Protection of Ti-Alloys against High Temperature Environmental Attack by a Two Step Process, Aluminization + Fluorination

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Abstract

Ti-alloys cannot be used at elevated temperatures above approximately 600°C in oxidizing environments. They suffer from accelerated oxidation and oxygen uptake in the subsurface zone, which deteriorates the mechanical properties. The addition of Al (usually < 10%) into standard Ti-alloys is not enough to form a protective alumina layer. Aluminization of technical Ti-alloys and formation of intermetallic Al-rich phases (e.g. $TiAl_3$) change the oxidation behavior from fast and non-protective rutile formation to slow growing alumina kinetics, but only for a limited period of time. A subsequent fluorination of the aluminized components gets the fluorine effect to operate. This is a way to improve the resistance of technical Ti-alloys against environmental attack, even for longer service times. In this paper the results of high temperature oxidation tests of several untreated and treated Ti-alloys will be presented and their behavior compared.

Keywords

Environmental Embrittlement, Fluorine Effect, Oxidation

Introduction

Titanium is a widely used material at ambient temperatures for several applications but it cannot be used at temperatures above approximately 600°C, even with the addition of other elements like Al [1]. Titanium has a high affinity towards oxygen. Therefore, passivation by the formation of a TiO_2-layer protects the material at ambient temperatures. On the other side, this protection does not work at elevated temperatures when fast oxygen diffusion through the disordered TiO_2 into the metallic substrate occurs [2]. This oxygen inward diffusion leads to an oxygen enriched subsurface zone which causes embrittlement [3]. Several methods to improve the environmental resistance of Ti-alloys at elevated temperatures are described in the literature e.g. coatings [4] but the success of these treatments so far has been rather limited [5]. Conventional overlay coatings can crack or delaminate so that the protective effect vanishes [6] and interdiffusion with the Ti-substrate from multi-elemental coatings can cause problems due to the formation of undesired intermetallic phases. To overcome these limitations and to increase the operating temperature of standard Ti-alloys a new concept was developed. A treatment combining Al-enrichment in a quite narrow surface zone e.g. by the powder pack process with subsequent fluorination was established. The Al-enrichment leads to the formation of an Al-rich intermetallic $TiAl_x$-diffusion zone [7] which has very low oxygen solubility, thus, preventing oxygen inward diffusion [8]. Noteworthy, technical γ-TiAl alloys with an Al-content between 40-50at.% form a mixed oxide scale during high temperature exposure in oxidizing environments due to similar thermodynamic stabilities of Al- and Ti-oxide [9]. This mixed scale does not show long term protective behavior.

The Al-content has to be above 55at.% to form Al_2O_3 only [10]. A protective Al_2O_3-layer reduces the oxygen inward diffusion. Therefore fluorine was applied onto the TiAl-diffusion layer. F-treated TiAl-alloys form such a protective Al_2O_3-layer during HT-oxidation in air due to the positive fluorine effect [11]. This alumina layer protects the substrate underneath even under thermocyclic conditions and in wet environments [12]. In this paper results of exposure tests with several untreated and treated Ti-alloys at 600°C and 700°C are presented and compared. The possible use of treated Ti-components in HT-applications will be discussed.

