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Improving the oxidation resistance of TiAl-alloys with fluorine

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Abstract

The technical TiAl-alloy γ-MET (Ti–46.5Al–4(Cr, Nb, Ta, B)) was oxidised thermocyclically (24 h-cycle-test) at 900 °C in wet and dry air. In this paper results of untreated and fluorine treated TiAl-samples are presented. Their oxidation behaviour will be shown. Several methods were used to apply the halogens to the surface, e.g. beamline ion implantation, spraying of or dipping into a halogen containing liquid. A pure protective alumina scale was found, e.g. after treatment with a fluorine containing polymer and thermocyclic oxidation up to 1 year at 900 °C in laboratory air. On the other side thick fast growing and non-protective mixed oxide scales were found on the untreated samples.

Keywords: Intermetallics; Oxidation; Metallography; Halogen effect; Titanium aluminides

1. Introduction

Alloys based on aluminium and titanium, intermetallic titanium aluminides, are promising materials for several high temperature applications due to their good mechanical strength at elevated temperatures which is comparable to that of Ni-based alloys. The specific weight of titanium aluminides is about 4 g/cm^3 and thus only half of that of high temperature Co- or Ni-alloys. The efficiency of e.g. automotive engines or aero turbines could be increased by using these light weight materials. Titanium aluminides with an Al-content of about 40–50 at% so called γ-TiAl-alloys are the most interesting [1]. The long term use of TiAl-alloys is limited to about 850 °C [2] because of their poor oxidation resistance despite their mechanical properties which would allow higher temperatures [3]. There are several ways to improve the oxidation resistance of TiAl-alloys. The alloying with other elements like Nb, Si, etc. (several at% = macro alloying) improves the oxidation resistance [4] but alloying of the whole bulk material influences the mechanical properties [5]. Surface treatments at the end of the processing route are much better because the components can be designed for their final use. Small amounts of halogens (some ppm = micro alloying) improve the oxidation resistance of TiAl-alloys significantly [6]. One method to apply the halogens is the ion implantation technique [7]. The halogens have to be at the metal/oxide interface to form gaseous aluminium halides, which are oxidised to Al_2O_3 while their outward diffusion due to the increasing oxygen partial pressure [8]. Cheaper methods for the halogenation of TiAl-alloys are dipping or spraying with halogen containing compounds. Especially fluorine containing organic compounds are proven to be the easiest way and also achieve the best results [9]. This fluorine effect is stable even under thermocyclic conditions and wet environments. The aim of this paper is to present recent results of the alloy Ti–46.5Al–4(Cr, Nb, Ta, B) with and without fluorine treatment after oxidation at 900 °C in dry and wet air.

2. Experimental

Coupons of the technical TiAl-alloy γ-MET (Ti–46.5Al–4(Cr, Nb, Ta, B)) were cut from 1 mm thick sheets. The dimensions of the coupons were 10 mm × 10 mm so the surface of the two faces was much larger than that of the other four sides. These samples were ground down to 1200 grit with SiC paper. After polishing the samples were cleaned ultrasonically in ethanol for 10 min. One set of such treated samples was sent to the research centre Dresden for beamline implantation, another set of untreated samples was directly oxidised to investigate their oxidation behaviour and finally some samples were sprayed with a fluorine containing compound (treatment I) or treated with fluorine via the gas phase after decomposition of a fluorine containing compound at elevated temperatures (treatment II). Thermocyclic oxidation tests were executed in two ways. Twenty four hours-cycle-tests included the exposure of the samples in an open chamber (=laboratory air) furnace at 900 °C for 24 h, cooling

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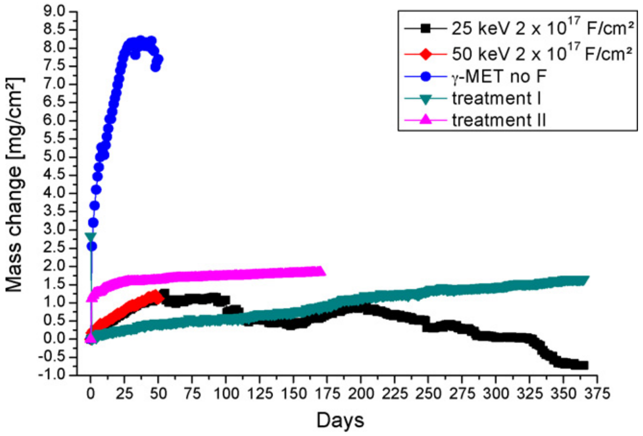


Fig. 1. Mass change behaviour of one untreated and four fluorine treated γ-MET samples (24 h-cycle-test/900 °C/dry air).

