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The growth of protective ultra-thin alumina layers on γ -TiAl(111) intermetallic single-crystal surfaces

V. Maurice^{a,*}, G. Despert^{a,b}, S. Zanna^a, P. Josso^b, M.-P. Bacos^b, P. Marcus^a

^a Laboratoire de Physico-Chimie des Surfaces, CNRS (UMR 7045), Université Pierre et Marie Curie, Ecole Nationale Supérieure de Chimie de Paris, 11 rue Pierre et Marie Curie, 75231 Paris Cedex 05, France

^b ONERA, Département Matériaux Métalliques et Procédés, BP 72, 29 avenue de la Division Leclerc 92322 Châtillon Cedex, France

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Abstract

An XPS and AES study of the early stages of oxidation of γ -TiAl(111) surfaces at 650 °C under 1.0×10^{-7} - 1.0×10^{-6} mbar O₂ is reported. The data evidence a first regime of oxidation characterized by the growth of a pure alumina layer followed by a second regime of simultaneous oxidation of both alloying elements. In the first regime, continuous alumina layers from ~ 0.4 to ~ 1.5 nm thick have been observed by angle-resolved XPS. The composition of the metallic phase underneath the growing oxide is modified by a depletion of Al and the injection of Al vacancies in the metal during the growth of the transient alumina formed at 650 °C. The onset of Ti oxidation was repeatedly observed for a critical concentration in the modified region of the alloy underneath the alumina layer: $Ti_{75\pm2}Al_{25\pm2}$ $(Ti_{50}Al_{17\pm2}V(Al)_{33\pm2})$, showing that decreasing the number of Ti–Al bonds in the modified intermetallic region increases the activity of Ti up to a critical point where its oxidation at the oxide/metal interface becomes competitive with that of Al. The growth of Ti^{3+} and Ti^{4+} oxide particles observed above the alumina layer by angle-resolved XPS indicates the transport of titanium cations trough the alumina layer and their subsequent reaction with oxygen at the outer gas/oxide interface. Improving structural ordering in the intermetallic phase slows down the growth kinetics of the alumina layer and the related Al-depletion of the substrate, and increases the resistance of the alloy to the subsequent oxidation of Ti. This is assigned to two combined effects: a slower diffusion of Al in the better ordered metallic phase and the growth of less defective alumina layers allowing to slow down the ionic transport through the oxide. Highly stable and corrosion resistant alloy surfaces covered by a 0.4 nm thick alumina layer have been obtained by slowly oxidizing the alloy at lower partial pressure ($\leq 5.0 \times 10^{-10}$ mbar O₂). © 2005 Elsevier B.V. All rights reserved.

Keywords: X-ray photoelectron spectroscopy; Intermetallics; Aluminium oxide; Titanium oxide; Corrosion; Protection; Single crystal surfaces; Surface defects

* Corresponding author. Tel.: +33 1 44276736; fax: +33 1 46340753. E-mail addresses: vincent-maurice@enscp.fr (V. Maurice), philippe-marcus@enscp.fr (P. Marcus).

1. Introduction

The use of lightweight TiAl intermetallic alloys in aeronautic applications is partly limited by their low resistance to high temperature corrosion (their mechanical properties is also a key issue). This is due to the growth of mixed oxide layers forming by competitive oxidation of the Ti and Al alloying elements [1-5], which prevents the formation of a continuous and dense α -alumina that would provide a more effective oxidation barrier in high temperature applications. In order to better understand the oxidation properties of these alloys, several studies of the initial stages of oxidation of the γ -TiAl intermetallic phase have been carried out on polycrystalline surfaces [6-12]. At room temperature, oxidation was reported to be preceded by the dissociative adsorption of oxygen, which was proposed to occur preferentially on the Ti atoms [7]. Titanium oxidation was observed afterwards and preceded aluminium oxidation [7,12]. The oxide was reported to be Ti(II) species [10]. For 100 °C < T < 600 °C, the simultaneous growth of titanium and aluminium oxides was reported [8,10,11] with the Ti(II), Ti(III), Ti(IV) and Al(III) oxidation states [10,11]. The amounts of Ti(II) and Ti(IV) decreased and increased with increasing temperature, respectively [10]. At 850 °C, the oxidation of aluminium was reported to precede the oxidation of titanium. Only Ti(IV) and Al(III) were observed in the following stage of simultaneous oxidation of the two alloying elements [9].

In this paper, we report a study of the initial stages of growth of the oxide layers at 650 °C on (111)-oriented γ -TiAl single-crystal surfaces. X-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES) were used. The sample was exposed to controlled doses of gaseous oxygen at low pressure ($P(O_2) = 1.0 \times 10^{-7} - 1.0 \times 10^{-6}$ mbar). The composition and thickness of the oxide layers as well as the modifications of the alloy substrate surface underneath the growing oxide scale were analysed by angle-resolved XPS. The results emphasize the effect of surface ordering on the mechanism of selective oxidation of the alloy to form a protective ultra-thin layer of alumina.

2. Experimental

2.1. Materials

The γ -TiAl single-crystal used in this study was supplied by Pr. Masaharu Yamaguchi (Department of Materials Science and Engineering, Kyoto University, Japan). Its bulk composition was $Ti_{49}Al_{51}$ (at%) corresponding to the γ phase. The chemically ordered structure of the y-TiAl intermetallic is based on a FCC lattice of parameter a = 0.402 nm. The stacking sequence along the [001] axis alternates pure Al or Ti atomic planes, thus creating a very small asymmetry along the c axis (c = 0.406 nm instead of 0.402 nm). The crystal was oriented along the [111] direction within $\pm 1^{\circ}$ as controlled by X-ray Laüe back diffraction. Each (111)-oriented plane is stoichiometric (Ti₅₀-Al₅₀) and alternates close-packed rows of Ti and Al. The surface was prepared by mechanical polishing with SiC paper down to a final grade of 4000 (4 μ m) for the XPS study and further with diamond paste down to 0.25 µm for the AES study. Afterwards, the sample was cleaned ultrasonically with acetone and ethanol and then thoroughly rinsed and dried before mounting on the sample holders for in situ treatments and analysis.