Experimental

Specimens of several Ti-alloys (table 1) were cut from sheets and bars into 10 x 10 x 1 mm³ coupons. Those coupons were ground prior to further treatment with SiC-paper to 1200 grit, rinsed with distilled water, ultrasonically cleaned in ethanol for 10 min and dried in air. Such prepared specimens were oxidized isothermally at 600°C and 700°C (HT) up to 1200h without further treatment to examine the oxidation behavior of the untreated material. Thermogravimetric analysis (TGA) was carried out within a closed tube furnace under a steady stream of synthetic air by connecting the samples with a balance so that the mass change at temperature was measured constantly during the short term isothermal oxidation (120h). The specimens remained within the furnace during heating up and cooling down to room temperature (RT) while the TGA-experiment was running. Long term tests (600h, 1200h) were performed by placing the samples in the open hot furnace (laboratory air) and removing them after the envisaged period of time so that cooling to RT happened outside the furnace. Al-enrichment was performed by the powder pack process [13]. The samples were exposed in a powder mixture of $Al_2O_3/Al/NH_4Cl$ or $Al_2O_3/Al/NH_4F$ at 600°C under a steady stream of Argon for 5 hours. As a result intermetallic $TiAl_3$-layers of about 5-20µm thickness depending on the activity of the powder pack were formed. Fluorination was performed by spraying F-containing polymer or by plasma immersion ion implantation (PI³) onto the Al-enriched sample surfaces. During high temperature exposure the polymer decomposes and the released fluorine reacts with the sample or the implanted fluorine reacts directly with Al. The exposed specimens were prepared metallographically. Cross sections were investigated by light optical microscopy (LOM), scanning electron microscopy (SEM) combined with standard less energy disperse X-ray spectroscopy (EDX), electron probe micro analysis (EPMA) and hardness measurements with a micro indenter.

Table 1. Compositions of the investigated Ti-alloys

Alloy	Composition (wt.%)
Cp-Ti	Ti-0.3O-0.3Fe
Ti 6242	Ti-6Al-2Zr-4Sn-2Mo
Ti 6246	Ti-6Al-2Zr-4Sn-6Mo

Results and discussion

The TGA-data of the untreated Ti6242 and Ti6246 samples oxidized isothermally at 600°C and 700°C in synthetic air are presented in figure 1. It can be seen that the oxidation behavior of the two technical alloys is similar. Their mass change at 600°C is very low. After a short incubation period with a slight mass increase the curves are almost flat. The mass gain at 700°C is much more pronounced. The curves reveal a steady mass increase and the slopes follow parabolic

kinetics. The final mass gain of Ti6242 (ca. 1mg/cm²) is lower than that of Ti6246 (ca. 1.2 mg/cm²) at 700°C.
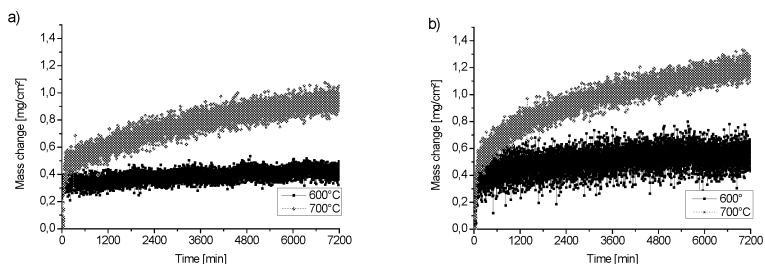

Figure 1a, b: *TGA-results of Ti 6242 (a) and Ti 6246 (b) during isothermal oxidation at 600°C and 700°C in synthetic air*

The scales for the alloys look similar. Hence, only the images of Ti6242 are presented in the following. After oxidation at 600°C the TiO_2-scale on the untreated Ti6242 specimen is hardly visible (fig. 2a). The thickness is below one µm. The exposure at 700°C leads to a much thicker TiO_2-scale (fig. 2b). This correlates with the higher mass gain during the TGA-measurement. After exposure for 1200h at 600°C a two layered TiO_2-scale was found (fig. 2c). The outer layer is porous and loosely attached and the inner layer appears homogeneous.
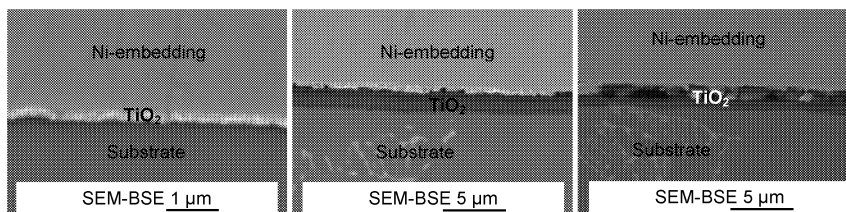

