

## On dipping of $\gamma$ -TiAl in low-concentration phosphoric acid solution and consecutive oxidation resistance at 800 °C

S.Y. Brou,<sup>a</sup> R. Siab,<sup>b</sup> G. Bonnet<sup>a</sup> and J.L. Grosseau-Poussard<sup>a,\*</sup>

<sup>a</sup>LEMMA, Pôle Sciences et Technologie, Université de La Rochelle, Av. M. Crepeau, 17042 La Rochelle, France

<sup>b</sup>Centre Universitaire El-Tarf, Wilaya d'El-Tarf, Algeria

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The oxidation behaviour of  $\gamma$ -TiAl previously treated in low-concentration phosphoric acid solution has been investigated at 800 °C in air. The chemical treatment promotes, instead of the usual TiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> mixed phase, the fast formation of a TiP<sub>2</sub>O<sub>7</sub> pyrophosphate layer with a subsequent large reduction in the oxidation rate.

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The titanium aluminide TiAl has been regarded as a promising high temperature structural material because of its low density and high strength for intermediate temperature (600–850 °C) aerospace applications [1–4]. However, TiAl has been reported to exhibit poor resistance to oxidation at the upper end of this temperature range (>750–800 °C) [5,6]. For applications at such temperatures, it is thus necessary to improve the resistance to oxidation, and attempts have been made by introducing alloying elements in the bulk or through ion implantation or surface coatings [7–17]. Different elements such as Mo, W, Nb or Si have been tested with relative success concerning high temperature efficiency, some of them leading to a decrease of mechanical properties. Recently, it was found that addition of chlorine, phosphorus and boron [12,18] has a significant effect on the oxidation behaviour of TiAl. Intensive studies on the oxidation mechanisms have been performed only for chlorine [12,18–22]. Concerning the phosphorus effect, only few results are available. On the raw aluminide, the oxide layer is formed of a non-protective phase of TiO<sub>2</sub> and a mixed phase containing TiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> [23,24]. Usually, the aim of the different treatments is to promote the unique formation of protective alumina or to slow down the development of TiO<sub>2</sub>. When the phosphorus was incorporated into the surface of TiAl

by ion implantation, the improvement of oxidation resistance at 900 °C is effective up to 100 h and the phosphorus effect is explained by doping of TiO<sub>2</sub>, which reduces the oxygen vacancies concentration and thus decreases the growth rate of titania [25]. An anodic coating has also been obtained on TiAl in phosphoric acid aqueous solution [26]: this amorphous film contains substantial amount of phosphorus, and it slows down the formation of titania and  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> during oxidation at 900 °C. It seems that the doping effect of phosphorus ions in titanium oxide also accounts for the improvement of the high temperature oxidation of Ti–Al. A chemical treatment, consisting in painting concentrated phosphoric acid (85 wt.% in water; 15 M) onto the aluminide and then calcining, has also been undertaken [27]. The reduced oxidation rate at 800 °C could be associated with a continuous or near continuous inner alumina layer, as compared with the usual mixed alumina/titania scale on the untreated material. However, for such highly concentrated solution (15 M), the surface resulting from a simple immersion treatment, is very inhomogeneous and thus it is very difficult to clearly identify the oxidation mechanism [17]. The aim of the present work was to investigate the oxidation behaviour at 800 °C of  $\gamma$ -TiAl treated by immersion in low concentrated (0.3 M) phosphoric acid, in order to check that the oxidation kinetics remains extremely reduced, and in the same way, to study the oxidation mechanism, in particular to determine if doping of TiO<sub>2</sub> is still present.

\* Corresponding author. Tel.: +33 5 46 45 86 12; fax: +33 54 64 57 272; e-mail: [jlgross@univ-lr.fr](mailto:jlgross@univ-lr.fr)

The specimens were prepared from a 12 mm diameter cylindrical bar of polycrystalline TiAl (Ti–54 at.% Al) supplied by ONERA (National Office for Aeronautical Research and Study). Before the chemical treatment, the surfaces were mechanically polished, from 600 to 4000 SiC grade, then ultrasonically washed for 5 min in ethanol, rinsed in ethanol + acetone solution and finally dried in air. According to the equilibrium diagram for TiAl [24] for such an atomic concentration, the alloy should be in the  $\gamma$  monophase domain. Finally, after polishing and chemical attack in a Kroll solution, the microstructure appears to be constituted of dendritic inclusions in the  $\gamma$  grains matrix, as previously observed by Desperet [24]. He showed that the dendrites usually contain the two phases:  $\gamma$ -TiAl, with  $\alpha_2$ -Ti<sub>3</sub>Al in a small proportion. This seems also to be the case in the present study, as in the corresponding X-ray diffraction (XRD) measurements only peaks originating from the  $\gamma$  phase were present.

