INVESTIGATION OF THE FLUORINE MICROALLOYING EFFECT IN THE OXIDATION OF TiAl AT 900°C IN AIR

Hans-Eberhard Zschau[1], Michael Schütze[1*], Horst Baumann[2] and Klaus Bethge[2]

[1]Karl Winnacker Institut der DECHEMA e.V., Theodor-Heuss-Allee 25,D-60486 Frankfurt am Main, Germany
[2]Institut für Kernphysik der Johann Wolfgang Goethe-Universität Frankfurt am Main, August-Euler-Str. 6, D-60486 Frankfurt am Main, Germany

High-temperature oxidation resistance of gamma titanium aluminides can be achieved by the formation of a continuous scale of slowly growing Al_2O_3. The formation of such a scale can be stimulated by the addition of small amounts of fluorine. In this study the fluorine is applied in two ways: treatment with diluted HF and ion implantation.

Cast γ-TiAl (Ti-50at.%Al) was prepared as coupons of dimensions 10x10x1 mm^3 and polished with SiC paper down to 4000 grit. Microstructural investigations show a minor amount of the α_2-Ti_3Al phase (lamellar structure) within the γ-TiAl phase.

In the first part of the investigations the samples were treated with different aqueous HF solutions of 0.0113 w.-%, 0.0565 w.-%, 0.113 w.-%, 0.565 w.-% and 1.13 w.-% HF. The HF was applied as a drop which covers one side of the samples. After drying the specimens were oxidized at 10h/900°C/air.

The post oxidation investigations started with optical microscopy followed by a morphologic surface study using SEM. Non destructive Ion Beam Analysis (PIGE-technique) was applied to determine the fluorine profile within the first 1.3 µm and to measure the elemental profiles of the main elements Ti, Al and O in the oxide layer down to the Al depleted sub-surface region (RBS-technique). These PIGE/RBS-investigations were also done at the samples after HF treatment but before oxidation. Finally a cross-section was prepared in order to study the layer structure by SEM.

For HF concentrations of 0.0113 w.-%, 0.565 w.-% and 1.13 w.-% a negative fluorine effect was observed. In these cases the oxide layers are at least 10 µm thick consisting of a pure TiO_2 top layer and a mixed Al_2O_3/ TiO_2 layer. For treatment with 1.13 w.-% HF a cross-section was prepared by a water-free method in order to measure the fluorine profile within the oxide by a scanning proton microprobe. A fluorine content of <2.000 w.-ppm was found at the oxide/metal interface.

A 0.8 µm layer rich in Al_2O_3 was found on the surface after 0.0565 w.-% HF and 0.113 w.-% HF treatment with oxidation showing a positive Fluorine effect. This effect is connected with fluorine amounts of about 20 - 22 w.-% at the surface before oxidation. After the oxidation a maximum of the fluorine concentration was found within the metal/oxide interface region with values up to 1.1 w.-%.

TGA measurements were carried out after dipping treatment in 0.113 w.-% HF for 600h/900°C/air which also showed a positive fluorine effect.

In the second part ion implantation was carried out using a 60 keV implanter. At 20 keV implantation energy (corresponding to a projected range of 34 nm) the following doses (in F-ions cm^{-2}) were implanted: 10^{15}, $5x10^{15}$, 10^{16}, $5x10^{16}$, 10^{17} and $5x10^{17}$. After isothermal oxidation (12 h/900°C/air) a positive fluorine effect was found for doses of $5x10^{16}$ and 10^{17}. Increasing the oxidation time to 120 hours a dose of 10^{17} gave the best results. Even after an oxidation time of 500h/900°C/air the implanted sample is covered by a layer rich in alumina. The measured profiles of F (fig.1), Ti, Al and O (fig. 2) are similar to those obtained for the positive fluorine effect after HF treatment. TGA measurements (650h/900°C/air) carried out after F implantation (10^{17} /40 keV) of the whole sample surface show slow alumina kinetics.

The measured fluorine concentrations in the oxide/metal interface are compared with the fluorine amounts required from thermodynamic calculations.

The loss of fluorine during the heating process was studied between 400°C and 1000°C in steps of 100 degreees for F-implanted and for HF-treated samples. The results show that the mechanism of the Fluorine effect is more complex compared to the other halides.

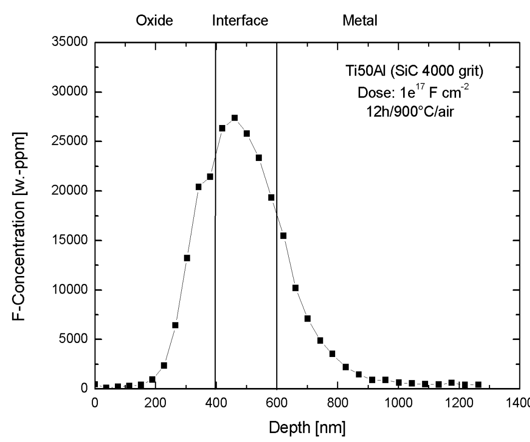

Fig. 1: F-Depth profile obtained by PIGE (10^{17} F cm^{-2} and 12h/900°C/air).

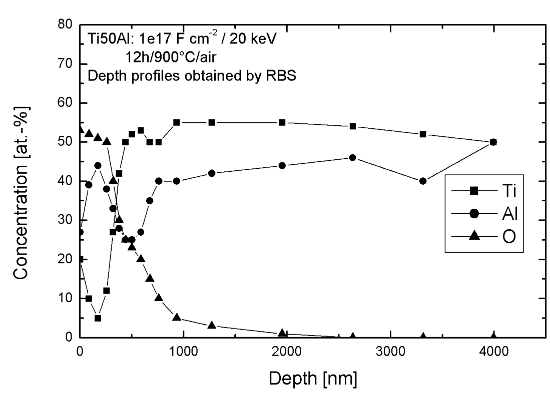

Fig. 2: Depth profiles of Ti, Al and O obtained by RBS (10^{17} F cm^{-2} and 12h/900°C/air).

* correspondence