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Effect of surface modification on the stability of oxide scales formed on TiAl intermetallic alloys at high temperature

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Abstract

TiAl intermetallic alloys have many interesting potential applications in the automotive and aerospace industry due to their low density and good mechanical properties at high temperature. Unfortunately they have a low oxidation resistance at temperature higher than 700 °C and the improvement of their oxidation behavior is still an open issue. In this work the surface of a TiAlCrNb alloy has been modified by means of either anodic coating or cerium conversion coating. Afterwards the stability of the oxide scale formed at 900 °C has been studied by analyzing crack formation and propagation, which is the phenomenon that can produce scale spallation during the alloy cooling.

1. Introduction

TiAl intermetallic alloys are very promising structural materials for aeroengine and automotive applications because of their low density coupled with good mechanical properties at high temperature. However, these alloys are not industrially used because of their low fracture toughness at room temperature and low oxidation resistance at elevated temperatures. One of the viable solutions for improving the oxidation resistance of TiAl alloys is alloying with ternary, quaternary or more elements such as Cr, Nb, Si and W, as described by Haanappel et al. (2002), Pilone et al. (2012), Pilone et al. (2013) and Kim et al. (2014). The most important problem related to this method is that in

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general elements that increase mechanical properties often have detrimental effect on the oxidation resistance. Although several efforts have been done to optimize the alloy composition Brotzu et al. (2014) showed that this is still an open issue.

Yang et al. (2003) said that protection against oxidation can be also obtained by using barrier coatings. The most interesting candidates for protecting TiAl alloys are treatments that promote the formation of an aluminum rich TiAl$_3$ layer. However this layer is brittle and often characterized by the presence of microcracks that may produce TiAl direct oxidation. Other tested superficial treatments are pre-oxidation that aims at producing a thin layer of alumina under a low-oxygen pressure and anodization that could produce the formation of a compact oxide layer. Anodization is a well-established technique used to improve the corrosion resistance of many aluminum alloys as described by Narayanan et al. (2007) and by Narayanan et al. (2008). Despite that Tsuchiya et al. (2007) and Yang et al. (2002) suggested that this method could also improve the oxidation resistance of TiAl alloys. Some authors showed that the high temperature cyclic oxidation resistance of Ti–50Al can be improved by anodic coating in 4 wt% phosphoric acid solution. Cyclic oxidation tests at 800°C highlighted that anodization can reduce the oxidation rate of the Ti–50Al alloy by affecting the rate constant that can be reduced to about 1/600 of that calculated for as-homogenized TiAl alloys. In fact it seems that the anodic coating hinders rutile formation and phosphorous ions improve the oxidation resistance by means of the doping effect. Another coating tested for improving the corrosion resistance of aluminum alloys is the cerium conversion coating that increases the corrosion resistance of the alloy because it inhibits both the cathodic and anodic reaction rates of the considered alloy in chloride environment by forming a mixed cerium-aluminum oxide. Those mechanisms were described by Wang et al. (2004), Kozhukharov et al. (2014) and Dabalà et al. (2004). This could be an interesting candidate to be tested for improving the oxidation resistance of TiAl intermetallic alloys.

In this work a TiAlCrNb alloy has been pretreated by means of either anodization or cerium conversion coating and afterwards isothermal oxidation tests have been carried out to compare their behavior with that of as-cast material.

2. Experimental

The TiAl alloys tested in this work were produced by induction melting after 8 vacuum-argon washing cycles both under an Ar atmosphere from pure Ti, Al, Cr, and Nb. The used crucibles were made of vitreous silica and zirconium oxide. The molten metal was cast directly into the rotating mold in order to obtain the specimens. The composition (% at.) of the considered samples was Ti-44.3 Al-2.6Cr-3.3Nb.

After degreasing the specimens, cerium conversion coatings were obtained by immersion in aqueous solution containing 10 g/L of Cerium trichloride and 100 mL/L of hydrogen peroxide at 50 °C. The immersion time was 60 min. Specimen's anodization was carried out at 25 °C either in 0.1 M H$_2$SO$_4$ solution or in 0.3 M H$_3$PO$_4$ solution by applying 150 V for 60 min.