The treatment solution was realised by diluting concentrated orthophosphoric acid (85 wt.%). For this preliminary study, a low-concentration of 0.3 M was used. The specimens are dipped into the solution at room temperature for 1 min, then dried in air for 24 h. The microstructure of the treated specimens and of the oxide scales were investigated by XRD, scanning electron microscopy (SEM) and microRaman spectroscopy. The compositions of the various phases were measured using energy-dispersive X-ray analysis (EDAX) in an electron microscope. The oxidation kinetics were investigated by thermogravimetric analysis in a Setaram TGA 92 thermobalance. The oxidation was performed under artificial air (20 vol.% O<sub>2</sub>; 80 vol.% N<sub>2</sub>) at a gas flow in the thermobalance of 0.61 h<sup>-1</sup>. For long-term oxidation prediction (around 500 h), cyclic experiments were also performed in an external furnace.

Before oxidation, the deposit remaining at the surface of the treated specimens looked like a homogeneous gel. SEM examination showed a featureless morphology. EDX analysis indicated that the surface is mainly constituted of phosphorus, titanium, aluminium and oxygen. Thus, the presence of a phosphate layer cannot be excluded a priori. Raman spectroscopy was undertaken on treated specimens (Fig. 1). It gave rise to two lines around 930 and 1000 cm<sup>-1</sup>, which are assigned to orthophosphate groups [28,29]. It must be outlined that the position of these two lines slightly differs from those directly observed with the H<sub>3</sub>PO<sub>4</sub> treatment solution.

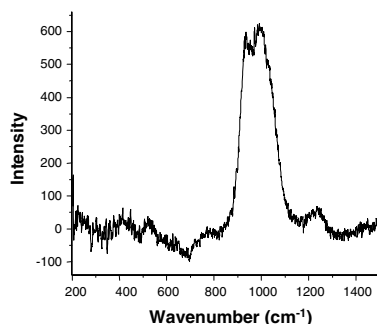


Figure 1. Raman spectra of TiAl dipped in 0.3 M phosphoric acid.

The treated specimens were also analysed by XRD measurements. Only peaks originating from the underlying substrate were detected, even on specimen observed at grazing incidence. This demonstrates that no crystallised compound was present at the surface, or was in too low a quantity to give noticeable XRD peaks.

At the temperature used in this work (800 °C), the weight change curves ( $\Delta m/S$ ) as a function of the exposure time are shown in Figure 2 for both raw and treated TiAl. From Figure 2 it clearly appears that at 800 °C the mass gain was drastically reduced for treated TiAl. For a given oxidation time of 48 h, the  $\Delta m/S$  ratio between both specimens was at least 10 as a consequence of the coating efficiency. As the two curves do not obey to any parabolic or linear regime, no kinetic constant could be extracted. Compared with the results obtained by Retallick [27], it can be noted that no initial weight reduction was observed at the beginning of oxidation. This could be because of the lower concentration of the orthophosphoric solution (0.3 M in the present work compared with 15 M for Retallick), which leads to a much thinner and more homogeneous deposit at the surface. Thus, the water outgasing and consequently the corresponding weight losses must be greatly reduced. In conclusion, it appears that even for low concentrated phosphoric solution, a significant reduction of the oxidation behaviour can be obtained. It should also be noted that if the surface is rinsed with water just after dipping treatment, no subsequent modification of the TiAl oxidation behaviour is observed. This result is contrary to the formation of a conversion layer, as is usually the case with iron alloys. Long-term oxidation experiments were also performed (Fig. 3). After 500 h oxidation at 800 °C the  $\Delta m/S$  ratio between both specimens was still of a value of 2. Thus, a protective transient oxidation stage seems to occur during the first 300 h. The  $\Delta m/S$  variation rate then becomes comparable to the one obtained for raw TiAl.

Figure 4 shows the SEM surface aspect of both raw and treated specimens after 48 h of oxidation at 800 °C. At this scale, the morphology of the oxidised surfaces for raw TiAl consists of a mixture of small rutile and alumina grains (Fig. 4a), which is not the case for the dipped specimen. Indeed, on the latter, a crack network is clearly visible (Fig. 4b). These cracks may be assigned to the departure of water during the temperature increase and subsequent oxidation. However, it should be mentioned that in spite of this phenomenon

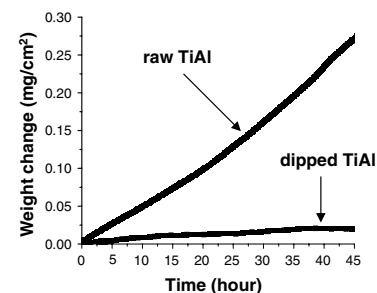


Figure 2. Effect of dipping in phosphoric acid on oxidation kinetics of TiAl alloys in synthetic air at 800 °C.