2.2. In situ surface preparation

Most oxidation experiments and analyses were performed in a VG ESCALAB Mark II spectrometer (VG Scientific). After introduction in the XPS preparation chamber, the surface was further treated by five cycles of Ar⁺ ion bombardment of 15 min and subsequent annealing (20 min) under the residual pressure of the UHV chamber $(\sim 5 \times 10^{-10} \text{ mbar})$. Bombardment with Ar⁺ ions $(P(Ar) = 1 \times 10^{-6} \text{ mbar})$ accelerated at 3 keV and giving a sample current of 100 µA was used to eliminate the presence of light contaminants (O, C and N). Annealing at 800 °C was used to eliminate the traces of Ar and C detected after ion bombardment and to re-crystallize the surface. During the last cycle, a milder ion bombardment treatment $(P(Ar) = 1 \times 10^{-6} \text{ mbar}, 3 \text{ keV}, 3 \mu \text{A}, t = 15 \text{ min})$ was performed and the surface was flash-annealed between 900 and 1000 °C. This last treatment at higher temperature was necessary in order to eliminate the residual traces of carbon (assigned to titanium carbide [13]) always observed after sputtering and/or annealing at 800 °C. An uptake of oxygen (mostly due to surface segregation from the bulk) was always observed after annealing in UHV. The analysis of the trace amounts of oxygen observed after preparation revealed the presence of two surface oxygen species adsorbed on the surface and of oxygen dissolved in the sub-surface [13,14].

The oxidation experiments were performed by background filling the UHV chamber to $P(O_2) =$ 1×10^{-7} mbar after setting the sample temperature at 650 °C. At the end of the exposure, oxygen inlet and sample heating were simultaneously stopped. The surface was cooled down to room temperature for analysis. The oxidation kinetics was measured by XPS by performing cumulative oxidation steps from 20 s up to a total time of 210 min. Their recording was ended when the metallic components corresponding to the substrate alloy could no longer be observed in the Ti 2p and Al 2p spectra due to the attenuation of the photoelectrons by the oxide scale. Different series of measurements were performed by varying the total pre-annealing time of the substrate before oxidation (110, 200, 350 and 550 min).

2.3. XPS analysis

The XPS analyses were performed using the Al K α X-ray source (1486.6 eV). Survey spectra were recorded with a pass energy of 100 eV and high resolution spectra of the Al 2p, Ti 2p and O Is core level regions were recorded with a pass energy of 20 eV. Angle-resolved measurements were performed by varying the take-off angle from 90° to 40° (angle of the analysed photoelectrons with respect to the surface plane). Peak fitting allowing to decompose the XPS spectra in different components assigned to different surface species was performed using the ECLIPSE software and a Shirley background. The procedure was established on reference spectra obtained on well-defined samples [13].

3. Results

3.1. Selective oxidation of aluminium

Fig. 1 shows a selection of spectra characteristic of the evolution of the Al 2p, O 1s and Ti 2p core level regions during the first 71 min of oxidation of the γ -TiAl(111) sample (pre-annealed for a total period of 110 min). The Al 2p spectrum consists of two peaks as revealed by the curve fitting shown in Fig. 2. The first peak, at a binding energy (BE) of 72.2 eV, is also observed before oxidation and



Fig. 1. XPS spectra of the Al 2p, O 1s and Ti 2p core levels for the γ -TiAl(111) sample exposed to $P(O_2) = 1.0 \times 10^{-7}$ mbar at 650 °C for 0, 2, 16 and 71 min.



Fig. 2. Curve fitting of the XPS Al 2p and Ti 2p spectra for the γ -TiAl(111) sample exposed to $P(O_2) = 1.0 \times 10^{-7}$ mbar at 650 °C for 2 min.

corresponds to the metallic signal of the substrate (Al_{2p}^0) . The second peak located at 75.5 eV is growing with increasing exposure to oxygen and corresponds to oxidised aluminium (Al_{2p}^{3+}) , in good agreement with previous observations on similar substrates [10,11,15–17]. The O 1s spectrum shows the growth of one peak centered at a BE of 532.1 eV assigned to the anions of the growing oxide layer (O_{1s}^{2-}) . At 2 min of oxidation, the Ti 2p spectrum remains unchanged, showing no higher BE component that could correspond to Ti(II), Ti(III) or Ti(IV) oxidation states. It consists of the two peaks at 454.4 and 460.6 eV (see Fig. 2 for curve fitting), corresponding to the $2p_{3/2}-2p_{1/2}$ spin-orbit doublet (intensity ratio of 2:1) for the metallic signal of the substrate $(Ti_{2p3/2}^0 and$ $Ti_{2p1/2}^{0}$, respectively). After longer exposures (>3 min, see below), the Ti 2p spectra show the growth of the additional higher BE components characteristic of the oxidation of titanium. At 71 min of exposure (following pre-annealing for 110 min), the two peaks at 454.6 and 460.6 eV, corresponding to the $2p_{3/2}-2p_{1/2}$ spin-orbit doublet for the metallic state Ti_{2p}^{0} , are strongly attenuated by the oxide layer. Instead, two sets of 2 peaks at 457.5 eV/463.2 eV and 459.6 eV/ 465.2 eV are observed, that are characteristic of the $2p_{3/2}-2p_{1/2}$ spin-orbit doublet for the Ti(III) and Ti(IV) oxidation states, respectively [8] (the curve fitting is described further on). At 71 min, the O 1s peak is centred at a BE of 531.4 eV characteristic of O^{2-} anions in titanium oxides [8], indicating a predominant growth of titanium oxides at this point. These spectra evidence a transient stage of selective oxidation of the alloy to form a pure alumina layer prior to the competitive oxidation of titanium, in agreement with the results obtained for polycrystalline samples [9,13,14].