Figure 2a- c: *SEM-images of untreated Ti6242 after oxidation at 600°C (a) and 700°C (b) for 120h in synthetic air and 1200h at 600°C in laboratory air(c)*

EPMA-investigations were conducted to analyze the elemental distribution of oxygen and its depth profile. The oxide scale is rather thin and the oxygen solubility in Ti is less than 20at.%. Therefore, the elemental mappings (fig. 3) do not give a clear answer about the oxygen inward diffusion. The EPMA oxygen depth profiles indicate the inward diffusion in the metal sub-surface zone (fig. 4a, b). A slight and narrow oxygen profile was found in the substrate adjacent to the oxide scale of the sample after 120h at 600°C but it reaches only about 10mm in depth (fig.4a). On the other hand, a much higher oxygen peak at the surface and an oxygen inward diffusion profile reaching up to more than 40µm in depth was observed on the sample after 1200h of oxidation. This causes embrittlement and an increased hardness of the oxygen influenced subsurface zone [14]. Consequently this oxygen inward diffusion has to be avoided because the observed embrittlement can cause failure of Ti-components in service under cyclic thermal or mechanical load.
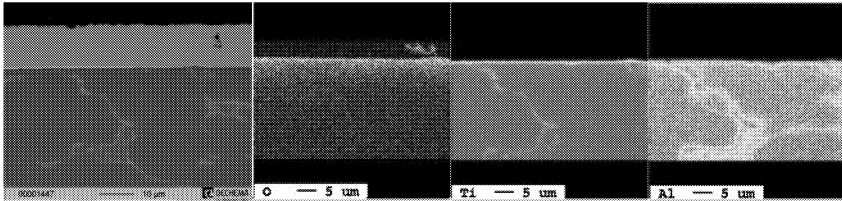
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Figure 3: EPMA-BSE-image (a) and elemental mappings of O (a), Ti (b) and Al (c) of the untreated Ti6242 sample after isothermal oxidation at 600°C for 120h in synthetic air
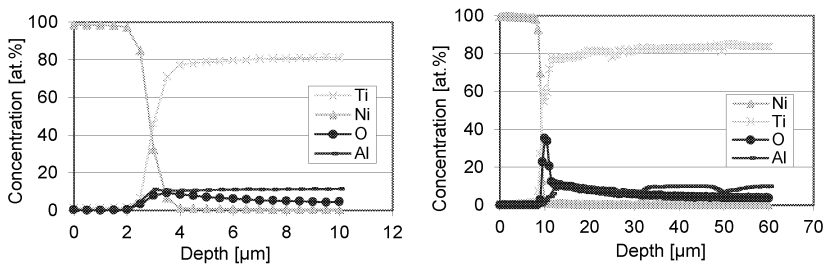

Figure 4a, b: EPMA-depth profiles of the oxidized untreated Ti6242 samples after oxidation at 600°C for 120h (a) and 1200h (b) in synthetic air

The Al-enrichment via the powder pack process led to an Al-rich intermetallic diffusion layer. In figure 5a a cross section of an aluminized Ti sample with thinner $TiAl_3$-diffusion zone is shown. The standard-less EDX-spectrum indicates the formation of the $TiAl_3$ phase (fig. 4b). The EPMA-profiles which are more precise than a simple EDX-measurement prove the $TiAl_3$-formation (fig. 5). By varying the pack parameters the thickness of the $TiAl_3$-diffusion zone can be controlled [14].
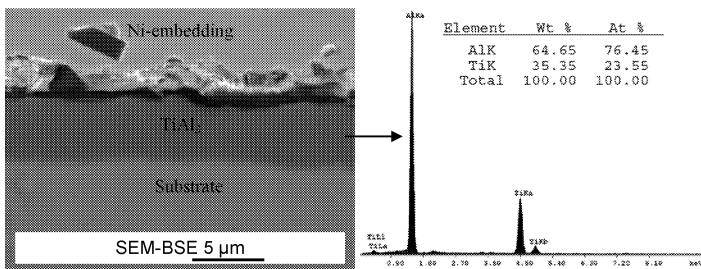

