Suppressing the Alpha-casing of Ti-alloys by a Combined Al-and F-treatment

Alexander Donchev[1], Michael Schütze[1], Andreas Kolitsch[2], Rossen Yankov[2]

1) DECHEMA e. V. Karl-Winnacker-Institut Theodor-Heuss-Allee 25; D-60486 Frankfurt/Main, Germany
2) Helmholtzzentrum Dresden-Rossendorf e. V. Institute of Ion Beam Physics and Materials Research Bautzener Landstraße 128, D-01328 Dresden, Germany

Oxygen inward diffusion into standard Ti-alloys during high temperature exposure in oxygen containing environments leads to an oxygen enriched surface zone which is detrimental under mechanical load. Therefore, the operating temperature of these alloys is limited. An enrichment of Al in the surface zone of Ti-alloys leads to an improvement by the formation of intermetallic Ti_xAl_y-phases with decreased oxygen solubility but this is not sufficient. Therefore, the combination of Al-enrichment in the surface zone to an extent that a TiAl-layer is formed and an additional F-treatment is proposed for the formation of a continuous stable alumina scale which prevents oxygen inward diffusion. In this paper the results of high temperature exposure tests in air of several Ti-alloys are presented without any treatment and treated with combined Al-enrichment plus fluorination. Post experimental investigations such as SEM revealed the formation of thin alumina layers on treated samples. Hardness measurements showed that no embrittlement was observed for the treated samples while untreated specimens showed increased hardness values corresponding with the oxygen diffusion profile in the subsurface zone.

Keywords: *Titanium, fluorine effect, high temperature oxidation*

1. Introduction

Titanium alloys are widely used as structural materials[1]. However, due to their high affinity to oxygen special procedures have to be undertaken during processing[2]. This high affinity to oxygen also causes problems during high temperature applications in oxidizing environments[3]. The rutile layer which is protective at lower temperatures looses its barrier properties due to increased disorder of the lattice[4]. Therefore oxygen can easily diffuse through this scale and becomes enriched in the subsurface zone. This enrichment the so called α-case is a very brittle phase and reduces the performance of Ti-components. Hence Ti-alloys cannot be used at temperatures above approximately 600℃. To overcome this problem coatings based on Al have been developed over the last decades but still these attempts are yet not sufficient[5]. A new concept is shown in this paper. The already known route of enriching the surface zone of Ti-alloys with Al is combined with the fluorine effect. Intermetallic TiAl-alloys form an alumina layer if the Al-content is above 60at. %[6]. This amount is too high for technical applications. Commercial TiAl-alloys therefore have an Al-content between 40 and 50at. %[7]. These alloys do not form an alumina layer but a mixed oxide/nitride scale ($TiO_2/Al_2O_3/TiN$) during high temperature oxidation in oxidizing atmospheres[8]. The thermodynamic stabilities of Ti-and Al-oxide are similar so that both oxides are formed side-by-side[9]. The addition of small amounts of fluorine applied onto the surface or within a quite thin surface zone changes the oxidation mechanism of TiAl alloys to pure alumina formation[10]. This so called fluorine effect is transferred to Ti-alloys with Al-enriched surfaces. The Al-enrichment leads to the formation of intermetallic TiAl-phases which are stabilized additionally by the fluorine effect. Results of oxidation tests show the positive effect of the combined treatment. Post experimental investigations as scanning electron microscopy are used to characterize the scales. The positive effect on the environmental stability will be discussed in the view of a technical application of the treatments for Ti-components to be used at elevated temperatures.

2. Experimental Procedure

Specimens of two Ti-based materials with no Al and 25at. % Al as a maximum limit (Table 1) were cut from sheets into 10 × 10 × 1 mm³ pieces. These were ground with SiC-paper before any further treatment to 1200 grit, cleaned ultrasonically with ethanol rinsed with distilled water and dried in air. Such prepared samples were oxidized at 600℃ in air to investigate their oxidation behavior. Al-enrichment was performed via the powder pack process. Specimens were stored in a sealed alumina crucible packed in an $Al/NH_4Cl/Al_2O_3$-powder. The mixture was heated to 600℃ under a steady stream of Ar for several hours. Fluorination was done either by spraying a fluorine containing polymer and subsequent heat treatment[11] or by plasma immersion ion implantation (PI^3)[12]. The fluorine profiles after PI^3 were measured by elastic recoil detection analysis (ERDA). Such samples were also oxidized and their performance was compared with that of the bare materials. Post experimental investigations included metallographic preparation, light microscopy (LM), scanning electron microscopy (SEM) with energy dispersive X-ray (EDX) and electron micro probe analysis (EPMA). Hardness measurements were performed with a micro indenter.

