DECHEMA FORSCHUNGSINSTITUT

High Temperature Materials

Minimization of the Oxygen Embrittlement of Ti-Alloys

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Introduction

Ti-alloys are widely used as structural materials in different industrial fields but their use at temperatures above about 500°C is limited due to oxidation/corrosion and environmental embrittlement by oxygen-, nitrogen- and/or hydrogen-uptake. This embrittlement can lead to premature failure of Ti-components.

The solubility of O_2 in Ti-alloys can go up to 25at.% which deteriorates the mechanical properties of the materials. An increasing Al-content limits the oxygen inward diffusion because Al_2O_3 is formed as well. At sufficiently high Al-contents a continuous, protective Al_2O_3-layer is formed on $TiAl_3$ during high temperature oxidation and no oxygen is found underneath (fig.1).

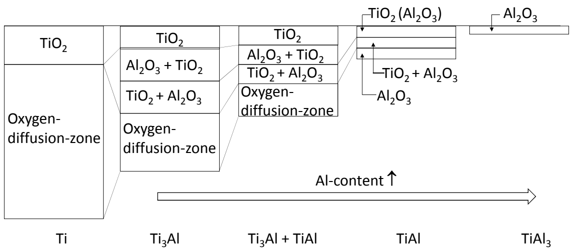

Figure 1: Schematic of the oxide layers and the oxygen diffusion zone of Ti and titanium aluminides (Smialek et al. 1985).

Note: The Al_2O_3-layer on TiAl does not provide long term protection unless a further treatment e.g. fluorine is applied.

Experimental

Several Ti-alloys were investigated with and without further treatment. The compositions of the alloys (wt.%) were as follows:

CP-Ti: Ti,
IMI 834: Ti-5.8Al-4Sn-3.5Zr-0.7Nb-0.5Mo-0.35Si-0.06C,
Ti6246: Ti-6Al-2Sn-4Zr-6Mo
Ti6242: Ti-6Al-2Sn-4Zr-2Mo-0.1Si

The alloys were enriched with aluminium at the surface by a powder pack process (fig. 2) or magnetron sputtering and the fluorine was applied afterwards by plasma immersion ion implantation (PI³) or other techniques like spraying, dipping, gas phase treatment etc. so that the fluorine effect could operate (fig. 3).

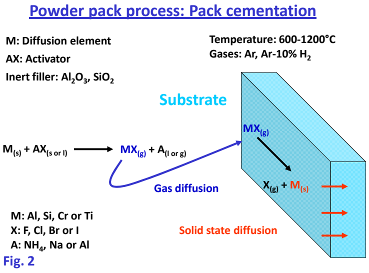

Fig. 2

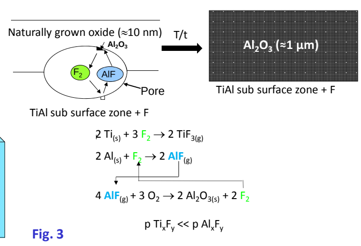

Fig. 3

$$2\,Ti_{(s)} + 3\,F_2 \rightarrow 2\,TiF_{3(g)}$$
$$2\,Al_{(s)} + F_2 \rightarrow 2\,AlF_{(g)}$$
$$4\,AlF_{(g)} + 3\,O_2 \rightarrow 2\,Al_2O_{3(s)} + 2\,F_2$$
$$p\,Ti_xF_y << p\,Al_xF_y$$

Figures 2 and 3: Schematic of the powder pack process (left) and the fluorine effect mechanism (right)

Results

Al-enrichment in the surface zone by powder pack led to the formation of a $TiAl_3$-layer on all tested alloys whose depth could be reduced by changing temperature, time or composition and activity of the pack. The thickness of the diffusion layer should remain below 5 µm, which was set to match industrial requirements. After optimization of the process, SEM-investigations (fig. 4) reveal that a thin and crack free diffusion layer could be achieved , whose composition was confirmed by EPMA (fig. 5).

