entering in solution into the metal is observed for oxidation in air [31].

The role of nitrogen might be explained by the formation of a thin layer of titanium nitride at the metal–oxide interface similar to that revealed during the oxidation in air of Ti–Si alloys [20]. This layer could modify the process of accumulation and/or release of stresses in the oxide layer, causing a low porosity level. The migration of oxygen into the voids would thus be reduced, which would encourage the extension of parabolic kinetics.

4. Conclusion

The relationship between the residual adhesion of thermal oxide films formed on titanium and the oxidation behaviour of this material has been studied. It is well known that several parameters can modify the accommodation of the stresses developed during the oxidation of a metal and consequently play an important role in maintaining the protective properties of oxide layers. Among these parameters we have studied the temperature, oxidation duration, thickness of the oxide layer and the nature of the oxidizing atmosphere.

The results show that the adhesion of the oxide layers to the metal substrate decreases as the layer thickness increases. The mechanical behaviour of the oxide layers thus depends on their thickness. However, the temperature, in addition to its effect on the
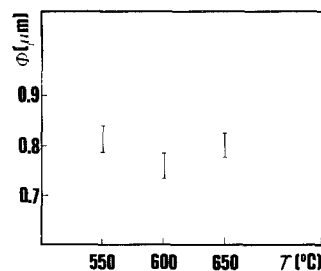
plasticity of the layers, also influence the kinetics and therefore modifies the thicknesses of these layers over a given time. In all cases, before comparisons are made, the results should hence be referred to identical oxide thicknesses. It was also shown that for equal weight increases, the adhesion of oxide layers decreases when the oxidation temperature increases, despite the increase in oxide plasticity. In addition, adhesion is greater for oxidation in air than in pure oxygen which illustrates the significant influence of nitrogen on the process. Moreover the study of the internal, external and total oxide layers thicknesses as a function of temperature, of oxidation time and of the composition of the oxidizing atmosphere, has allowed us to show the close correlations between oxide growth rates, structure and adhesion of oxide layers.

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