The thickness, *d*, of the alumina layer can be calculated from the intensity ratio of the Al_{2p}^{3+} and Al_{2p}^{0} signals with:

$$\begin{split} d &= \lambda_{\mathrm{Al}_{2p}}^{\mathrm{Al}_{2D}} \times \sin \theta \\ &\times \ln \left[1 + \frac{I(\mathrm{Al}_{2p}^{3+})}{I(\mathrm{Al}_{2p}^{0})} \times \frac{D_{\mathrm{Al}}^{\mathrm{TiAl}}}{D_{\mathrm{Al}}^{\mathrm{Al}_{2D}}} \times \frac{\lambda_{\mathrm{Al}_{2p}}^{\mathrm{TiAl}}}{\lambda_{\mathrm{Al}_{2p}}^{\mathrm{Al}_{2D}}} \right], \end{split}$$

where $\lambda_{Al_{2p}}^{Al_{2O_3}}$ ($\lambda_{Al_{2p}}^{TiAl}$) is the attenuation length of the Al_{2p} photoelectrons in the oxide layer (substrate), θ the take-off angle of the photoelectrons with respect to the surface plane, and $D_{Al}^{Al_2O_3}$ the atomic concentration of aluminium in the oxide layer [13]. D_{Al}^{TiAl} is the concentration of aluminium in the modified alloy underneath the oxide (see below). In this expression, it is assumed that the oxide layer is continuous and has an homogeneous thickness. Fig. 3 shows the equivalent thickness of the alumina layer obtained after 2 min of exposure to oxygen (for the sample pre-annealed for 110 min) calculated from the XPS spectra recorded at various take-off angles θ . The measured value is constant, which confirms the model of a continuous oxide layer.

Fig. 4 shows the evolution of the equivalent thickness of the alumina layer with increasing exposure to oxygen after pre-annealing time periods of 110, 200, 350 and 550 min. The plot is limited to the stage of selective oxidation during



Fig. 3. Equivalent thickness of the alumina layer and modified concentration of the underlying metallic phase as a function of the take-off angle θ for the γ -TiAl(111) exposed to $P(O_2) = 1.0 \times 10^{-7}$ mbar at 650 °C for 2 min.



Fig. 4. Kinetics of growth of the alumina layer on γ -TiAl(111) exposed to $P(O_2) = 1.0 \times 10^{-7}$ mbar at 650 °C. Four series of measurements performed after pre-annealing for (a) 110 min, (b) 200 min, (c) 350 min and (d) 550 min are shown. The inset shows the first 9 min of oxidation.

which no titanium oxide particles are detected in the oxide layer. In all series, the thickness of the alumina layer increases rapidly after the first exposure to oxygen to reach 0.7–0.8 nm after less than 3 min of exposure, and levels off afterwards to reach 1.3–1.5 nm at the most. This range of thickness is typical for the alumina layers formed under UHV conditions on other aluminide alloys (NiAl) [16–22]. It amounts to oxide films consisting of 3–7 monolayers of oxide. The effect of the pre-annealing time is discussed further on.

The composition of the modified alloy region underneath the oxide, D_{Al}^{TiAl} , and $D_{Ti}^{TiAl} = 1 - D_{Al}^{TiAl}$,

can be calculated from the intensity ratio of the Ti_{2p}^0 to Al_{2p}^0 signals (assuming an homogeneous depth distribution in the metallic phase) with:

$$\frac{I(\mathrm{Ti}_{2p}^{0})}{I(\mathrm{AI}_{2p}^{0})} = \frac{T_{\mathrm{Ti}_{2p}}}{T_{\mathrm{Al}_{2p}}} \times \frac{\sigma_{\mathrm{Ti}_{2p}}}{\sigma_{\mathrm{Al}_{2p}}} \times \frac{\lambda_{\mathrm{Ti}_{2p}}^{\mathrm{TiAl}}}{\lambda_{\mathrm{Al}_{2p}}^{\mathrm{TiAl}}} \times \frac{1 - D_{\mathrm{Al}}^{\mathrm{TiAl}}}{D_{\mathrm{Al}}^{\mathrm{TiAl}}}$$
$$\times \left[\frac{\exp\left(\frac{-d}{\lambda_{\mathrm{Ti}_{2p}}^{-d} \times \sin\theta}\right)}{\exp\left(\frac{-d}{\lambda_{\mathrm{Al}_{2p}}^{-d} \times \sin\theta}\right)}\right],$$

where $T_{\text{Ti}_{2p}}(T_{\text{Al}_{2p}})$ and $\sigma_{\text{Ti}_{2p}}(\sigma_{\text{Al}_{2p}})$ are the transmission factor and photoionisation cross section of the Ti_{2p} (Al_{2p}) electrons, respectively [13]. D_{Al}^{TiAl} is the concentration of aluminium in the modified alloy region underneath the oxide. Fig. 3 shows the Al concentration calculated from measurements at various take-off angles of the photoelectrons, after 2 min of exposure to oxygen (i.e., below the 0.8 nm alumina film). The measured values are lower than 50 at%, showing that the metallic phase underneath the oxide layer is depleted in Al, which is consistent with the selective oxidation of the alloy. Since the escape depth of the photoelectrons ($\approx 3 \times \lambda \times \sin \theta$) decreases with decreasing take-off angle, the decrease of the average value of the Al concentration with decreasing take-off angle indicates that the Al depletion is limited to the nearest substrate layers below the metal/oxide interface and that there is a concentration gradient.

