Advanced Materials Research *Online: 2011-07-04*
ISSN: 1662-8985, Vol. 278, pp 485-490
doi:10.4028/www.scientific.net/AMR.278.485

Formation of a protective alumina scale on Ni-base superalloys by using the halogen effect

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Key words: Ni-base superalloys, oxidation protection, halogen effect, ion implantation, alumina scale

Abstract. A new method is proposed to achieve a dense protective alumina scale for Ni-base superalloys with an Al-content lower than 10 wt.% at temperatures above 1000°C. The method is based on the halogen effect. Thermodynamical calculations show the existence of a region for a positive fluorine effect at temperatures between 900-1200°C for the alloys IN738 and IN939. By using fluorine ion implantation in combination with Monte Carlo simulation of the fluorine profiles these results were transformed into a region of F-concentrations at the metal surface. A dense protective alumina scale was formed for IN738 after oxidation at 1050°C. Due to the very low Al-content no alumina scale was found for IN939.

Introduction

Technical Ni-based alloys with an Al-content significantly lower than 10 wt.% show a fast growing Ni, Cr, Al-oxide scale on the surface during oxidation at temperatures above 1000°C [1]. Beneath this oxide scale a discontinuous non-protective internal alumina scale is formed. The halogen effect was proposed as a new method to form a thin, continuous and dense protective alumina scale [2]. In this work the influence of the Al-content of the alloy is studied. The results of thermodynamical calculations for IN738 and IN939 show the existence of a region for a positive F-effect at temperatures between 900-1200°C. As F-treatment the beam-line ion implantation was chosen. A dense protective external alumina scale was established for IN738 revealing a protective behaviour at least up to 1000h/1050°C. For the alloy IN939 no protective alumina scale was formed. The limits of thermodynamical predictions are discussed.

Materials and Methods

The elemental composition of the used alloys IN738 and IN939 is summarized in table 1. The material was cut into pieces of size 10 x 10 x 1 mm followed by polishing down to 4000 grit SiC. The fluorine treatment was done by ion implantation using a plasma source at the 60 keV ion implanter of the Institute of Nuclear Physics (IKF) of the Goethe-University in Frankfurt/Main. The expected fluorine implantation profiles were calculated using the software package T-DYN [3] and variation of the implantation parameters (fluence, energy). The F-fluences cover the range between

10^{16} and 4 x 10^{17} F cm^{-2}, whereas the chosen F-ion energy of 38 keV corresponds to a mean projected range of about 35 nm in both alloys as calculated by using SRIM [4]. Only one side of the samples was implanted, whereas the untreated sides served as comparison. The non-destructive measurement of the F-implantation profiles is possible with the help of the PIGE (Proton Induced Gamma-ray Emission) method, which belongs to the ensemble of ion beam analysis. The PIGE-measurements were done at the 2.5 MV Van de Graaff-accelerator at the IKF. The resonant nuclear reaction $^{19}F(p, \alpha\gamma)^{16}O$ at a proton energy of 484 keV allowed the F-depth profiling up to a depth of 1 µm. By choosing an incidence angle of 60 degrees a depth resolution of 10 nm near the surface could be reached. The high-energetic 5..7 MeV γ-rays were registered by a 5" NaI-detector. The oxidation tests were performed in a furnace under lab air at 1050°C up to 1000 hours. Metallographic cross-sections were prepared to study the structure of the oxide scales by using light microscopy as well as SEM and EDX-spectrometry.

Table1: Composition of the Ni-base alloys IN738 and IN 939 (in wt.%).

Alloy	Ni	Co	Cr	Al	W	Mo	C	Ti	Ta	Others
IN 738	61.13	9.0	16.00	3.30	1.70	2.60	0,17	3.50	1.70	0.90 Nb
IN 939	48.35	20	22	1.4	2		0.15	3.8	1.3	1.0 Nb

Results of Thermodynamical Calculations

A dense protective alumina scale can be formed on the surface if the Al-content of the alloy is above the "critical" Al-concentration according to Wagner's oxidation theory [5]. The low Al-contents shown in tab. 1 hinder the formation of a dense protective alumina scale. However, if the Al-activity on the surface is increased "artificially", the oxidation mechanism can be changed. The halogen effect was found to realize an "artifical" increase of the Al-activity leading to the formation of a protective alumina scale [2]. After doping the surface with a halogen, e. g. fluorine, and heating the alloy to high temperatures, a preferred formation of gaseous Al-fluorides can be obtained. These Al-fluorides migrate to the surface and, after disintegration due to the increasing oxygen partial pressure, the formation of alumina proceeds. The free gaseous fluorine is able to return into the metal and maintains a cycle process leading to the alumina scale formation. This model originally developed for the case of TiAl-alloys [6] is consistent with the experimental results. The key point for the occurance of this " positive F-effect" is the existence of a region with a preferred formation of gaseous Al-fluorides.