Isothermal oxidation tests were carried out at 900 °C in static laboratory air. The specimens used in the oxidation tests were polished up to 600 grit SiC papers and cleaned with acetone before oxidation. The weight of the specimen being oxidized was measured by using a Cahan microbalance in conjunction with a computer. Metallographic examinations were carried out prior to and after oxidation tests on specimens ground to a mirror-like surface using SiC papers up to 1200 followed by 1 μm alumina. In order to perform cross-section analyses specimens were first embedded in a cold mounting resin. Metallographic structure, scale morphology and specimen cross sections were inspected by scanning electron microscope (SEM) and microanalyses were carried out by energy dispersion spectroscopy (EDS).

3. Results and discussion

Fig. 1 shows SEM micrograph of the studied alloy. Grains are composed of alternating lamellae of α$_2$-Ti$_3$Al and γ-TiAl. Lamellar structure of TiAl intermetallics is considered as beneficial in relation to mechanical properties. After surface modification either by means of anodization or cerium conversion coating, specimens of the treated alloy were subjected to isothermal oxidation tests at 900 °C.

Fig. 2 shows thermogravimetric oxidation curves obtained at 900 °C in air. The results reported in Fig. 2 clearly show that at 900 °C the mean oxidation kinetics are higher for the treated alloy in comparison with the as-cast alloy. The weight gain after about 70 h reaches 4.5 mg/cm^2 for the untreated specimen, while all the treated specimens show a faster oxidation kinetic.
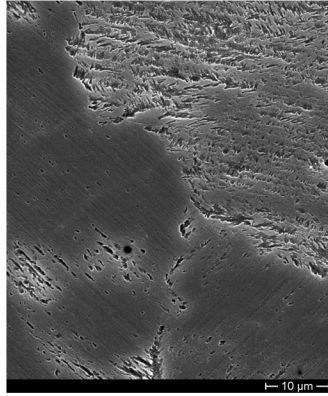

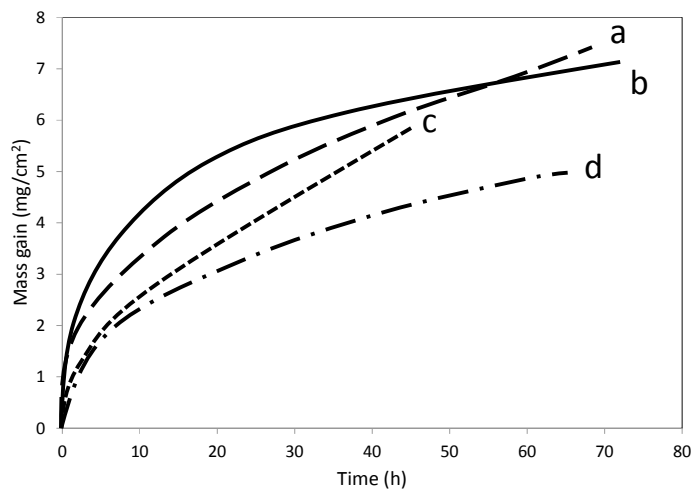Fig. 1. SEM micrograph showing the alloy microstructure.

Fig. 2. Isothermal oxidation kinetics at 900 °C in air of specimens anodized in phosphoric acid (a), anodized in sulfuric acid (b), coated with a cerium conversion coating (c) and in as-cast conditions (d) .

