Karl-Winnacker-Institut High Temperature Materials

Oxidation protection of new high temperature light weight materials by ion implantation

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Introduction


Alloys based on γ-TiAl are of great interest for several high temperature applications due to their properties (good high temperature strength and coeval low specific weight). TiAl-components in e.g. aero engines would be 40% lighter compared to now used made of Ni-alloys and this would reduce fuel consumption, noise and CO_2 emissions.

The long term use of TiAl-alloys is limited to temperatures of about 700°C because of their poor oxidation resistance. The oxidation resistance can be improved significantly by small amounts of halogens in the subsurface zone (so called halogen effect). The halogens form gaseous Al-halides which are finally oxidised to Al_2O_3. So a protective alumina scale is formed which is stable under thermocyclic conditions and in wet environments.

Experimental

Several technical TiAl-alloys were investigated with and without fluorine treatment. The compositions of the investigated TiAl-alloys (at.%) were as follows:

γ-MET: Ti-46.5Al-4(Cr, Nb, Ta, B),
MoCuSi: Ti-45Al-0.35Mo-0.65Cu-0.2Si,
PX-3500: Ti-46Al-5Nb,
TNB-V3: Ti-45Al-8Nb-0.2B-0.2C,
XD-4722: Ti-47Al-2Cr-2Nb.

Fluorine was applied by BLI² (beamline-ion-implantation) and also by the PI³-technique (plasma-immersion-ion-implantation). Additional ways to apply fluorine were treating the samples via the liquid phase with a F-containing compound at RT and subsequent heating at elevated temperatures or a gas phase treatment directly at elevated temperatures.

Isothermal thermogravimetric measurements were performed to study the oxidation kinetics of the alloys with and without fluorine. Thermocyclic 25h-oxidation tests were done under laboratory air at 720°C and 900°C. The samples were heated for 24 hours. Then they were removed from the furnace, cooled to room temperature and weighed. This took one hour. Finally the samples were put back into the hot furnace so the duration of one cycle was 25h.

Results

The halogen effect reduces the oxidation kinetics. This can be seen in figs. 1 and 2. During thermocyclic oxidation spallation of oxide particles can occur. This explains the mass losses of the untreated sample after about 40 days (fig. 3). The halogen effect is stable for oxidation times up to 365 days (= 8640 h) and longer in dry environment. The optimum implantation dose is 2×10^{17} F/cm². The implantation energy plays a minor role. The halogens can also be incorporated by other techniques e.g. dipping or spraying. The treatment with a fluorine containing polymer leads to even better results than the beamline implantation with the optimum fluorine dose (fig. 4). The treatment with the polymer protects the whole surface while only the planar faces are implanted during the beamline process so accelerated oxidation can be observed at the unprotected corners and edges of the implanted samples. The mass loss after the first day of the polymer treated samples is due to the evaporation of the organic rest of the polymer during the first heating up. The gas phase treated sample shows an even better behaviour.

The halogen effect works also on complex components. Several TiAl turbine blades have been investigated during a 25h-cycle test at 720°C and 900°C in lab air. Light microscopy and SEM images of the surface of an untreated sample and a F-PI³ implanted sample before oxidation and after 10 days exposure were made. (Figs. 5 – 8, a + b). EDX-measurements revealed no difference between the two samples before oxidation except the additional appearance of F on the implanted one but after oxidation a mixed oxide layer was found on the untreated sample while a Al_2O_3-scale has formed on the PI³-sample (Figs. 5 – 8, c).

Metallographic cross sections of small coupons proved these results. Untreated TiAl-alloys form a thick mixed oxide ($TiO2/Al_2O_3$ + TiN) or can be even totally oxidized during high temperature exposure in air while a thin alumina layer is found on F-treated samples (figs. 9 – 11).

Conclusions

Fluorine surface treatment leads to a significant increase of the oxidation resistance of TiAl-alloys without infecting their good mechanical properties. The oxidation resistance is no limiting factor anymore so the long term use of TiAl-alloys after fluorination at temperatures above 700°C could be possible now. The halogen treatment would be the last step in the processing route of TiAl-components so they can be designed and processed for their final application before.