Figure 4a, b: SEM- image of an Al-enriched Ti-sample after pack with thinner $TiAl_3$ diffusion layer (a) and EDX-spectrum of the diffusion layer (b)
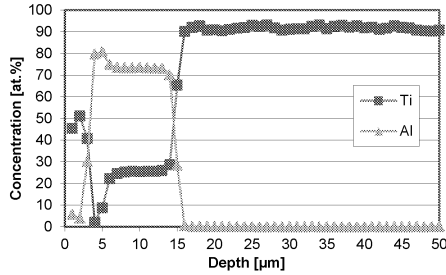
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Figure 5: EPMA-profiles of the Al-enriched Ti-sample with thicker TiAl₃ diffusion layer after pack

The intermetallic Al-rich diffusion layer protects the Ti-based substrate underneath during HT-exposure in oxidizing environments. A protective alumina layer has formed on the outer surface due to the sufficient Al-content in the diffusion zone after 600h of exposure at 600°C in laboratory air (fig. 6a). The formation of a thicker diffusion zone (ca. 15μm) by varying the pack parameters is possible so that the $TiAl_3$-phase formed during the pack process is still present after HT-exposure. Interdiffusion with the substrate due to the Al-concentration gradient triggered the formation of other intermetallic phases with a lower Al-content ($TiAl_2$, TiAl and Ti_3Al) and the original thickness of the $TiAl_3$-diffusion zone was reduced, too (fig. 6a). This was also proven in the EPMA-profile. Additionally oxygen was only found on the surface on top of the diffusion zone but not within the diffusion zones or the substrate (fig. 6b). The oxygen ingress into the Ti-substrate and hence its' embrittlement was avoided by the presented treatment.
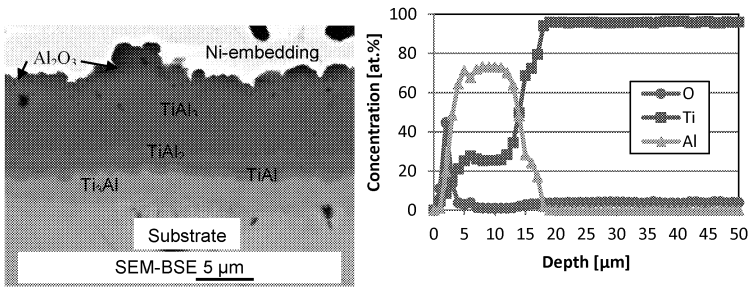

Figure 6a, b: SEM-image (a) and EPMA-profiles (b) of an Al-treated Ti-sample (thick diffusion layer) after oxidation (600°C/600h/laboratory air)

If the originally formed TiAl$_3$-diffusion zone is rather thin (< 5µm) the TiAl$_3$-phase can be converted fast into TiAl$_2$ during HT-exposure: another exposed Ti- sample treated with Al plus F after 120h of oxidation at 600°C in air where nor TiAl$_3$ was identified by EDX anymore (fig. 7a, b). Oxygen was detected by EPMA on the surface and fluorine was detected underneath. The Al-content has dropped from 75at.% directly after pack to about 60at.% and interdiffusion of Al with the Ti-substrate is observable. After 120h of exposure the Al-content in the subsurface zone is still high enough to form pure alumina but proceeding interdiffusion reduces the Al-content in the diffusion zone so that finally also TiO$_2$ will be formed if the Al-content drops below 55at.% [10]. Therefore the desired thin alumina layer has to be stabilized with fluorine for longer exposure times so that the protective effect of the desired thin Al diffusion zone does not vanish after short operating times at elevated temperatures.
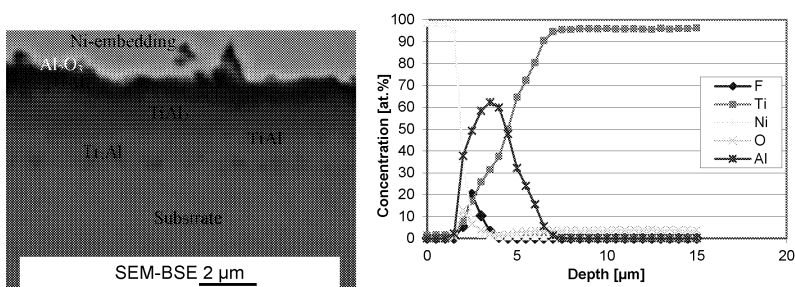