As far as the untreated specimen is concerned although the weight gain is contained, the oxide scale tends to spall off during cooling. Fig. 3 shows that the scale, which is about 25 µm thick, is not adherent to the metallic substrate and that it is constituted by alternate layers of different oxides. In Fig. 3a it can be seen that after spalling three layers are visible: an outer TiO_2 layer (A), an inner Al_2O_3 layer (C) and an intermixed intermediate layer (B). In order to verify the effect of a superficial pre-treatment on the oxide formation and growth at high temperature specimens have been either anodized or covered by a cerium conversion coating. Fig. 4 shows the specimen appearance both after pretreatment and after oxidation at 900 °C. This figure highlights that anodization in sulfuric acid and cerium conversion coating do not improve the alloy behavior at high temperature, in fact in both cases it is characterized by severe spalling during cooling. The specimen anodized in phosphoric acid slightly spalls off close to the edges and corners.

Many intermetallics rely on Al_2O_3 scales for protection against high temperature oxidation. In general the formation of such scales is promoted by a high aluminum content in the alloy or by the presence of other alloying elements whose content should be optimized. In TiAl intermetallic alloys the oxide layer is not protective because it

contains Ti and Al oxides. The outermost layer is rich of TiO_2, followed by a layered structure made of Al_2O_3 and TiO_2. Aim of the alloy pretreatment is the preliminary formation of a compact and adherent anodic coating that should hinder diffusion of metal cations and oxygen.

Fig. 5 shows the morphology of the anodic coating formed in phosphoric acid. It appears characterized by the presence of some cracks that do not seem to affect the oxide scale stability. A research carried out by Brou et al. (2009) highlighted the positive effect of bringing phosphorus bearing species at the surfaces of TiAl samples by means of dipping and drying. This result was attributed to the barrier effect of the TiP_2O_7 layer formed at high temperature. Also in this case phosphorous seems to have a positive effect on the studied alloy: although the oxide thickness is about 30 µm it does not spall off during cooling probably because the growth mechanism of the scale is changed by the presence of the compact anodic coating. Figs. 5 and 6 show that the oxide scale is characterized by a layered structure made of Al_2O_3 and TiO_2. X-ray mappings highlight that the oxide is richer in aluminum in the inner portion, while in the outer portion it is richer in titanium. Chromium oxide seems to be uniformly distributed throughout the scale.
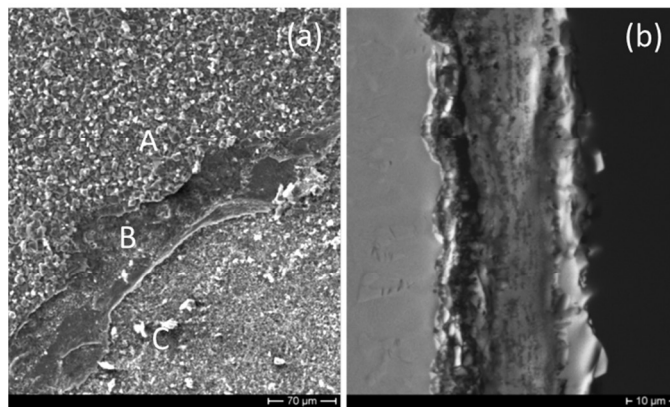

Fig. 3. SEM micrographs showing the oxide morphology (a) and the transverse section (b) of the as-cast specimen treated at 900 °C.
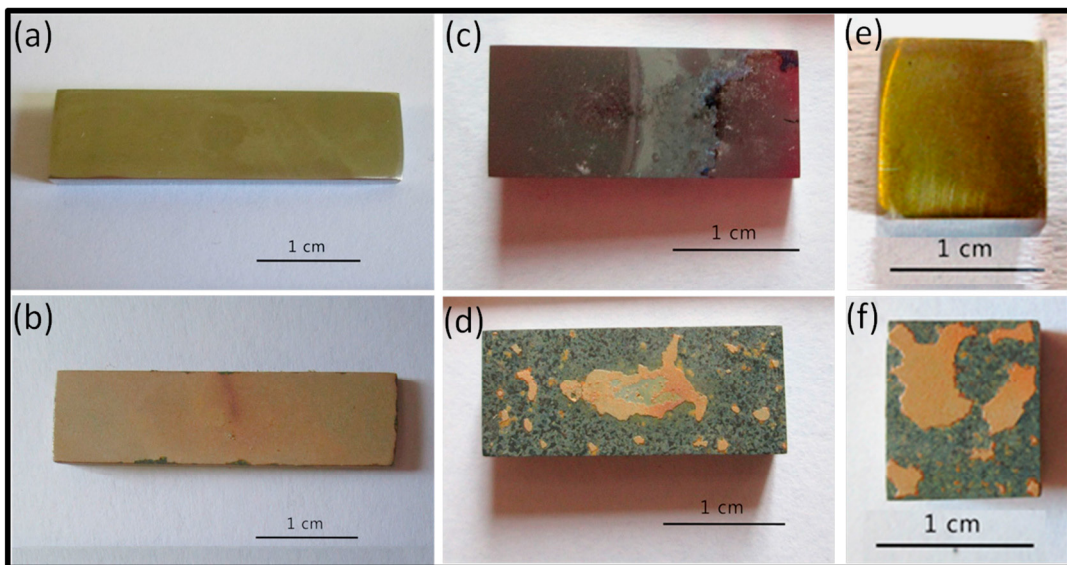