Fig. 5 shows the evolution of the composition of the modified alloy region underneath the growing oxide layer. The relative concentration in Al $(\tilde{D}_{Al}^{TiAl} + D_{Ti}^{TiAl} = 1)$ is plotted. A decrease of the Al concentration is observed, from 50 at%, measured prior to oxidation, to 25 ± 2 at% measured at the end of the stage of selective oxidation (i.e., before the oxidation of titanium). The fact that this decrease is observed shows that the growth of the oxide is too fast to allow the metallic phase to re-homogenize, Al being consumed too rapidly by the growth of the oxide. This indicates that the growth of the alumina layer is limited by the diffusion of Al to the metal/oxide interface, and not by its diffusion in the oxide layer (the transient alumina formed in this temperature regime is



Fig. 5. Changes of the composition of the modified alloy region underneath the alumina layer for γ -TiAl(111) exposed to $P(O_2) = 1.0 \times 10^{-7}$ mbar at 650 °C. Four series of measurements performed after pre-annealing for (a) 110 min, (b) 200 min, (c) 350 min and (d) 550 min are shown.

growing predominantly by outward cation diffusion [23,24]).

3.2. Onset of Ti oxidation

The detection of the onset of oxidation of titanium was based on angle-resolved XPS measurements. Fig. 6a and b show the superposition of Ti 2p spectra measured at 90° and 45° take-off angles after 3 and 4 min of exposure to oxygen, respectively. For titanium oxides growing above the metallic substrate, the corresponding higher BE components of the Ti 2p signal must increase at lower take-off angles, for which the signal is more surface sensitive. This is not the case after 3 min of oxidation (the two spectra nearly perfectly superimpose (Fig. 6a)), whereas after 4 min of oxidation (Fig. 6b), the spectrum obtained at 45° take-off angle reveals a significant increase on the high BE side of the peaks, suggesting the growth of titanium oxide particles at the surface of the alloy and therefore the onset of oxidation of titanium.

In Fig. 7 we have plotted the full width at half maximum (FWHM) of the experimental Ti $2p_{3/2}$ peak as a function of $d \times \sin \theta$, i.e., the distance in the aluminium oxide that the collected photoelectrons must go through. The two series of measurements performed at 90° and 45° during the



Fig. 6. Ti 2p XPS spectra recorded at 90° and 45° take-off angle for the γ -TiAl(111) sample exposed to $P(O_2) = 1.0 \times 10^{-7}$ mbar at 650 °C for 3 min (a) and 4 min (b). The spectra obtained after background subtraction are shown.



Fig. 7. Full width at half maximum of the Ti $2p_{3/2}$ peak measured at 90° and 45° take-off angles during the initial stages of oxidation of the γ -TiAl(111) sample exposed to $P(O_2) = 1.0 \times 10^{-7}$ mbar at 650 °C.

growth of the oxide layer are shown. The thickness, d, of the alumina layer was obtained as de-

scribed above. It can be seen that the two series of measurements superimpose up to a value of $d \times \sin \theta = 0.9$. The increase of the FWHM (i.e., broadening of the Ti 2p signal) observed up to this point is assigned to the inelastic scattering of the photoelectrons through the alumina layer, increasing with increasing thickness of the oxide. Above $d \times \sin \theta = 0.9$, the two series of measurements in Fig. 7 diverge, indicating that the broadening of the Ti $2p_{3/2}$ cannot then be explained by the increase of the inelastic scattering only, but also corresponds to the growth of titanium oxides at the surface This confirms the onset of oxidation of titanium since the thickness of 0.9 nm was attained after 3 min of oxidation (for the sample pre-annealed for 110 min). Note that above the onset of Ti oxidation the thickness of the alumina layer still increases indicating the simultaneous oxidation of the two alloying elements.

Fig. 8 shows the curve fitting of the Ti 2p XPS spectrum obtained after 16 min of exposure of the γ -TiAl sample to oxygen. It can be seen that the experimental curves can be fitted by 3 sets of $2p_{3/2}-2p_{1/2}$ peaks (2:1 intensity ratio) at 454.6 and 460.6 eV, 457.5 and 463.2 eV, and 459.6 and 465.2 eV. These 3 sets correspond to the Ti(0), Ti(III) and Ti(IV) oxidation states, respectively [8]. Their observation evidences the transient growth of Ti³⁺ oxides after the onset of oxidation of titanium. After prolonged exposure to oxygen, the formation of Ti⁴⁺ oxides was found to dominate.



Fig. 8. Curve fitting of the XPS Ti 2p spectrum for the γ -TiAl(111) sample exposed to $P(O_2) = 1.0 \times 10^{-7}$ mbar at 650 °C for 16 min.

Angle-resolved measurements were also used to elucidate the location of the nucleation and growth of the titanium oxides: below the alumina layer (oxide/metal interface) or at the alumina surface (gas/oxide interface). Assuming the growth of two distinct continuous layers of aluminium and titanium oxides, the density ratio $D_{\text{Ti}}^{\text{TiOx}}/D_{\text{Al}}^{\text{AlOx}}$ of the two layers can be extracted from the intensity ratio $I(\text{Ti}_{2p}^{\text{Ox}})/I(\text{Al}_{2p}^{\text{Ox}})$. If the titanium oxide layer grows below the alumina layer, the expression is

$$\frac{I(\mathrm{Ti}_{2\mathrm{p}}^{\mathrm{Ox}})}{I(\mathrm{Al}_{2\mathrm{p}}^{\mathrm{Ox}})} = \frac{D_{\mathrm{Ti}}^{\mathrm{TiOx}}}{D_{\mathrm{Al}}^{\mathrm{AlOx}}} \times \frac{\sigma_{\mathrm{Ti}_{2\mathrm{p}}}}{\sigma_{\mathrm{Al}_{2\mathrm{p}}}} \times \frac{\lambda_{\mathrm{Ti}_{2\mathrm{p}}}^{\mathrm{TiOx}}}{\lambda_{\mathrm{Al}_{2\mathrm{p}}}^{\mathrm{AlOx}}} \times \frac{T_{\mathrm{Ti}_{2\mathrm{p}}}}{T_{\mathrm{Al}_{2\mathrm{p}}}} \\ \times \frac{\left(1 - \exp\left(\frac{-d_{\mathrm{TOx}}}{z_{\mathrm{Ti}_{2\mathrm{p}}}^{\mathrm{TiOx}} \times \sin\theta}\right)\right) \times \exp\left(\frac{-d_{\mathrm{AlOx}}}{z_{\mathrm{Ti}_{2\mathrm{p}}}^{\mathrm{AlOx}} \times \sin\theta}\right)}{\left(1 - \exp\left(\frac{-d_{\mathrm{AlOx}}}{z_{\mathrm{Al}_{2\mathrm{p}}}^{\mathrm{AlOx}} \times \sin\theta}\right)\right)},$$