Table 1. Compositions of the investigated alloys

Alloy	Ti-content (wt. %)	Additional elements (wt. %)
Ti	99.4	0.3O-0.3Fe
Ti_3Al	75	24Al

3. Results and Discussion

Thermogravimetric mass change data obtained during isothermal tests give a first impression of the oxidation behavior. Thermocyclic tests are more reliable because they are closer to technical application of real components which always includes heating up and cooling during their life time. Additional information is obtained from metallographic cross sections. In Figure 1 (a, b) the cross sections of untreated Ti-specimens of several investigated Ti-alloys after oxidation are presented.

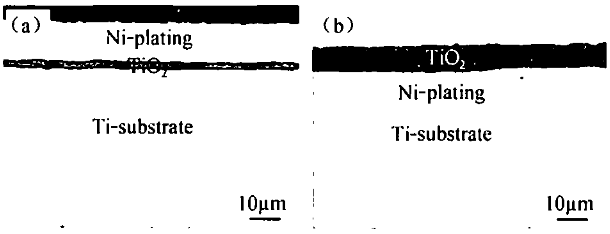

Figure 1. a, b. LM-images of the metallographic cross sections of Ti samples oxidized at 600℃ in air (left 120h, right 1000h)

The rutile layers are not dense and their thicknesses change from 3 μm (120h) to 7 μm (1000h). Oxygen was found underneath this defective layer on all untreated samples. In Figure 2 the elemental EPMA-profiles are presented showing the oxygen diffusion profile which reaches up to about 40 μm into the substrate. This indicates the easy diffusion of oxygen through the TiO_2-scale and the high solubility within titanium.

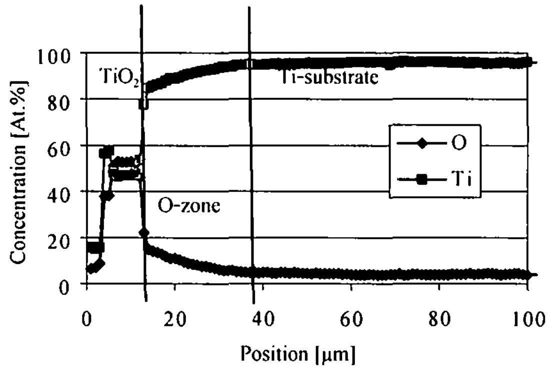

Figure 2. EPMA-profiles of O and Ti in the surface zone of an untreated Ti-sample after 600h oxidation at 600℃ in air

The oxygen affected zone has a much higher hardness than the substrate. Figure 3 shows the hardness profile of the untreated Ti-sample after 600h of oxidation which follows the observations of the oxygen concentration in Figure 2. The hardness directly underneath the surface where the oxygen content is the highest is up to 800 Vickers while the hardness of the substrate is only about 250 Vickers.

After aluminizing an intermetallic $TiAl_3$-layer had formed on all Ti-alloys. This was proven by EDX (Figure 4). The thickness of this layer can be determined by varying the parameters (temperature, time, Al-activity) of the powder pack process (Figure 5(a), (b)).

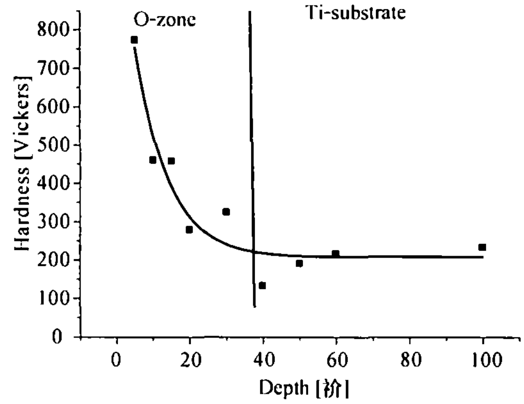

Figure 3. Hardness profile of the untreated Ti-sample after 600h oxidation at 600℃ in air