Fig. 4. Macrographs showing the specimens anodized in phosphoric acid prior to (a) and after oxidation (b), in sulfuric acid prior to (c) and after oxidation (d) and the specimen covered by the cerium conversion coating prior to (e) and after oxidation (f).
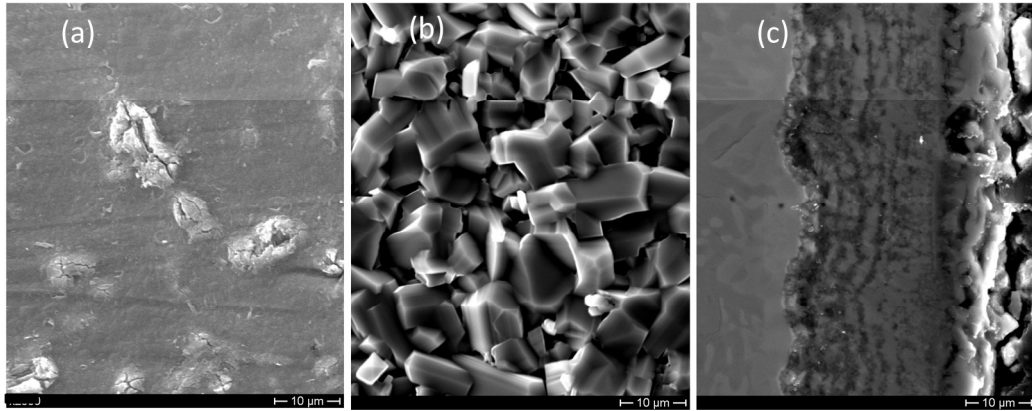
Fig. 5. SEM micrographs showing the specimen surface morphology after anodization with phosphoric acid (a)and after oxidation at 900 °C (b). The specimen transverse section after oxidation at 900 °C is visible in figure (c).
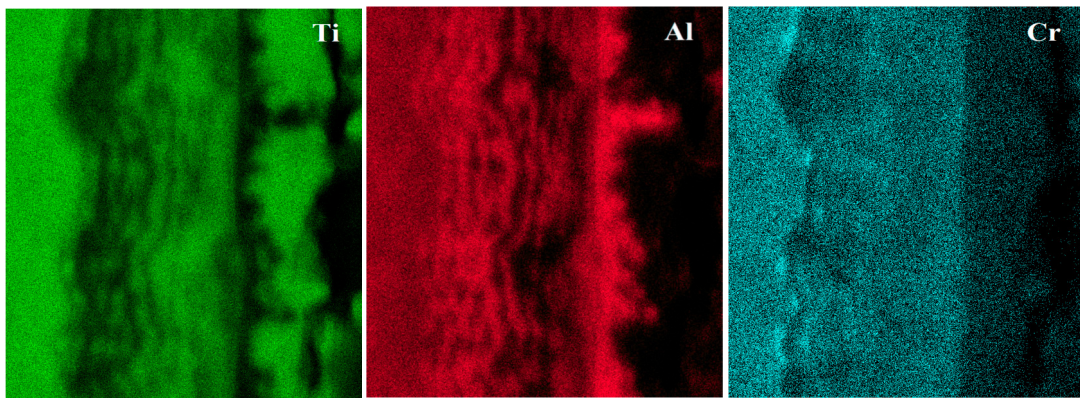

Fig. 6. X-Ray mappings highlighting Ti, Al and Cr distribution on the cross section shown in Fig. 4c.