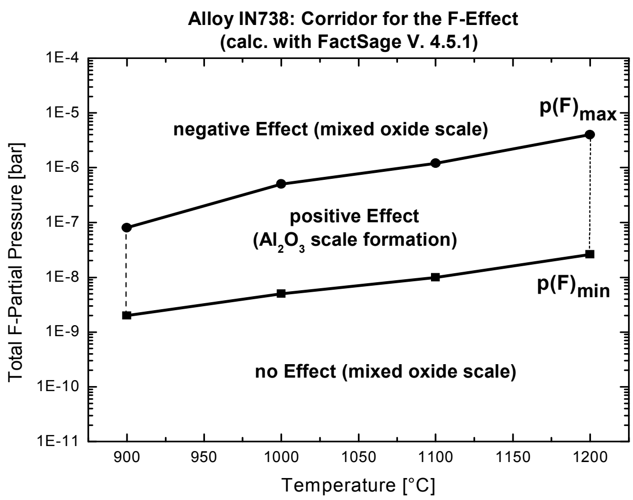


Fig. 1: Corridor for a positive F-effect for the alloy IN738 (calc. with FactSage [8]).

Otherwise the gaseous fluorides of the other alloying elements will take part in this process leading to the formation of a non-protective mixed oxide scale. In ref. [2, 7] the existence of such a corridor for F and the alloy IN738 was shown for temperatures of 900-1200°C (fig. 1) by using the software package FactSage V. 4.5.1 [8].
The calculations were extended to the alloy IN939. Even for this alloy with a low Al-content a corridor for the positive F-effect was predicted for the temperature range of 900-1200°C similar as for IN738. The thermodynamical predictions suppose equilibrium, therefore a possible F-loss during heating is not considered.
However practical applications require the knowledge of suitable F-concentrations on the metal surface. There is no direct equation between total F-partial pressure and F-concentration. Therefore a screening was necessary to transform the F-total partial pressures into F-concentrations.

F-treatment using Ion Implantation

The beam line ion implantation was chosen as method of F-treatment because of its good accuracy and high reproducibility. The maximum of the F-implantation profile was determined to be in a depth of about 35 nm similar to the case of TiAl. This corresponds to an energy of 38 keV for the Ni-based alloys according to SRIM [4]. The implantation depth profiles were calculated by variation of the F-fluence between 10^{16} and 4 x 10^{17} F cm^{-2} using the Monte Carlo software package T-DYN [3]. The calculated F-profiles for IN738 are summarized in fig. 2, whereas the fig. 3 shows the results for alloy IN939.

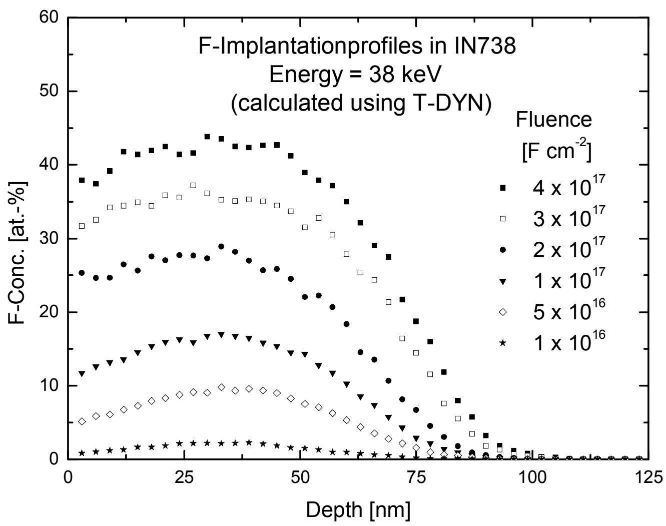


Fig. 2: F-implantation profiles in the alloy IN738 calculated by using T-DYN [3].

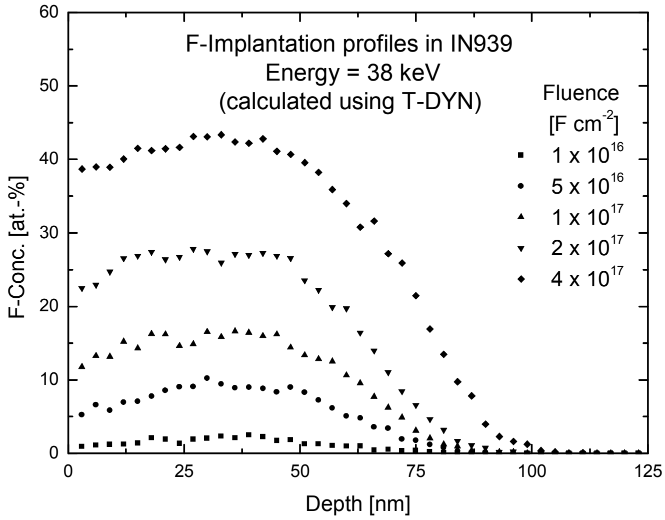


Fig. 3: F-implantation profiles in the alloy IN939 calculated by using T-DYN [3].

The calculated profiles reveal a similar behaviour for both alloys. The maximal F-concentration varies between 2-45 at.% within the depth of 35-45 nm. Due to the high sputtering yield of about 1.6 a saturation effect occurs at a fluence of 4×10^{17} F cm^{-2}. Hence higher fluences were not considered. Based on these results for both alloys the implantations were performed on one side of the samples for 38 keV and fluences between 10^{16} and 4×10^{17} F cm^{-2}. The non-implanted sides served as a baseline.