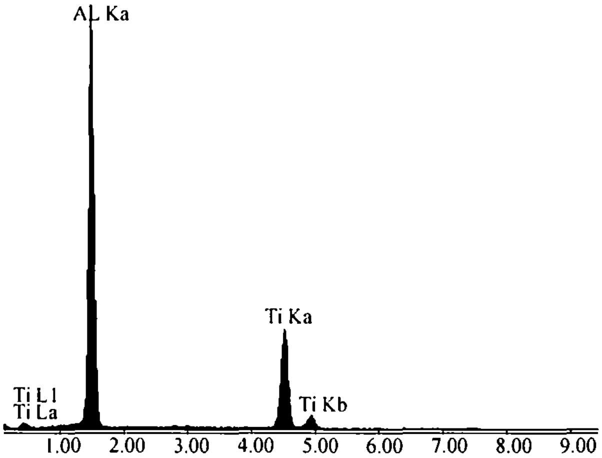

Figure 4. EDX-spectrum of the $TiAl_3$-layer (74% Al+26% Ti) after aluminizing

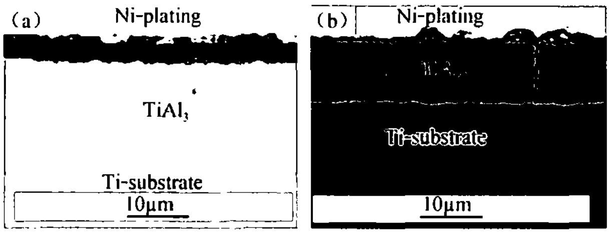

Figure 5. a, b. SEM-images of a thicker $TiAl_3$-layer (left, 700℃) and a thinner $TiAl_3$-layer (right, 600℃) after aluminizing with the same Al-activity for 5h at different temperatures

EPMA-investigations of the elemental distributions in the surface zone revealed that no oxygen could be observed underneath the intermetallic layer (Figure 6).

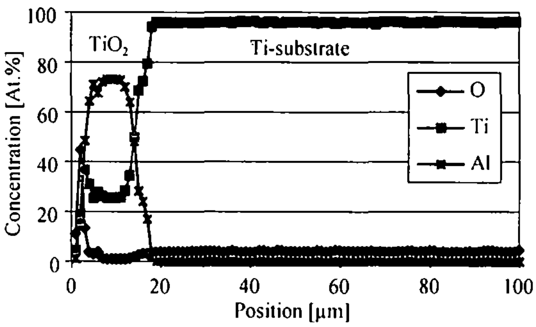

Figure 6. EPMA-profiles of Al, O and Ti in the surface zone of an treated Ti-sample after 600h oxidation at 600℃ in air

On top of the intermetallic diffusion zone an alumina layer had formed. This was proven by EDX (Figure 7). The alumina layer is quite thin therefore the signal of Ti from the underlying $TiAl_3$-coating was detected, too.

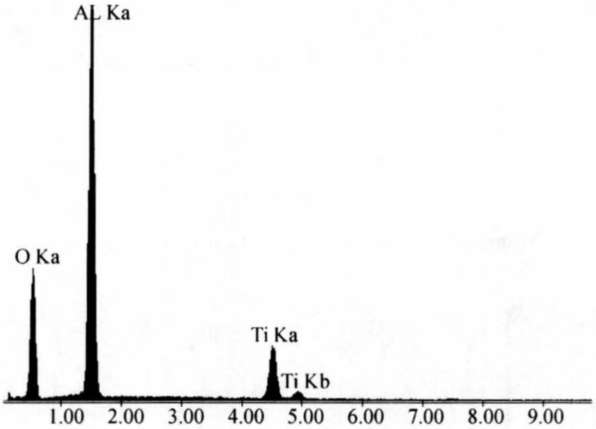

Figure 7. EDX-spectrum of the Al_2O_3-layer on top of the $TiAl_3$-diffusion zone after 600h oxidation in air

The hardness of the substrate zone underneath the intermetallic diffusion layer was found to be the same as that of the bulk. No increase in hardness was measured (Figure 8).

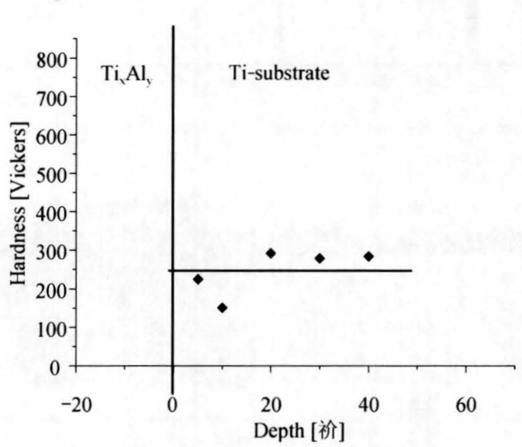

Figure 8. Hardness profile of a treated Ti-sample after 600h oxidation at 600℃ in air

All the results so far indicate the potential of an Al-enrichment of the surface zone to suppress the oxygen inward diffusion and hence the alpha-case formation during high temperature exposure of Ti-components in oxidizing environments. The solubility of oxygen in the Al-rich intermetallic $TiAl_x$ phases (x=1,2,3) is very low[13]. Furthermore the Al_2O_3-layer is protective, slowly growing and prevents oxygen inward diffusion.