As far as the anodic coating obtained in sulfuric acid solution is concerned, it has a very fine morphology (Fig.7). At 900 °C the oxide scale grows with a fast kinetic and it spalls off almost completely during cooling. SEM micrographs in Figs. 7(b) and (c) highlight that the oxide layer is really porous and not adherent to the substrate, in particular Fig. 7(b) shows the external TiO_2 rich layer and the internal Al_2O_3 rich layer after breakaway oxidation. Even after cerium conversion treatment the studied alloy is subjected to breakaway oxidation. Fig. 8 shows the very fine morphology of the cerium conversion coating and the layered structure of the oxide scale. In this case the very fast oxidation kinetic (Fig. 2) and the porous oxide structure justify the poor protectiveness of the oxide at high temperature. Fig. 7(c) shows also oxide intrusions at the metal-scale interface with localized thickening resulting probably from the formation of rapid diffusion paths for metal cations, oxygen or both species.

As explained by Schütze et al. (1995) there are two mechanisms leading to oxide spallation: when the oxide-metal interface is strong the failure occurs by shear cracking, while when there is decohesion at the oxide-metal interface spallation proceeds in an unstable way. The oxide growth at high temperature on the studied alloy involves inward transport of oxygen along the scale grain boundaries and the outward diffusion of aluminum and titanium. This mechanism enables new oxide to form within the bulk scale close to the grain boundaries. The expansion resulting from this growth causes stress development within the scale and when the specimen cools off the differential contraction between the metallic substrate and the scale determines the scale spallation.

From the literature it is well known that the tensile scale failure can be described by a fracture mechanics approach as:

$$\varepsilon_c = \frac{K_{Ic}}{f \, E_{ox} \, \sqrt{\pi c}} \qquad (1)$$

where ε_c is the critical strain for scale failure, K_{Ic} is the oxide fracture toughness, f can take different values depending on the shape and size of defects, c is half the length of an embedded defect and E_{ox} is the elastic modulus of the oxide scale. K_{Ic} can be easily calculated, by knowing tabulated values of surface fracture energy γ_0, by using the following equation:
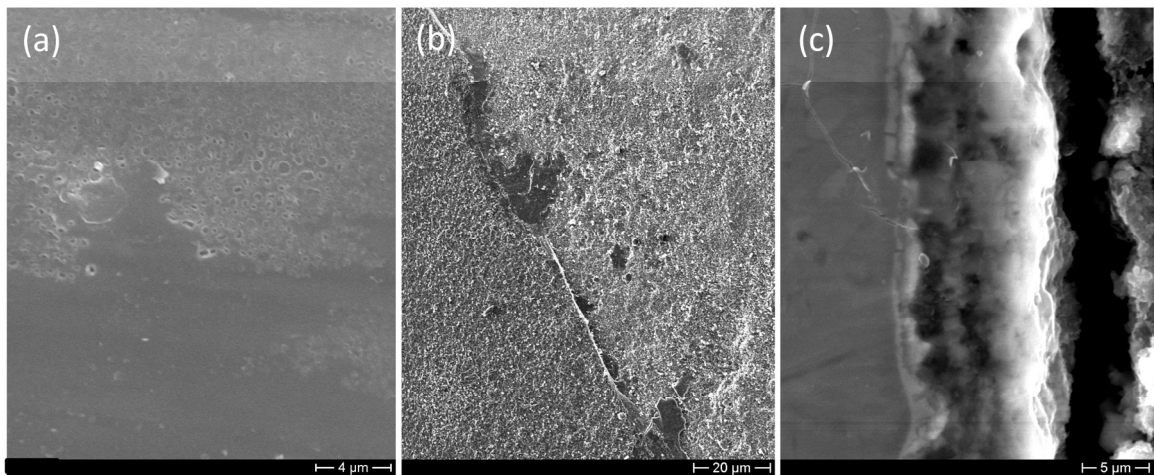
$$K_{Ic} = \sqrt{2 \, \gamma_0 \, E_{ox}} \qquad (2)$$