where d_{AIOx} (d_{TiOx}) is the thickness of the aluminium (titanium) oxide layer calculated as described above. If the titanium oxide layer grows above the alumina layer, the expression is

$$\frac{I(\mathrm{Ti}_{2p}^{\mathrm{Ox}})}{I(\mathrm{Al}_{2p}^{\mathrm{Ox}})} = \frac{D_{\mathrm{Ti}}^{\mathrm{TiOx}}}{D_{\mathrm{Al}}^{\mathrm{AIOx}}} \times \frac{\sigma_{\mathrm{Ti}_{2p}}}{\sigma_{\mathrm{Al}_{2p}}} \times \frac{\lambda_{\mathrm{Ti}_{2p}}^{\mathrm{TiOx}}}{\lambda_{\mathrm{Al}_{2p}}^{\mathrm{AIOx}}} \times \frac{T_{\mathrm{Ti}_{2p}}}{T_{\mathrm{Al}_{2p}}} \times \frac{\left(1 - \exp\left(\frac{-d_{\mathrm{TiOx}}}{\lambda_{\mathrm{Ti}_{2p}}^{\mathrm{TiOx}} \times \sin\theta}\right)\right)\right)}{\left(1 - \exp\left(\frac{-d_{\mathrm{AIOx}}}{\lambda_{\mathrm{Al}_{2p}}^{\mathrm{AIOx}} \times \sin\theta}\right)\right) \times \exp\left(\frac{-d_{\mathrm{TiOx}}}{\lambda_{\mathrm{Al}_{2p}}^{\mathrm{AIOx}} \times \sin\theta}\right)}.$$

In both cases, the values of the density ratio obtained by varying the take-off angle θ must remain constant if the assumption made is valid. The values of $D_{\text{Ti}}^{\text{TiOx}}/D_{\text{Al}}^{\text{AlOx}}$ obtained after 8 min of exposure to oxygen are 0.73 and 1.07 at 90° and 45°, respectively, if one assumes that titanium oxide grows below the alumina layer, and 0.36 and 0.37 at 90° and 45°, respectively, if one assumes that titanium oxide grows above the alumina layer. The significant difference obtained in the first case allows us to exclude this possibility. In the second case, the values are nearly equal which validates the assumption that titanium oxide is formed above the alumina layer. This result is in agreement with other results obtained on polycrystalline samples [13,14], where the growth of titanium oxide particles above the

alumina layer was determined from ion-sputtering experiments. The equivalent thickness (0.17 nm) of the titanium oxide layer obtained after 8 min of exposure to oxygen is extremely low, smaller that the equivalent thickness of ~0.2 nm estimated for one monolayer of oxide. This indicates that islands partially covering the substrate are formed in this initial stage of growth following the nucleation of the titanium oxide.

3.3. Effect of pre-annealing

In the experiment described above the alloy was annealed for 110 min prior to oxidation. The effect of the pre-annealing time has been investigated. Figs. 4 and 5 show respectively the evolution of the equivalent thickness of the alumina layer and of the composition of the modified alloy region with increasing exposure to oxygen after preannealing time periods of 110, 200, 350 and 550 min. It is observed in Fig. 4 that the longer the pre-annealing time of the sample, the slower the growth kinetics and the longer the duration of the stage of selective oxidation of the alloy (i.e., growth of Al_2O_3 only). For the sample preannealed for 550 min, a slightly smaller thickness of 1.3 nm is obtained after 210 min of exposure at which point no oxidation of titanium was observed. In this case, the slow growing alumina layer provided a better protection of the alloy against the oxidation of titanium, under the low oxygen pressure used here.

Fig. 5 shows that a striking effect of the preannealing time is to decrease the kinetics of Al depletion in the modified metallic region under the oxide. This is consistent with the decrease of the growth kinetics of the oxide layer. Note also that for the sample pre-annealed for 550 min, for which no titanium oxidation was observed even after 210 min of exposure to oxygen, the Al concentration in the modified metallic phase is higher (Ti₇₀Al₃₀) than that measured in the other series (Ti₇₅Al₂₅). The alumina layer formed in this case being slightly thinner than the less protective layers formed after shorter pre-annealing periods, it can be concluded that the onset of oxidation of titanium is related to a critical concentration of the modified metallic phase underneath the oxide. The composition of $Ti_{75\pm2}Al_{25\pm2}$ obtained in the present study right before the oxidation of titanium is in excellent agreement with the value of $Ti_{75}Al_{25}$ obtained on polycrystalline samples [13,14], showing that this is really a critical concentration for the onset of oxidation of titanium on γ -TiAl.