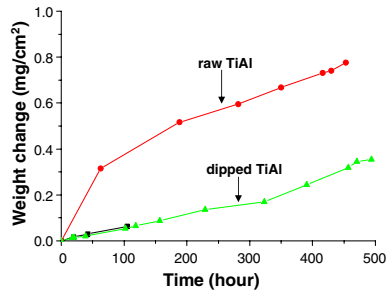


Figure 3. Effect of dipping in phosphoric acid on long-term oxidation kinetics of TiAl alloys in synthetic air at 800 °C.

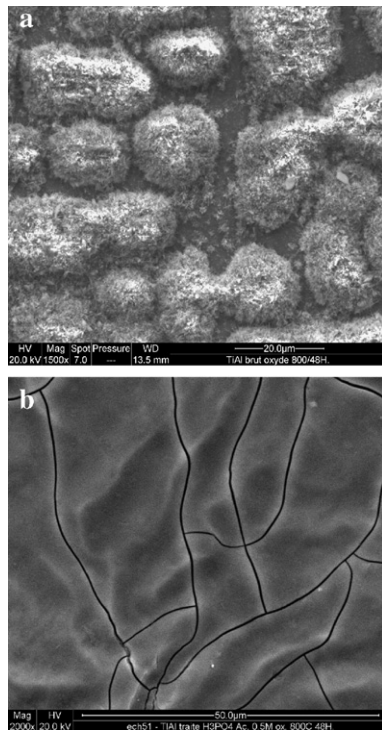


Figure 4. SEM image of oxide scale on TiAl after oxidation in synthetic air for 48 h at 800 °C: (a) raw TiAl; (b) dipped TiAl.

a large reduction in the oxidation kinetic was observed during the transient oxidation period. In Figure 5, cross-sectional SEM examinations of both raw and treated

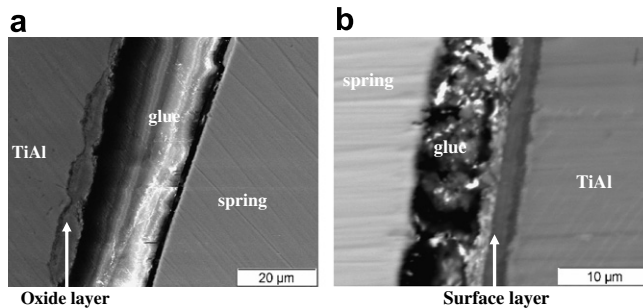


Figure 5. Cross-sectional SEM image of oxide scale on TiAl after oxidation in synthetic air for 48 h at 800 °C: (a) raw TiAl; (b) dipped TiAl.

ted TiAl oxidised at 800 °C for 48 h are presented. For raw TiAl (Fig. 5a) there is an irregular oxide layer (between 2 and 6 μm thick), which contains Ti, Al and O. On the other hand, for dipped TiAl (Fig. 5b), a much more homogeneous surface layer is visible (less than 2.5 μm thick). It contains the elements Ti, Al, P and O. It seems that the phosphorous concentration increases at the external surface.

XRD patterns recorded on raw and treated TiAl specimens oxidised at 800 °C for 48 h are presented in Figure 6. On raw TiAl, it appears that TiO<sub>2</sub> and a low quantity of Al<sub>2</sub>O<sub>3</sub> are present, together with peaks characteristic of the substrate. So, as already observed, the mixed alumina/titania scale has developed. On the treated specimen, no peaks characteristic of these two oxide phases could be identified. On the other hand, three peaks were visible at low 2θ angles (22.5, 25.5 and 28°) and are ascribed to the pyrophosphate TiP<sub>2</sub>O<sub>7</sub> (JCPDS 038 1468). This compound is assumed to be responsible for the drastically decreased kinetic, at least during the transient oxidation period. As a consequence, and as already observed in the oxidation kinetic study, the oxide layer grown on the treated specimen must be thinner than the oxide layer grown on the raw specimen. Indeed, from the examination of the TiAl lines in the scans, it is obvious that the peak intensities are smaller on the raw specimen compared with the treated one (see the peak at 2θ = 21.5°). This corresponds to an increasing absorption of the X-ray through the thickest oxide layer for the raw specimen. Moreover, in Figure 5b the superficial layer is less than 2.5 μm thick and contains the four elements Ti, Al, O and P. Thus, it may be constituted of one part corresponding to the TiP<sub>2</sub>O<sub>7</sub> pyrophosphate and another part corresponding to a thin oxide layer.