Fig. 7. SEM micrographs showing the specimen surface morphology after anodization with sulfuric acid (a)and after oxidation at 900 °C (b). The specimen transverse section after oxidation at 900 °C is visible in figure (c).
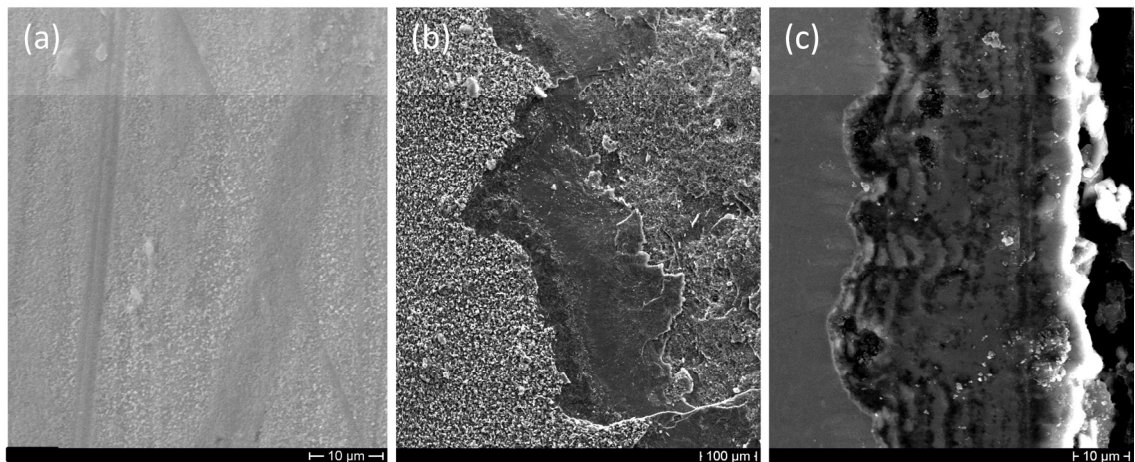

Fig. 8. SEM micrographs showing the specimen surface morphology after cerium conversion treatment (a)and after oxidation at 900 °C (b). The specimen transverse section after oxidation at 900 °C is visible in figure (c).

Different oxides are characterized by different values of the elastic modulus that affects the scale fracture toughness. In general aluminum oxide has both an elastic modulus and a K_{Ic} which are higher than those of titanium oxide. In fact for the considered oxides the K_{Ic} values vary over the range 1.5-2.5 $MPa \sqrt{m}$ and increase progressively going from TiO_2 to Cr_2O_3 to Al_2O_3. Despite that in our study, where the scale is made of different

components, the most important factor affecting scale spallation during cooling is defect size. In fact scales with low defect size have a higher critical strain to cracking in comparison with those having large defects.

The presence of interfacial voids generated by outward transport of cations in a metal-deficient scale favors scale spallation. In the case of specimens anodized in phosphoric acid, as suggested in literature, phosphorous ions improve the oxidation behavior by means of the doping effect that decreases oxygen vacancies and hinders ion diffusion throughout the scale. After anodization in phosphoric acid the oxide growing mechanism changes and the oxide scale is more compact and then characterized by a higher critical strain value. That is the reason why the oxide does not spall off during cooling. On the other hand, the fact that specimens anodized in sulfuric acid show breakaway oxidation can be justified considering that sulfur segregation to the metal-scale interface, unlike phosphorus segregation, weakens it and causes scale spallation as highlighted by Stott et al. (1995). In fact a comparison among Figs. 5(c), 7(c) and 8(c) reveals that the oxide with the lowest defect sizes is the one grown on the specimen anodized in phosphoric acid.