3.4. Corrosion protection under low oxygen pressure

Longer exposures of the alloy at 650 °C and $P(O_2) = 1 \times 10^{-7}$ mbar and 1×10^{-6} mbar were performed in a separate UHV system. In these experiments, the sample was pre-annealed between 650 and 750 °C for 20 h under a residual pressure of $\sim 3 \times 10^{-10}$ mbar in order to optimise the surface structural ordering. UHV-STM revealed the terrace and step topography of the surface after this pre-treatment, allowing atomic scale measurements on the terraces [13,25]. Fig. 9 shows the AES spectrum obtained after this pre-treatment. The peak at 506 eV (O_{KLL} transition) shows the surface uptake of oxygen. The peaks at 43 and 56 eV (Al_{LMM}) correspond to oxidized Al detected in addition to the metallic Al signal at 68 eV (Al_{LMM}). Some residual carbon contamination is detected at 272 eV (CKLL). The small carbon contamination is due to the fact that, in this UHV chamber, the sample could not be flashannealed between 900 and 1000 °C like in the XPS chamber. The peaks at 30 eV (Ti_{KLL}), 386 eV (Ti_{LMM}) and 416 eV (Ti_{LMM}) are assigned



Fig. 9. AES spectrum of the γ -TiAl(111) sample after preannealing at 650 °C under UHV for 20 h.

to Ti. The detection of the Al_{LMM}^{Ox} signals, combined with the selective oxidation of the alloy evidenced by XPS, indicates the presence of an ultrathin layer of alumina covering the alloy surface (the low-energy Al_{LMM}^{Met} signal at 68 eV is still observed). Its formation results from the interaction of the surface with residual oxygen traces out-gassing from the sample holder during the prolonged annealing treatment.

Fig. 10 shows the peak-to-peak height ratio (i.e., intensity ratio) for the Al_{LMM}^{Ox} and Al_{LMM}^{Met} , Ti_{LMM} and O_{KLL} , and Ti_{LMM} and Al_{LMM}^{Met} signals obtained after pre-treatment, and their evolution after subsequent exposures to oxygen at $P(O_2) =$ 1×10^{-7} and 1×10^{-6} mbar at 650 °C (up to a cumulated exposure time of 20 h). The result obtained after annealing the oxidized surface at 750 °C for 15 h under UHV is also included in this figure. A slow increase from ~ 1.5 to ~ 2.0 is observed for the $Al_{LMM}^{Ox}/Al_{LMM}^{Met}$ ratio with some fluctuation in the data. This suggests a slight thickening of the alumina layer covering the alloy. However, this trend is not confirmed by the Ti_{LMM}/O_{KLL} ratio which remains constant, indicating that there is no further uptake of oxygen by the alumina covered surface during these oxidation treatments and that the Ti concentration of the metallic phase underneath the alumina layer does not vary. The fluctuations of the data for the $Al_{LMM}^{Ox}/Al_{LMM}^{Met}$ ratio are paralleled by fluctua-



Fig. 10. AES intensity ratios for the γ -TiAl(111) sample preannealed at 650 °C under UHV for 20 h, and subsequently exposed to (a) $P(O_2) = 1.0 \times 10^{-7}$ mbar, (b) $P(O_2) = 1.0 \times 10^{-6}$ mbar at 650 °C for a cumulated time of 20 h, and (c) finally annealed at 750 °C under UHV for 15 h.

tions of the Ti_{LMM}/Al_{LMM}^{Met} ratio. They are attributed uted to some dispersion resulting from the measurement of the low intensity Al_{LMM}^{Met} peak at 68 eV rather than to actual fluctuations of the Al concentration in the modified metallic phase underneath the alumina layer. This assignment is supported by the structural analysis of this surface [25] that showed an unchanged structure of the pre-annealed surface after subsequent exposure to oxygen and also after further annealing under UHV, thus confirming the high stability of this surface in these low pressure oxidizing conditions. The equivalent thickness of the alumina layer, calculated from the $Al_{LMM}^{Ox}/Al_{LMM}^{Met}$ intensity ratio as described above and assuming an unmodified concentration in the metallic phase, is estimated to ~ 0.4 nm. This suggests the formation of an extremely thin alumina layer (~ 2 oxide monolayers) protecting the alloy against the oxidation of titanium.

4. Discussion

The results obtained in the present study on γ -TiAl(111) single-crystal surfaces evidence that a stage of selective oxidation of the alloy to form a pure alumina layer precedes the oxidation of titanium. Other data obtained in the same oxidizing conditions on polycrystalline surfaces are consistent [13,14]. In the previous studies of the initial stages of oxidation of γ -TiAl alloys at low oxygen pressure, this stage of selective oxidation of aluminium has only been observed for experiments performed at 850 °C [9]. We note that, for the oxidation experiments performed at 600 °C [8,10,11], the first analyses were performed after several minutes of oxidation, very likely not allowing the observation of the transient stage of selective oxidation which can be short ($\sim 3 \min$) depending on the pre-annealing treatment of the sample as shown in the present study.

Our results also show that the alumina layers formed in this transient stage of selective oxidation are extremely thin (≤ 1.5 nm). Thinner (~0.4 nm) and protective layers can be prepared by prolonged pre-annealing of the substrate. Angleresolved XPS measurements performed on a 0.8 nm thick film give evidence of the formation of a continuous layer of alumina. The formation of islands covering partially the metallic substrate was not observed, although it is expected after nucleation of the oxide particles. This range of thickness is consistent with that observed on polycrystalline surfaces [13,14] and typical for the alumina layers formed under UHV conditions on other aluminide alloys (NiAl) [16–22]. It corresponds to oxide films consisting of 2–7 monolayers of oxide.

The data obtained after different pre-annealing treatments show that the thickness of the alumina layer does not seem to be critical to optimise the protection of the alloy by a pure alumina layer. Indeed, no oxidation of titanium at $P(O_2) = 1 \times 10^{-7}$ mbar and 650 °C was observed by XPS for a 1.3 nm thick film whereas it was observed for 1.5 nm films. The protective film analysed by AES was only 0.4 nm thick. This is consistent with the fact that the more protective the oxide layer the slower its growth for equal conditions of oxidation.

The onset of oxidation of titanium was repeatedly observed for a critical value of the concentration of the modified metallic phase underneath the oxide film. The critical value of $Ti_{75\pm2}Al_{25\pm2}$ for the relative concentration measured in the present study is also found for polycrystalline alloy surfaces [13,14].