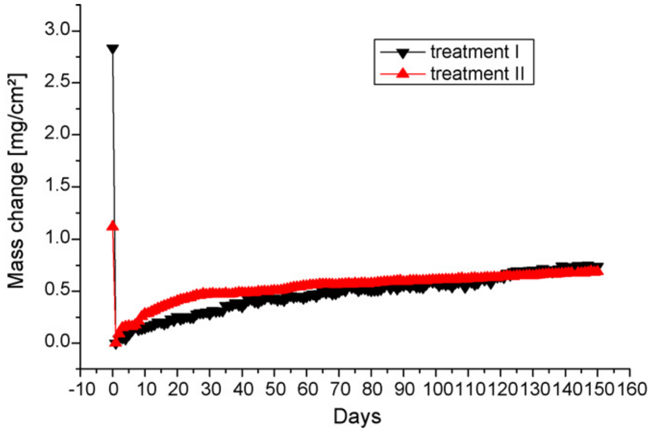


Fig. 2. Comparison of the standardised mass change behaviour of the two γ-MET samples after treatment I and II (24 h-cycle-test/900 °C/dry air).

to room temperature, weighing and finally putting them back into the furnace after 1 h. During a second test series the atmosphere was moistened with 10% water vapour. Post experimental investigations included metallographic observations, EPMA (Electron Probe Micro Analysis) and SEM (Scanning Electron Microscopy) to inspect the form, composition and thickness of the oxide scales.

3. Results and discussion

The untreated samples could be recognised easily by viewing. They showed a brownish surface, which was identified as a mixed oxide/nitride of TiO_2/TiN/Al_2O_3 [10]. Halogen treated TiAl-alloys showed either a grey surface (after implantation) or a yellow/white surface (after liquid or gas phase treatment). These surfaces were identified as a thin protective Al_2O_3-scale [11]. The oxidation kinetics of these samples was several orders of magnitude lower than that of untreated TiAl-alloys [12]. This effect was independent of the halogen used if the tests were performed isothermally [13]. The halogen effect worked also in wet environments [14]. Under thermocyclic conditions only fluorine showed a positive effect [15]. The effect of chlorine worked only for the first hot dwell period [16]. In Fig. 1 the results of some γ-MET samples are shown. The samples were oxidised thermocyclically in a 24 h-cycle-test at 900 °C in laboratory air for up to 1 year. The untreated sample showed the highest mass gain within its test duration of 50 days and some spallation, which was caused by the mismatch of the thermal expansion coefficients of the metallic substrate and the oxide scale during cooling. This mismatch led to tensions within the oxide scale, which were released by cracking or rumpling and finally by the spallation of oxide flakes if the oxide scale was to thick. The atmosphere diffused faster through these cracks within the oxide scale to the metallic substrate than through a compact oxide layer. This caused enhanced oxidation. The spallation was observed visibly and it was revealed by the mass losses during the last days of the test. The beamline implantation of fluorine with one dose (2×10^{17} F/cm^2) at two energies (25 and 50 keV) showed no spallation within 50 days. The test with the higher energy was stopped after this period. The second sample was exposed for 1 year, i.e. 365 days. After about 55 days the first mass loss occurred. This loss was due to the spallation of flakes of the oxide scale formed at the untreated edges and corners of the coupon. The beamline implantation was limited to flat sample geometries so that the edges were not implanted. During the beamline process a focussed ion beam was scanned over the surface of the sample so the samples had to be turned to implant the two faces. The implantation of the four small sides was not done due to time restrictions. On the other side a total protection of a fourth sample was achieved by a liquid phase treatment with a fluorine containing organic compound. This sample showed a mass loss after the first day because of the evaporation of the organic residues during heating up for the first time but after that no further mass loss, i.e. no spallation was observed within the test duration of 1 year. Therefore, the fluorine effect was present at least for this time period. The compound decomposed and the fluorine was released. The released fluorine reacted with the aluminium of the substrate to form fluorides which were finally oxidised to Al_2O_3. The total mass gain after 1 year was less than 2 mg/cm^2. This was related to a slow growing Al_2O_3 scale. This scale was very thin and did not tend to spall. So it was very protective. The sample treated with fluorine via the gas phase is still under investigation. The mass gain after 150 days was about 2 mg/cm^2, which was almost