Figure 7a, b: *SEM-image (a) and EPMA-profiles (b) of an Al- + F-treated Ti-sample (thin diffusion layer) after oxidation (600°C/120h/laboratory air*

No oxygen is found after oxidation underneath the diffusion layer (fig. 7b). This observation was made for all samples which were enriched with Al and fluorinated [14]. The intermetallic TiAl$_x$-diffusion zone plus the alumina layer evolving during HT-exposure act as a barrier for oxygen inward diffusion and hence no embrittlement is observed in the subsurface zone in contrast to the untreated samples. The kinetics of the alumina growth is much smaller than those of titania so that the metal loss due to oxidation is minimized. This means that Ti-components could be used at temperatures much higher than today in service after the combined treatment, Al-enrichment and fluorination.

4 Conclusions

The combination of Al-enrichment within a thin zone and subsequent F-treatment leads to highly improved environmental stability of standard Ti-alloys at elevated temperatures by the formation of a protective alumina layer which reduces the oxidation rate and suppresses the oxygen inward diffusion. Otherwise, this oxygen ingress leads to subsequent embrittlement of the components. Additionally the intermetallic TiAl-phases underneath the oxide scale have low oxygen solubility which also hinders the oxygen inward diffusion. The use of Ti-components at temperatures above 600°C in oxidizing environments could become possible with this combined treatment.

Acknowledgements

References

[1] F.H. Froes, T.-L. Yau, H.G. Weidinger, *Materials Science and Technology* Vol. 8, ed. R.W. Kahn, P. Haasen, E.J. Kramer, VCH Weinheim **1996** p.399

[2] G. Lütjering, J.C. Williams, *Titanium*, Springer Berlin **2003** p. 48

[3] O. Schauerte, A. Gysler, G. Lütjering, S. Mailly, Y. Chabanne, C. Sarrazin-Baudoux, J. Mendez, J. Petit, *Fatigue Behavior of Titanium Alloys,* TMS Warrendale **1999** p. 191

[4] C. Leyens, *Titanium and Titanium Alloys,* ed. C. Leyens, M. Peters, Wiley-VCH Weinheim **2003** p. 189

[5] B. Cockeram, R.A. Rapp, Ox. Met. **1996**, 45, 427

[6] J.K. Tien, J.C. Chesnutt, D.H. Boone, G.W. Goward, *Titanium Science and Technology,* ed. R.I. Jaffe, H.M. Burke, Plenum Press New York **1973** p. 2517

[7] N. Birks, G.H. Meier, F.S. Pettit, *High-Temperature Oxidation of Metals*, Cambridge University Press Cambridge **2006** p.271

[8] J.L. Smialek J.A. Nesbitt, W.J. Brindley, M.P. Brady, J.K. Doychak, R.M. Dickerson, D.R. Hull, Mat. Res. Soc. Symp. Proc. **1995**, 364, 1935

[9] H. Kestler, H. Clemens, *Titanium and Titanium Alloys,* ed. C. Leyens, M. Peters, WILEY-VCH Weinheim **2003** p. 351

[10] A. Rahmel, P.J. Spencer, Ox. Met. **1991**, 35, 53

[11] A. Donchev, B. Gleeson, M. Schütze, Intermetallics **2003**, 11, 387

[12] A. Donchev, E. Richter, M. Schütze, R. Yankov, J. of Alloys and Compounds **2008**, 452, 7

[13] R. Mevrel, C. Duret, R. Pichior, Mat. Sci. Techn. **1986**, 2, 201

[14] A. Donchev, R. Yankov, A. Kolitsch, M. Schütze, Key Eng. Mat. **2013**, 551, 109