Study of the Mechanisms of Initial Oxidation and of the Interaction with Reactive Elements in the Halogen Effect for Ni-base Alloys

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Funded by: DFG
Period: 01.07.2011 - 30.06.2013

Deutsche Forschungsgemeinschaft
DFG

Introduction

Ni-base super alloys with Al-contents of less than 10 wt.-% are widely used in high temperature technology due to their beneficial mechanical properties. In contrast to this their oxidation behaviour is insufficient at temperatures above 1000°C.
Oxidation of Ni-base alloys in air at temperatures above 1000°C does not form a dense protective Al_2O_3-scale on the surface, but rather a complex layer structure as shown in fig. 1. The alumina scale is characterized by internal oxidation, i. e. it grows into the metal showing a discontinuous structure.

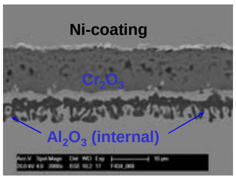

Fig. 1: Oxide scale of IN738 after isothermal oxidation of 24h/1050°C/air.

Fig. 2: The turbine blades for aircraft engines and gas fired power stations are manufactured with an Al-rich bond coat and a TBC.

Oxidation protection can be achieved by the formation of a dense alumina scale. Usually Ni-base alloys are covered with Al-rich coatings (bond coat).

➡ State of the art (fig. 2).

F-effect: change of the oxidation mechanism

Formation of a "self-supporting" alumina scale:
Wagner´s oxidation theory: Formation of a dense alumina scale can be achieved, if the Al-activity is sufficiently high.

„Artificial" increase of the Al-amount by using the **halogen effect**.
This concept works in the case of TiAl-alloys. Fluorine is chosen due to the good results obtained with TiAl.

In fig. 3 the possible reactions in a cavity at the oxide/metal interface are illustrated. The Al-amount at the metal surface can be increased by a selective formation of gaseous Al-fluorides in pores and microcracks and their migration towards the surface. Due to the increasing oxygen partial pressure the Al-fluorides disintegrate and the Al is oxidized forming a dense protective layer of Al_2O_3 (fig. 4-6).

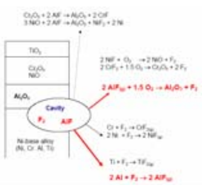

Fig. 3: Possible reactions for the formation of gaseous metal halides in a cavity. The selective formation of gaseous Al-halides is the key condition for the halogen effect.

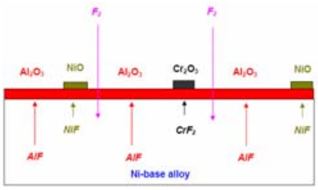

Fig. 4: The halogen effect achieves an artifical increase of the Al-activity and stimulates the formation of a dense protective alumina scale.

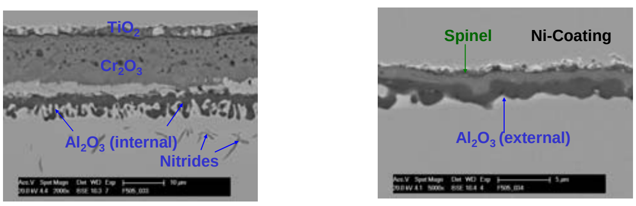

Fig. 5: Left micrograph: Oxide scale of IN 738 (untreated) after oxidation (24h/1050°C/air). Right micrograph: The implanted sample (10^{17} F cm^{-2}) after oxidation (60h/1050°C/air) shows the change from internal to external oxidation of Al.

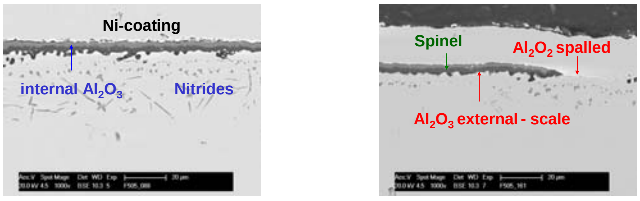

Fig. 6: Left micrograph: Oxide scale of IN 738 (untreated) after oxidation (1000h/1050°C/air). Right micrograph: The implanted sample (5 x 10^{16} F cm^{-2}) shows the change from internal to external oxidation of Al. Only few nitrides are visible. The protective alumina scale formed can partly spall during cooling.