4. Conclusions

In this work the surface of a TiAlCrNb alloy has been modified by means of either anodic coating or cerium conversion coating. The results reported in this paper highlighted that only anodization in phosphoric acid seems to be effective in improving high temperature oxidation behavior of the studied alloy. In fact after anodization the anodic coating avoids decohesion at the metal-oxide interface and scale spalling during cooling. Despite that none of the tested surface modification methods promotes the formation of a self-healing protective alumina layer.

References

Brotzu, A., Felli, F., Pilone, D., 2014. Effect of alloying elements on the behaviour of TiAl-based alloys. Intermetallics 54, 176-180.

Brou, S.Y., Bonnet, G., Grosseau-Poussard, J.L., 2009. Formation and evolution of phosphorus-containing species during high-temperature oxidation of TiAl dipped in a low-concentrated phosphoric acid solution. Surface and Coatings Technology 203, 1138-1143.

Dabalà, M., Ramous, E., Magrini, M., 2004. Corrosion resistance of cerium-based chemical conversion coatings on AA5083 aluminium alloy. Materials and Corrosion 55, 381-386.

Haanappel, V.A.C., Clemens, H., Stroosnijder, M.F., 2002. The high temperature oxidation behaviour of high and low alloyed TiAl-based intermetallics. Intermetallics 10, 293-305.

Kim, D., Seo, D., Huang, X., Sawatzky, T., Saari, H., Hong, J., Kim, Y.-W., 2014. Oxidation behaviour of gamma titanium aluminides with or without protective coatings. International Materials Reviews 59, 297-325.

Kozhukharov, S.V., Acuña, O.F., Machkova, M.S., Kozhukharov, V.S., 2014. Influence of buffering on the spontaneous deposition of cerium conversion coatings for corrosion protection of AA2024-T3 aluminum alloy. Journal of Applied Electrochemistry 44, 1093-1105.

Narayanan, R., Seshadri, S.K., 2007. Phosphoric acid anodization of Ti-6Al-4V - Structural and corrosion aspects. Corrosion Science 49, 542-558.

Narayanan, R., Seshadri, S.K., 2008. Point defect model and corrosion of anodic oxide coatings on Ti-6Al-4V . Corrosion Science 50, 1521-1529.

Pilone, D., Felli, F., 2012. Isothermal oxidation behaviour of TiAl-Cr-Nb-B alloys produced by induction melting. Intermetallics 26, 36-39.

Pilone, D., Felli, F., Brotzu, A., 2013. High temperature oxidation behaviour of TiAl-Cr-Nb-Mo alloys. Intermetallics 43, 131-137.

Schütze, M., 1995. Mechanical properties of oxide scales. Oxidation of Metals 44, 29-61.

Stott, F.H., Wood, G.C., Stringer, J., 1995. The influence of alloying elements on the development and maintenance of protective scales. Oxidation of Metals 44, 113-145.

Tsuchiya, H., Berger, S., Macak, J.M., Ghicov, A., Schmuki, P., 2007. Self-organized porous and tubular oxide layers on Ti Al alloys. Electrochemistry Communications 9, 2397-2402.

Wang, C., Jiang, F., Wang, F., 2004. Cerium chemical conversion coating for aluminum alloy 2024-T3 and its corrosion resistance. Corrosion 60, 237-243.

Yang M.-R., Wu S.-K., 2003. Oxidation resistance improvement of TiAl intermetallics using surface modification. Bulletin of the College of Engineering, N.T.U. 89, 3–19.

Yang, M.-R., Wu, S.K., 2002. The improvement of high-temperature oxidation of Ti-50Al by anodic coating in the phosphoric acid. Acta Materialia 50, 691-701.