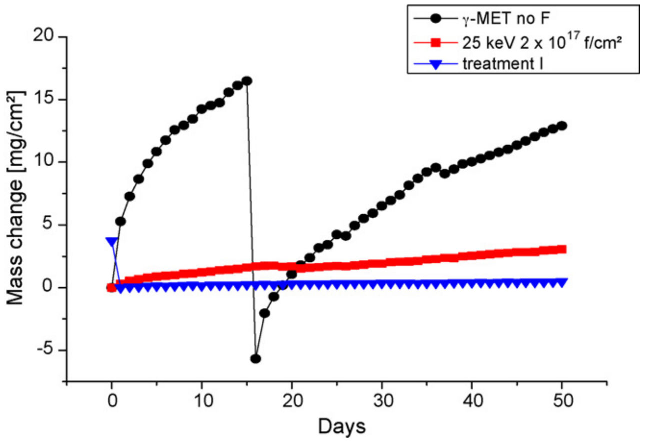
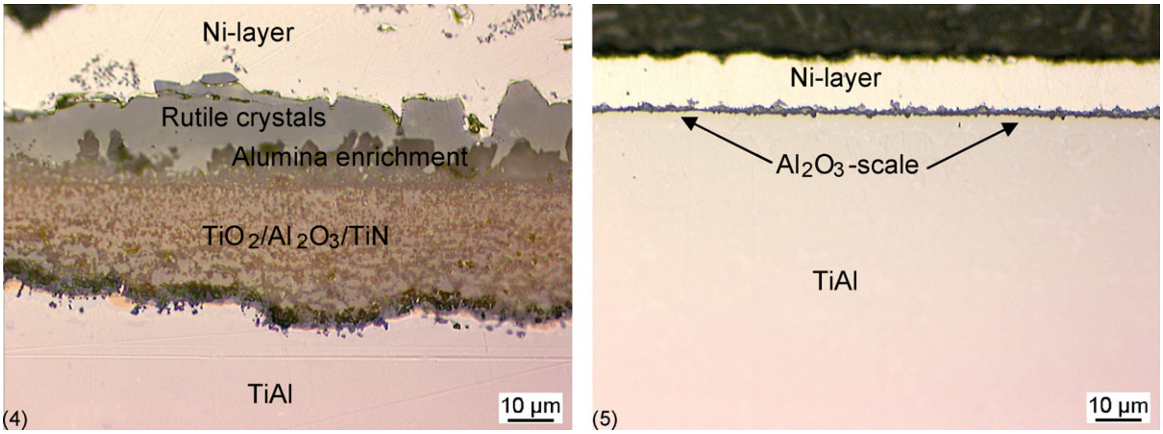


Fig. 3. Mass change behaviour of one untreated and two fluorine treated γ-MET samples (24 h-cycle-test/900 °C/wet air).



Figs. 4 and 5. Metallographic cross sections of the untreated γ-MET sample (left) and the fluorine implanted sample (right) after 50 days cyclic oxidation at 900 °C in wet air showing the oxide scales on the faces (the Ni-layer is a result of the metallographic preparation).

the same as the final value of the sample with treatment I but it has to be taken into account that the mass gain after the first day was more than 1 mg/cm$_2$. This higher mass gain at the beginning was related to the uptake of fluorine via the gas phase. The mass gains of the different fluorine treatments were compared by setting the mass gain after the first day to zero. These standardised mass changes of treatment I and II are shown in Fig. 2. The mass change behaviour of the two samples was almost the same during the first 150 days of testing.

Water vapour accelerates the oxidation rate due to the reaction with TiO_2 of the normally grown mixed oxide scale. This reaction leads to the formation of H_2, which can diffuse through the oxide scale and deteriorate it, so oxygen can attack the metallic substrate more easily [17]. However, the fluorine effect worked also under thermocyclic conditions in wet environments (Fig. 3). The mass gain of an untreated γ-MET sample was much higher than in dry atmosphere and after 14 days there was an immense mass loss due to the spallation of the whole oxide scale from one side of the specimen. No spallation and only a slight mass gain was observed after treating with fluorine. The Al_2O_3 scale after fluorine treatment did not react with the water vapour, so no H_2 could form and thus no change in the oxidation behaviour occured [18]. The mass gain of the beamline implanted sample was again higher than that of the one after treatment I because of the enhanced oxidation at the unprotected four small sides after beamline implantation but still much lower than without any treatment due to the protection by implantation of the two faces. In Figs. 4 and 5 the oxide scales formed on the faces of the untreated and the fluorine implanted sample can be seen. The magnification of the metallographic images was the same. The mixed oxide scale (TiO_2/Al_2O_3) on the untreated sample was very thick and wavy (up to 100 μm). This scale had a layered structure with some rutile on top, an alumina enrichment underneath, a fine grained mixed oxide and finally some yellow nitrides (especially TiN) have been found at the oxide/metal interface which was concurrent with older results [19]. There were also some voids at the metal/oxide interface. The protective Al_2O_3 scale on the faces of the coupon after fluorine implantation was quite thin (less than 5 μm) and no nitrides were found (Fig. 5). The scale was also good adherent and free of cracks. Thicker scales equal to those on the untreated sample were found on the unprotected edges and corners. The result for treatment I looked the same but with the difference that the sample was totally covered with the thin alumina scale. This sample was perfectly protected despite of the enhanced oxidation conditions. The fluorine effect was not influenced by the water vapour.

4. Conclusions

The presented results are a step towards an industrial use of TiAl-components. The oxidation resistance of TiAl-alloys can be improved by a treatment with fluorine up to temperatures of at least 900 °C. The fluorine effect works under enhanced oxidation conditions such as wet environments and thermo cycling where untreated components would fail quite quickly at this temperature. The effect works up to at least 8760 h. The fluorine treatment would be the last step in the processing route of TiAl-components so they can be designed and optimised for their later use before.

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