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Application of ion beam analysis for the control of the improvement of the oxidation resistance of TiAl at 900 °C in air by fluorine ion implantation and HF-treatment

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Abstract

The oxidation resistance of TiAl at elevated temperatures >750 °C can be improved by the addition of small amounts of fluorine. The fluorine is applied in two ways: ion implantation and wetting with diluted HF. Using non-destructive Ion Beam Analysis the fluorine depth concentration profiles in the near surface region are determined before and after oxidation. The fluorine maximum is found to be at the metal/oxide interface, which supports the theoretical explanation of the fluorine microalloying effect. The time dependent behaviour of the fluorine content is characterized by a fast decrease of the fluorine concentration during the first hours of oxidation followed by a moderate decrease. The results offer the possibility for a technical application of the fluorine microalloying effect to improve the oxidation resistance of TiAl-alloys at temperatures >750 °C.

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1. Introduction

γ-TiAl is of increasing interest in gas turbine industries because of its good mechanical properties and low density. However, due to the poor high-temperature oxidation resistance of TiAl at temperatures above 750 °C, the lifetime of

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components is limited. Indeed, under such conditions, a non protective oxide layer consisting of TiO_2 and Al_2O_3 is formed during oxidation. This mixed oxide exhibits faster oxidation kinetics than a continuous protective alumina scale [1].

One method used to improve the γ-TiAl oxidation behaviour is the so-called microalloying effect. In [2], it was reported that very small amounts of chlorine improve dramatically the oxidation behaviour of γ-TiAl. This "chlorine effect" is explained by a thermodynamically driven selective transport of volatile Al_xCl_y species towards the metal/oxide interface [3]. The chlorine effect was investigated in detail in [4–6] using Cl ion implantation. It was shown that this effect occurs even for Cl concentrations lower than 500 ppm. In contrast to this first investigation, the treatment with F showed no positive effect. Since theoretical considerations would lead to the conclusion that also for fluorine a "halogen effect" should exist [7] a detailed investigation concerning the fluorine effect was needed. It was predicted that the fluorine effect should occur within a certain fluorine concentration interval. The aim of the present study is to improve the oxidation behaviour of γ-TiAl using the fluorine microalloying effect and to determine experimentally the optimal fluorine content.

2. Materials and methods

Cast γ-TiAl (Ti-50 at.%Al) was prepared as sheets of dimensions $8 \times 8 \times 1\ mm^3$ and polished with SiC paper down to 4000 grit.

In the case of HF treatment the TiAl specimens were treated with different diluted HF solutions by a droplet and dried before oxidation, whereas the other side remained untreated.

The implantation of fluorine ions was carried out one-sided with several fluences using 20 keV ion energy. All implantations were performed at the 60 kV implanter of the Institute of Nuclear Physics (IKF) of the Johann Wolfgang Goethe-University in Frankfurt/Main.

All specimens were characterized both prior to and after oxidation by surface analytical and ion beam techniques. Metallographic cross-sections were prepared after the oxidation tests. Optical microscopy and SEM (Scanning Electron Microscopy) were used to study the surface structure and oxide morphology. The integral oxide growth during oxidation was measured by simultaneous recording the mass gain using a thermobalance (Thermogravimetric Analysis TGA). In these cases all sides of the specimens were treated.

The PIGE (Proton Induced Gamma-ray Emission) technique [8] with the reaction $^{19}F(p,\alpha\gamma)^{16}O$ at resonances of 340 keV and 484 keV was used to determine the fluorine concentration depth profiles within the first 1.4 μm. The depth resolution near the surface is about 20 nm. The PIGE measurements were carried out using a proton beam of 0.5 mm diameter from the 2.5 MV Van de Graaff accelerator of the IKF. A high purity CaF_2 single crystal served as standard and the ion fluence was measured using a monitor detector. The high energetic γ-rays (5–6 MeV) were detected using a 10 inch NaJ-detector which was more efficient than a former used BGO detector. The RBS (Rutherford Backscattering Spectrometry) technique [9] was suitable to measure the elemental composition at the sample surface and depth profiles of Ti-Al-O within the first micrometers. The RBS-measurements were carried out at the 7 MV Van de Graaff accelerator of the same institute using a 3.52 MeV ^{4}He-ion beam of 0.5 mm diameter and a surface barrier detector.

3. Results and discussion

3.1. Fluorine microalloying effect after ion implantation

Detailed experimental investigations were performed to study the fluorine microalloying effect. From thermodynamics the amount of fluorine required for establishing a protective alumina layer was not known exactly. Because of this a screening using several fluorine implantation fluences was started to find the optimal fluorine implantation condition. The TiAl-samples were implanted at 20 keV implantation energy with the following fluences (in F-ions cm^{-2}): 10^{15}, 5×10^{15}, 10^{16}, 5×10^{16} and 10^{17}. The resulting fluorine depth profiles were calculated using the computer code T-DYN [10].