A depletion of Al in a modified metallic phase underneath the oxide film has previously been observed in oxidation studies performed at atmospheric pressure [1-3,5]. In the present work we have shown that the Al depletion under the oxide film requires not only the selective oxidation of Al but also a growth kinetics of the alumina layer limited by the diffusion of Al in the substrate (otherwise, a near equilibrium Al concentration would be measured in a re-homogenized metallic phase). At 650 °C transient alumina layers are formed and have been actually observed to grow on TiAl substrates [26]. They grow by a cationic outward diffusion mechanism requiring the injection of Al vacancies at the metal/oxide interface [23,24]. Therefore, the Al depletion of the metallic phase measured in our study can be related to the injection of Al vacancies by the growth mechanism of the oxide.

In the (111) orientation, each atomic plane of the γ -TiAl structure has a Ti₅₀Al₅₀ concentration and alternates close-packed $\langle 1 \overline{1} 0 \rangle$ rows of Al and Ti atoms. Assuming, in first approximation, that the Ti concentration is not modified in an Al-depleted metallic phase, the concentration of injected Al vacancies (V(Al)) can be deduced from the measured relative concentration of the modified phase and compared with the number of injected vacancies required to form the alumina layer. For the 0.8 nm thick alumina layer formed after 2 min of oxidation (Fig. 3), the modified relative concentration measured at 45° take-off angle is Ti₇₂Al₂₈ which amounts to an average value of the concentration of Al vacancies of 31% $(Ti_{50}Al_{19}V(Al)_{31})$ for each atomic plane of the alloy below the 0.8 nm oxide film. The probed depth in the XPS measurement can be estimated to $2 \times \lambda \times \sin \theta$ (corresponding to 89% of the signal). It amounts to 2.8 nm in this experiment $(\lambda_{Al_{2p}}^{Al_{2}O_{3}} = \lambda_{Al_{2p}}^{TiAl} = 2 \text{ nm } [13,14]; \theta = 45^{\circ}).$ The oxide layer being 0.8 nm thick, a depth of 2.0 nm is therefore measured in the alloy, which amounts to ~ 9 atomic planes given the reticular distance of 0.232 nm of the (111)-oriented γ -TiAl structure. The total amount of Al vacancies is therefore estimated to 3.75×10^{15} cm⁻² (2.7 equivalent monolayers (ML)). If one takes the relative concentration of Ti₆₃Al₃₇ (Ti₅₀Al₂₉V(Al)₂₁) measured at 90° take-off angle, one obtains a value of $4.06 \times 10^{15} \text{ cm}^{-2}$ of vacancies (2.9 ML). These values are in good agreement with the total number of injected vacancies estimated from the thickness of the alumina layer. Indeed the value of 0.8 nm corresponds to \sim 4 oxide monolayers, which, given the Al₂O₃ stoichiometry, amounts to 3.73×10^{15} cm⁻² of Al vacancies (2.66 ML) injected to grow the oxide layer.

These calculations confirm that the modification of the metallic phase underneath the oxide layer results from the presence of Al vacancies injected in the metal by the growth mechanism of the oxide. The observed accumulation of the vacancies at the metal/oxide interface shows that the growth kinetics is limited by the diffusion of Al to the metal/oxide interface, in a process, which is too slow to allow the re-homogenisation of the metallic phase during the oxidation. Recent STM results obtained on this system have confirmed the presence of 2D and 3D interfacial defects assigned to the presence of metal vacancies at the metal/oxide interface [25]. These measurements provided direct observations of the interfacial vacancies produced by injection at the metal/oxide interface, in agreement with the conclusions of the present study. The concentration of the interfacial vacancies was significantly lower than the total number of injected vacancies required to grow the ultra-thin alumina layer because, in the reported case, the metallic phase was re-homogenized by prolonged annealing treatments.

A marked effect of pre-annealing the substrate before oxidation is to slow down the growth rate of the alumina layer. Pre-annealing was performed to improve structural ordering by re-crystallization of the highly defective surfaces obtained after the mechanical polishing and Ar ion bombardments. The LEED measurements performed in the separate structural study confirmed that at least 10 h of annealing at 750 °C were necessary to produce relatively sharp diffraction spots [13,25]. A higher structural ordering of the substrate is consistent with the decrease of the growth kinetics of the oxide measured in the present study. Diffusion of the alloying elements is slow in intermetallics due to their strong interaction that provides structural and chemical ordering in these phases (the diffusion coefficient of Al in γ -TiAl is 5×10^{-22} m²/s at 650 °C [27]). Diffusion is expected to significantly increase in the highly defective non-ordered surface layer produced by mechanical polishing and ion bombardments. Therefore, increasing structural order will decrease the rate of diffusion of Al from the bulk to the alloy/oxide interface where Al is consumed by oxidation.

Another effect of the increase in structural ordering of the alloy surface achieved by annealing is to optimise the epitaxial growth of ordered transient alumina layers. The exact structure of the alumina layer is not determined in this system. Based on the identical symmetry and small lattice mismatch (1.4%) of γ -TiAl(111) planes and (111) planes of the FCC oxygen sub-lattices of the transient alumina, the parallel (or anti-parallel) orientation of the FCC oxygen sub-lattice of a γ -like Al₂O₃ layer can be expected on γ -TiAl(111),

as observed on Ni₃Al(111) [28-31] and NiAl(111) [21] surfaces. Optimising the epitaxial growth of the oxide layer decreases the density of defects that form preferential diffusion pathways for the ionic transport through the film.

The results reported in this paper show that the oxidation of titanium is characterized by the formation of Ti³⁺ and Ti⁴⁺ oxide species, indicating the transition from a selective oxidation regime to a simultaneous oxidation regime of both elements. This simultaneous oxidation regime was also observed in previous studies performed at 600 °C under low oxygen pressure [8,9,11]. No Ti^{2+} species are observed in our study in contrast with other observations [8,10]. This may be an effect of temperature on the stability of the Ti²⁺ oxide species at 650 °C. Indeed, a previous study [10] has shown that whereas Ti^{2+} species are formed at 30 °C, Ti³⁺ and Ti⁴⁺ species are formed above 600 °C, indicating the instability of the Ti^{2+} oxide species with increasing temperature.