It has to be taken into account that the Al-content in the diffusion layer declines due to interdiffusion with the substrate. The Al-gradient at the interface leads to the formation of phases with a lower Al-content. In Figure 9 the different interdiffusion layers can be distinguished on a Ti-sample oxidized at 600℃ for 600h. The interdiffusion at 600℃ is slow but measurable.

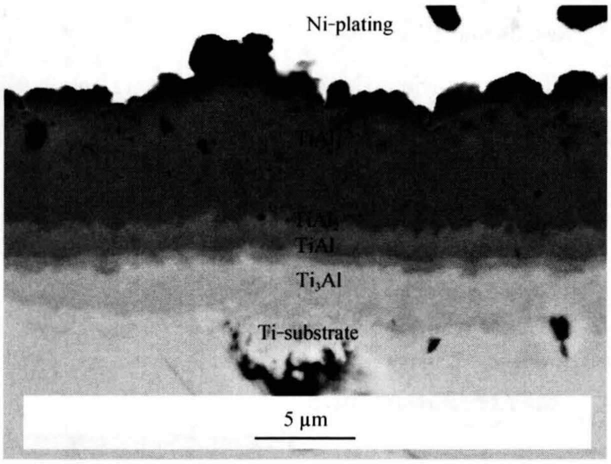

Figure 9. SEM-image of the different Ti_yAl_x-layers formed by interdiffusion between the $TiAl_3$-zone and the Ti-substrate after 600h oxidation in air

The alumina layer can be stabilized even for Al-contents below a critical value where also TiO_2 would be formed in addition to a discontinuous Al_2O_3-layer. This can be achieved by the fluorine effect. The fluorine effect leads to the exclusive formation of Al_2O_3 during high temperature oxidation of TiAl-alloys if the fluorine concentration is within a defined range which was thermodynamically calculated in advance[10]. Isothermal thermogravimetric measurements (TGA) have been performed at 800℃ with fluorinated and non-fluorinated specimens (Figure 10). This higher temperature was chosen to accelerate interdiffusion. These tests show the beneficial effect of the additional fluorine treatment. The mass gain of untreated Ti_3Al is steady and follows parabolic behavior. The final mass gain was about 8 mg/cm^2. Single aluminizing with a low activity Al-pack at 600℃ leads to a thin $TiAl_3$-layer on the Ti_3Al-sample. Therefore, the mass gain at the beginning of the oxidation is lower than that of the untreated specimen. But after about 25h the mass gain of this specimen accelerates and at the end of the test the mass gain is even higher than that of the untreated sample (9 mg/cm^2). The oxidation rate had probably increased after the $TiAl_3$-layer was consumed by oxidation and interdiffusion. The additional F-treatment

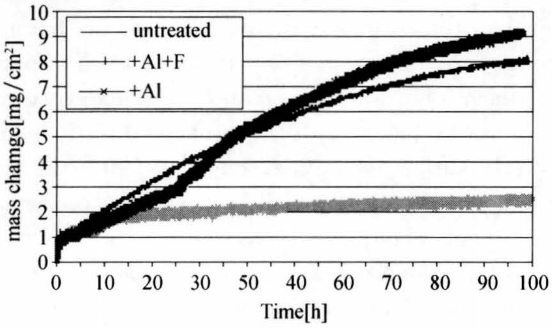

Figure 10. TGA-results of untreated, aluminized and aluminized plus F-treated Ti_3Al-samples oxidized isothermally at 800℃ in synthetic air for 100h

showed a much lower mass gain over the whole test period following alumina kinetics and indicating a stable and protective alumina layer. Hence single Al-enrichment is not enough for a long term protection of Ti-components.