Combined treatment with F and reactive elements

Small additions of reactive elements (Y, Hf, Ce…) are beneficial for the adhesion of protective alumina scales. An improved adhesion of the protective alumina scale formed by the fluorine effect should be achieved by a combination of the fluorine treatment and the reactive element effect. To find the optimum additions ion implantation was used because of its high accuracy and reproducibility. The implantations were performed at the 60 kV-implanter, whereas the non-destructive analysis of F-and Y/Hf-profiles was carried out by using the PIGE/RBS-techniques at the 2 MV Van de Graaff accelerator of the Institute of Nuclear Physics of Frankfurt University. The implantations were planned by doing comprehensive Monte Carlo simulations of the implantation profiles using the software T-DYN (fig. 7-10).

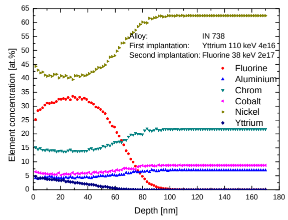

Fig. 7: Element profiles in the alloy IN 738 after implantation of Y (4 x 10^{16} Y cm^{-2}/110 keV) and F (2 x 10^{17} F cm^{-2}/38 keV). Calc. by T-DYN.

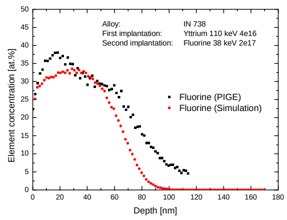

Fig. 8: Comparison of the implanted F-profile (measured by using PIGE) and the simulated (T-DYN) for data of fig. 7.

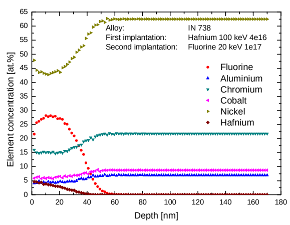

Fig. 9: Element profiles in the alloy IN 738 after implantation of Hf (4 x 10^{16} Hf cm^{-2}/100 keV) and F (10^{17} F cm^{-2}/20 keV). Calc. by T-DYN.

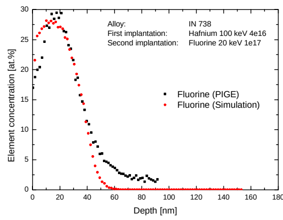

Fig. 10: Comparison of the implanted F-profile (measured by using PIGE) and the simulated (T-DYN) for data of fig. 9.

The implantations of Y resp. Hf, followed by implantation of F show a distinct change of the element profiles within the near-surface region of the alloy IN 738 as illustrated in fig. 7 and 9. The measured F-depth profiles are in good agreement with the calculated F- implantation profiles (fig. 8 and 10). Based on these results first experiments show an adherent protective alumina scale (fig. 11). Future work is planned to determine the optimum parameters for several reactive elements in combination with F.

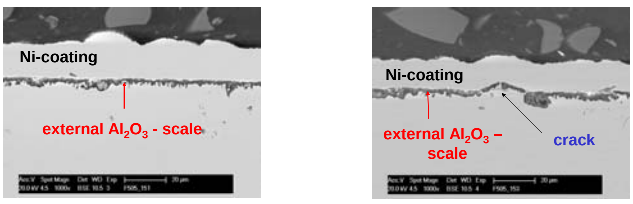

Fig. 11: Implanted sample of IN 738 after oxidation (60h/1050°C/air). Left micrograph: 4 x 10^{16} Y cm^{-2} /110 keV and 1 x 10^{17} F cm^{-2} / 38 keV. Right micrograph: 1 x 10^{16} Y cm^{-2} / 110 keV and 1 x 10^{17} F cm^{-2} / 38 keV.