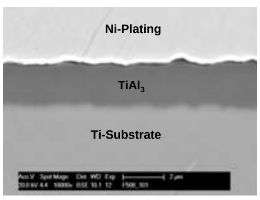

Fig. 4

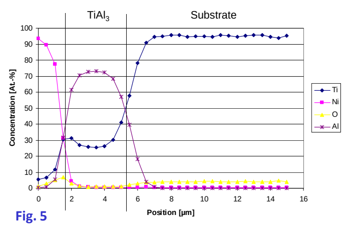

Fig. 5

Figures 4 and 5: SEM-image of a thin $TiAl_3$-diffusion layer on Ti after pure low activity aluminizing (left) and corresponding EPMA-profiles (right)

Oxidation tests were performed to reveal the oxidation behaviour of the untreated material and the effect of the coating procedure. Post experimental investigations of the metallographic cross sections showed a thick, cracked TiO_2-scale on the untreated sample (fig. 6), while a thin Al_2O_3-layer on the TiAl-diffusion layer of the sample after aluminizing and fluorination appeared (fig. 7). Oxygen was found underneath the oxide scale on the untreated sample (fig. 8). Interdiffusion of Al into the Ti-substrate led to the formation of the intermetallic phase TiAl with no oxygen in the sub surface zone (fig. 9).

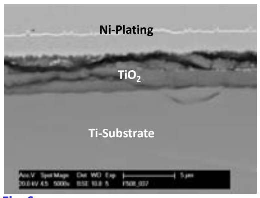

Fig. 6

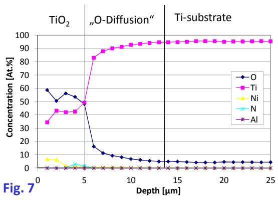

Fig. 7

Figures 6 and 7: SEM-image of the untreated sample after 120h of oxidation at 600°C in air (left) and EPMA-profiles (right)

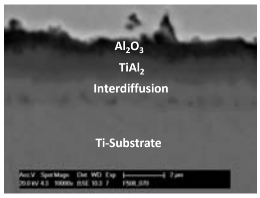

Fig. 8

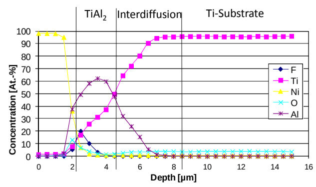

Fig. 9

Figures 8 and 9: SEM-image of the Al/Ti-pack-sample after 120h of oxidation at 600°C in air (left) and EPMA-profiles (right)

Sputtering of Al plus subsequent heat treatment (vacuum annealing VA) led to the formation of a very thin intermetallic TiAl-layer (1-2 µm) on different Ti-alloys (fig. 10), as was proven by XRD (fig. 11). After oxidation at 600°C in air for 120h a double layer scale was found on the annealed and F-PI³ implanted Ti-sample consisting of an outer Al_2O_3 layer and a TiO_2-layer underneath (fig. 11). No oxygen was found underneath the oxide layers of the Al- + F-treated sample (fig. 12), proving that this treatment is also suitable for the protection of Ti-alloys against high temperature attack and environmental embrittlement.

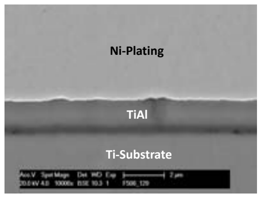

Fig. 10

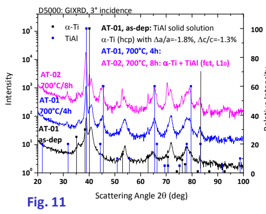

Fig. 11

Figures 10 and 11: SEM-image of the sputtered and annealed Ti-sample (left) and XRD-spectra showing the formation of TiAl by VA (right)

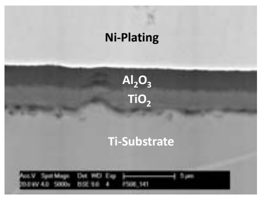

Fig. 12

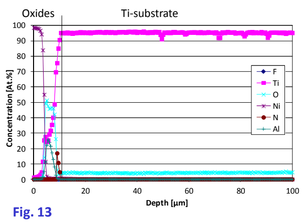

Fig. 13

Figures 13 and 14: SEM-image of the double layer oxide scale (left) and EPMA-profiles (right) after 120h of oxidation at 600°C in air

Conclusions

The oxygen uptake of Ti-alloys during high temperature exposure in oxidizing environments can be suppressed by a combined Al- plus F-treatment. Single Al-enrichment is not enough for long term exposure. This combination widens the application possibilities of Ti-alloys so that they could be used at temperatures above 600°C.

Introduction

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