The stabilization of the Al_2O_3-layer via F-treatment is necessary. This Al_2O_3-layer on F-treated TiAl-alloys can protect these alloys under thermocyclic conditions for long exposure times even in wet environments[14]. The fluorine profiles within the Al-enriched surface zone after PI^3 are the same as in TiAl-alloys[12]. Figure 11 shows an ERDA-profile of the elements in this zone. O and C are coming from the precursor (CH_2F_2) and some residues of air in the vacuum chamber, respectively. They have their maximum at the surface and do not deteriorate the F-effect[12]. The implanted fluorine dose was 5.15×10^{17} F/cm^2 which is in the same order of magnitude as for TiAl-alloys[12]. The drop of the Al-concentration was caused by the limited detection depth for this element.

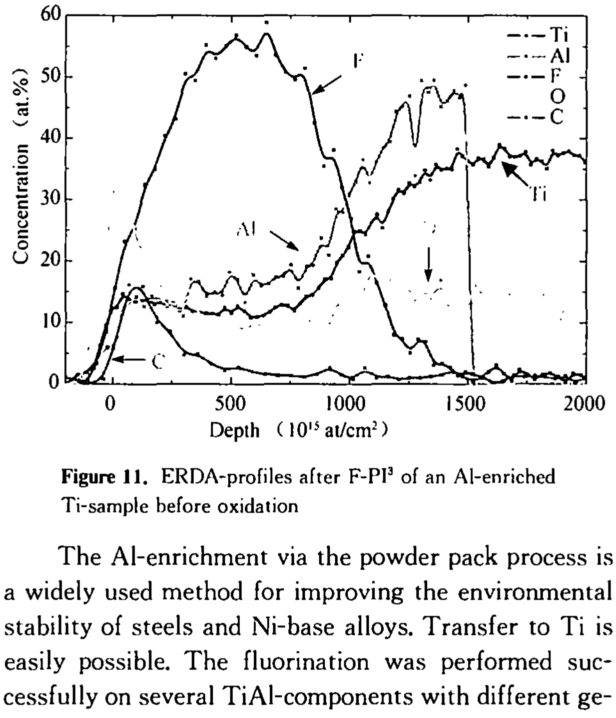

Figure 11. ERDA-profiles after F-PI^3 of an Al-enriched Ti-sample before oxidation

The Al-enrichment via the powder pack process is a widely used method for improving the environmental stability of steels and Ni-base alloys. Transfer to Ti is easily possible. The fluorination was performed successfully on several TiAl-components with different geometries[15] so that these parameters could also be used for components made of Ti-alloys.

4. Conclusions

The alpha-case formation of Ti-alloys during high temperature exposure in oxidizing atmospheres can be suppressed by a combined Al-enrichment plus F-treatment. This leads to the formation of a stable and protective alumina layer on top of intermetallic TiAl-phases which would allow the use of Ti-components at temperatures higher than those actually setting the maximum operation limit.

Acknowledgements

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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. 51ff.
3) R. I. Jaffee, H. M. Burte, *Titanium Science and Technology*, Plenum Press New York 1973.
4) G. Lütjering, J. C. Williams, *Titanium*, Springer Berlin 2003 p. 48.
5) C. Leyens, Titanium and *Titanium Alloys*, ed. C. Leyens, M. Peters, Wiley-VCH Weinheim 2003 p. 189.
6) M. Eckert, K. Hilpert, Materials and Corrosion, 1997, 48: pp. 10-12.
7) F. Appel, M. Oehring, *Titanium and Titanium Alloys*, ed. C. Leyens, M. Peters, Wiley-VCH Weinheim 2003 p. 89.
8) A. Rahmel, W. J. Quadakkers, M. Schütze, Materials and Corrosion, 1995, 1995: pp. 271-285.
9) A. Rahmel, P. J. Spencer, Oxidation of Metals, 1991, 35: pp. 53-68.
10) A. Donchev, B. Gleeson, M. Schütze, Intermetallics 2003, 11: pp. 387-398.
11) A. Donchev, E. Richter, M. Schütze, R. Yankov, Journal of Alloys and Compounds, 2008, 452: pp. 7-10.
12) A. Donchev, A. Kolitsch, M. Schütze, R. Yankov, Plasma Processes and Polymers, 2009, 6: pp. 434-439.
13) J. L. Smialek, J. A. Nesbitt, W. J. Brindley, M. P. Brady, J. K. Doychak, R. M. Dickerson, D. R. Hull, Materials Research Society Symposium Proceedings, 1995, 364: pp. 1273-1284.
14) A. Donchev, M. Schütze, Materials Science Forum, 2010, 638-642: pp. 1294-1299.
15) A. Donchev, R. Pflumm, M. Schütze, Materials Research Society Symposium Proceedings, 2008, 1128: pp. 209-214.