Raman spectroscopy was also undertaken after oxidation (Fig. 7). Concerning raw TiAl, the response was homogeneous whatever the region of analysis, and

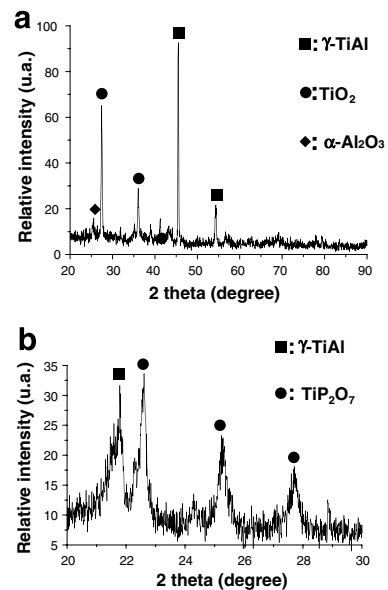
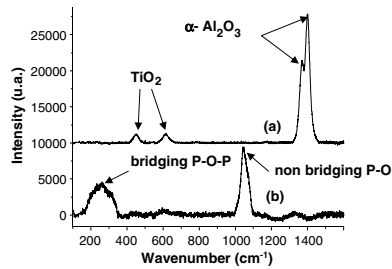


Figure 6. XRD scans after oxidation in synthetic air for 48 h at 800 °C of TiAl: (a) raw TiAl, (b) dipped TiAl.



**Figure 7.** Raman spectra after oxidation in synthetic air for 48 h at 800 °C of TiAl: (a) raw TiAl, (b) dipped TiAl.

three bands located at 450, 620 and around 1400  $\text{cm}^{-1}$  were observed and assigned to  $\text{TiO}_2$  and  $\text{Al}_2\text{O}_3$  [26], in agreement with the XRD results. For the treated specimen, two different spectra were obtained. For the homogeneous region between the cracks, the spectrum is constituted of two broad bands, located, respectively, in the region 200–400  $\text{cm}^{-1}$  and around 1050  $\text{cm}^{-1}$ . According to Lipinska-Kalita [30], these two bands are, respectively, ascribed to bridging P–O–P and non-bridging P–O bonds in the crystallised  $\text{TiP}_2\text{O}_7$  pyrophosphate. Compared with spectra obtained before oxidation, it appears that the phosphate groups are now interconnected and titanium cations are also embedded in the structure. When the Raman analysis was performed in the cracks, only lines corresponding to  $\text{Al}_2\text{O}_3$  and  $\text{TiO}_2$  were visible. This indicates that the pyrophosphate film had already cracked at the beginning of the oxidation period and that the underlying metallic surface had been locally oxidised. As the size of the Raman analysis probe is around 1  $\mu\text{m}^2$ , versus 10  $\text{mm}^2$  for X-ray analysis, it accounts for the absence of the alumina and titania lines in the XRD scans, and indicates that the main contribution comes from the  $\text{TiP}_2\text{O}_7$  compound.

Compared with previous results concerning the phosphorus effect in titanium aluminides [25,26], it appears that in the present case the phosphorus doping effect cannot be put forward, as at 800 °C titania was not present in the scale. Moreover, the suggestion of Retallick [27] implying the formation of a protective alumina layer cannot be considered here as no alumina could be detected after oxidation. Thus, the decreased kinetic can only be relied on in the presence of the  $\text{TiP}_2\text{O}_7$  compound. It should be mentioned that  $\text{TiP}_2\text{O}_7$  has already been obtained in different environmental conditions. The study of Rotole [31] showed that such a pyrophosphate film can be obtained when a clean metal surface is subjected to electrochemical treatment in aqueous orthophosphoric acid and subsequently exposed to air. Then, it was stable for indefinite period under atmospheric conditions. In the present study, the SEM observation of the pyrophosphate film obtained after oxidation at 800 °C (Fig. 4b) clearly shows its featureless character: it looks like a glassy phase. This film acts as an efficient diffusion barrier at high temperature. Moreover, its formation prevents that of a non-protective  $\text{TiO}_2$  scale. Complementary investigations are currently in progress in order to determine the way the

$\text{TiP}_2\text{O}_7$  forms and how it modifies the reactive species diffusion.

Titanium aluminide was dipped in 0.3 M phosphoric acid solution in order to study the associated oxidation behaviour at 800 °C. The surface treatment gave rise to a homogeneous deposit containing orthophosphates groups. The subsequent high temperature oxidation mainly induces the formation of the pyrophosphate  $\text{TiP}_2\text{O}_7$  that is responsible for the drastically reduced oxidation kinetic during the transient oxidation stage.

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