The angle-resolved XPS measurements performed in this study allowed us to precisely determine the onset of oxidation of titanium, and to characterize the oxide islands partially covering the surface of the alumina layer. The formation of the titanium oxide particles at the outer oxide/ gas interface suggests that titanium atoms, oxidized at the internal interface, diffuse as Ti³⁺ cations through the alumina lattice to react with oxygen at the external (oxide/gas) interface. Thus, when slower growing and better ordered alumina scales are formed, the lower density of preferential diffusion pathways in the oxide film decreases the rate of transport of cations to the outer interface, thus decreasing the growth rate of the oxide and the Al depletion in the underlying metallic phase. If the critical concentration of Ti₇₅Al₂₅ (Ti₅₀Al₁₇-V(Al)₃₃) is reached in the metallic phase, the related increase of the activity of titanium leads to a competitive oxidation of the Ti and Al atoms with transfer of both cations to the outer interface to form Al(III) and Ti(IV) oxides. The comparison with similar measurements performed on polycrystalline $\alpha 2$ -Ti₇₅Al₂₅ samples, for which the onset of Ti oxidation is observed for a modified concentration of $Ti_{82}Al_{18}$ [13,14], shows that the decrease of the number of Al-Ti bonds in the Al-depleted

 γ -phase, rather than just the nominal Ti concentration of 75 at%, determines the Ti activity in the modified intermetallic.

In contrast, if the growth kinetics is slow enough to keep the Ti content below the critical concentration of $Ti_{75}Al_{25}$ for the modified γ -phase, only Al atoms are oxidized and their transport to the outer interface is hindered by the structural ordering of the oxide layer, eventually nearly stopping the growth of the oxide. Ordering of the surface of the oxide layer may also decrease the adsorption of the oxygen species at the surface, thus also contributing to hinder the growth of the oxide. Full protection of the alloy against the oxidation of titanium under low oxygen pressure conditions was observed in our study for ultra-thin layers of pure alumina (1.3 and 0.4 nm), covering completely the substrate, and annealed to optimise their structural order.

5. Conclusion

The early stages of oxidation of γ -TiAl(111) surfaces have been studied at 650 °C under low oxygen pressure (1.0×10^{-7} - 1.0×10^{-6} mbar). The thickness of the oxide layers, the modifications of the alloy substrate underneath the growing oxide scale, and the corrosion protection were investigated by XPS and AES. The data evidence two distinct oxidation regimes.

The first regime is characterized by the growth of a pure alumina layer resulting from the selective oxidation of aluminium. Continuous alumina layers completely covering the substrate have been obtained, as evidenced by angle-resolved XPS data. Their thickness ranges from ~ 0.4 to ~ 1.5 nm, which amounts to 2-7 monolayers of oxide. The composition of the metallic phase underneath the growing oxide is modified by a depletion of Al, forming a concentration gradient below the oxide/ metal interface. The observation of vacancies underneath the growing oxide indicates a growth kinetics limited by the diffusion of Al to the oxide/metal interface, and is consistent with the injection of Al vacancies in the metal during the growth of the transient alumina at 650 °C. Underneath a 0.8 nm thick oxide layer, a modified

concentration of Ti₇₂Al₂₈ (Ti₅₀Al₁₉V(Al)₃₁), corresponding to the injection of 3.75×10^{15} vacancies/ cm^{-2} , has been measured, in excellent agreement with the total number of Al vacancies required to grow 4 monolayers of oxide $(3.73 \times 10^{15} \text{ vacan-}$ $cies/cm^{-2}$). Improving the structural ordering of the substrate by prolonged annealing pre-treatments slows down the growth kinetics of the oxide and the related Al-depletion of the substrate, and increases the resistance of the alloy to the subsequent oxidation of titanium. This is assigned to a combined slower diffusion of Al in the less defective ordered metallic phase and to the growth of better ordered alumina layers allowing to slow down the ionic transport through the oxide. Good protection of the alloy against the oxidation of titanium has been observed at 650 °C under 1.0×10^{-7} mbar of gaseous oxygen for a 1.3 nm thick alumina layer, despite an average modified concentration of Ti₇₀Al₃₀ (Ti₅₀Al₂₁V(Al)₂₉) in the metallic phase underneath the oxide. Highly stable and corrosion resistant alloy surfaces covered by a 0.4 nm thick alumina layer have been obtained by slowly oxidizing the alloy at lower partial pressure $(<5.0 \times 10^{-10} \text{ mbar}).$

The second oxidation regime corresponds to the simultaneous oxidation of aluminium and titanium. The determination of the onset of oxidation of titanium was based on angle-resolved XPS data allowing to discriminate the influence of inelastic scattering through the growing alumina layer from the formation of titanium oxide particles, both contributing to increase the high BE signal in the Ti2p_{3/2}-Ti2p_{1/2} spectra. Angle-resolved XPS data also provide evidence that the Ti oxide particles grow above the alumina layer at the oxide/gas interface. The onset of titanium oxidation was repeatedly observed for a critical concentration of Ti in the modified region of the alloy underneath the alumina layer: $Ti_{75\pm 2}Al_{25\pm 2}$ ($Ti_{50}Al_{17\pm 2}V(Al)_{33\pm 2}$), showing that the depletion in Al decreases the number of Ti-Al bonds and increases the activity of the Ti atoms up to a critical point where the oxidation of Ti at the oxide/metal interface becomes competitive with that of Al. The growth of titanium oxide particles above the alumina layer indicates the transport of Ti³⁺ cations through the alumina layer and subsequent reaction with oxygen at the outer interface. Slower growing and better ordered alumina layers decrease the density of preferential pathways and the ionic transport through the film thus allowing some re-homogenisation of the underlying metallic phase limiting the Al depletion and maintaining the Ti concentration below a critical value. This is a way to obtain improved resistance of the alloy to high temperature oxidation.

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