Acknowledgements

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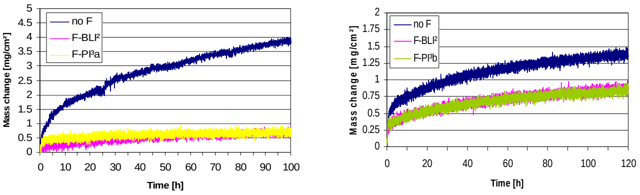
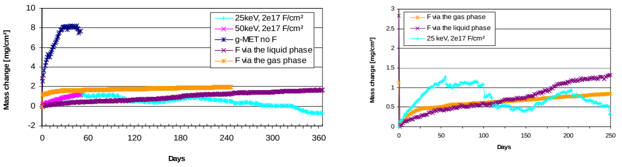


Figures 1 and 2: TGA-results of γ-MET (left) and TNB-V3 (right) during isothermal oxidation at 900°C in synthetic air with and without F-implantation (BLI²: 25 keV, 2×10^{17} F/cm²; PI³-a: 10 µs, 30 kV, 300 W, 500 Hz, 1×10^6 Pulse; PI³-b: 10 µs, 30 kV, 400 W, 750 Hz, 7.5×10^5 Pulse)



Figures 3 and 4: Results of γ-MET under thermocyclic oxidation (25h-cycle-test) at 900°C in laboratory air (left: measured mass change; right: standardized mass change)

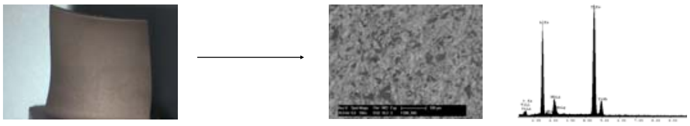


Figure 5 a- c: Magnified photo of the untreated blade (left), SEM-image of the surface (middle) and EDX-spectra of the surface (right) before oxidation

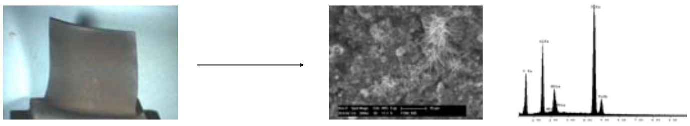


Figure 6 a- c: Magnified photo of the untreated blade (left), SEM-image of the surface (middle) and EDX-spectra of the surface (right) after oxidation for 10 days at 720°C in air

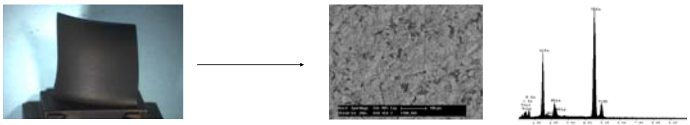


Figure 7 a- c: Magnified photo of the F-PI³ blade (left), SEM-image of the surface (middle) and EDX-spectra of the surface (right) before oxidation

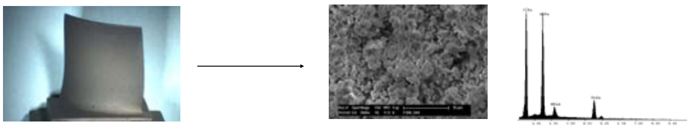
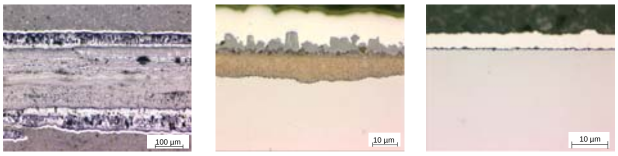


Figure 8 a- c: Magnified photo of the F-PI³ blade (left), SEM-image of the surface (middle) and EDX-spectra of the surface (right) after oxidation for 10 days at 720°C in air



Figures 9 - 11: Metallographic cross sections of MoCuSi (left, totally oxidized, no implantation), γ-MET (middle, mixed oxide scale, no implantation) and MoCuSi (right, Al_2O_3-scale, F-BLI²) after oxidation at 900°C in dry synthetic air for 120 h.