The PIGE-technique was applied in order to prove the accuracy and reproducibility of the implantation. The comparison between the simulated and the measured F-implantation profile in fig. 4 shows a good agreement. The small deviations on the surface are caused by the surface sputtering, whereas differences in the used stopping power data may be the reason for the small differences in the depth. The measured F-dose of 6.5×10^{16} F cm^{-2} corresponds to the fluence.

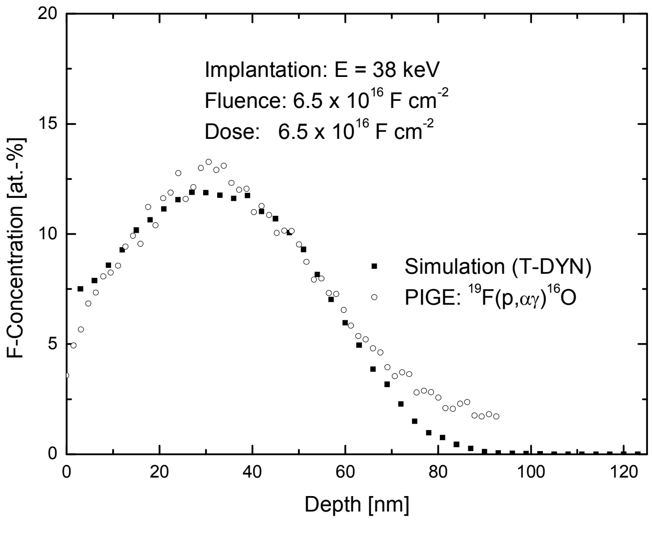


Fig. 4: Calculated (6.5×10^{16} F cm^{-2}) by using T-DYN [3] and implanted (obtained by using PIGE) fluorine implantation profile in alloy IN738.

Results and Discussion

The screening for the alloy IN738 started with the highest fluence of 4 x 10^{17} F cm^{-2} down to 10^{16} F cm^{-2}. The samples were oxidized at 1050°C lab air and for oxidation times between 24h and 168 h. In all cases metallographic cross-section preparation has been performed. The formation of a dense protective oxide scale was obtained partially at high fluences of 2-4 x 10^{17} F cm^{-2}. For longer oxidation times a fluence between 5 x 10^{16} and 10^{17} F cm^{-2} showed the best results. In fig. 5 the results for a fluence of 1 x 10^{17} F cm^{-2} (38 keV) after oxidation (60h/1050°C/air), are shown.

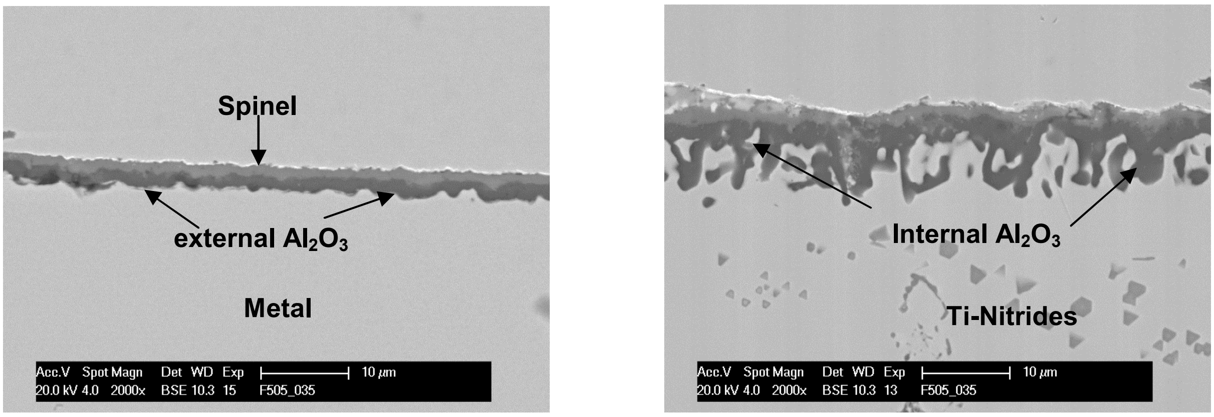


Fig. 5: Left micrograph: Metallographic cross-section of an implanted sample of IN738 (1 x 10^{17} F cm^{-2} / 38 keV) after oxidation (60h/1050°C/air). Right micrograph: Untreated side.

A 1 µm thin external growing alumina scale was formed on the surface of the implanted side. This scale is covered by a 1 µm thick scale of Al-Ni-spinel. The protective nature of the formed alumina scale is revealed by a comparison with the untreated side of the sample in fig. 5. The non-protective internal alumina scale of 10 µm thickness cannot hinder the inward diffusion of nitrogen forming Ti-nitrides within the oxide/metal zone. After extending the oxidation time to 1000h/1050°C the external protective alumina scale still exists as illustrated in fig. 6. Only a few nitrides occur. Partial spalling of the thin (1-2 µm) external alumina scale indicates that scale adhesion must be improved.

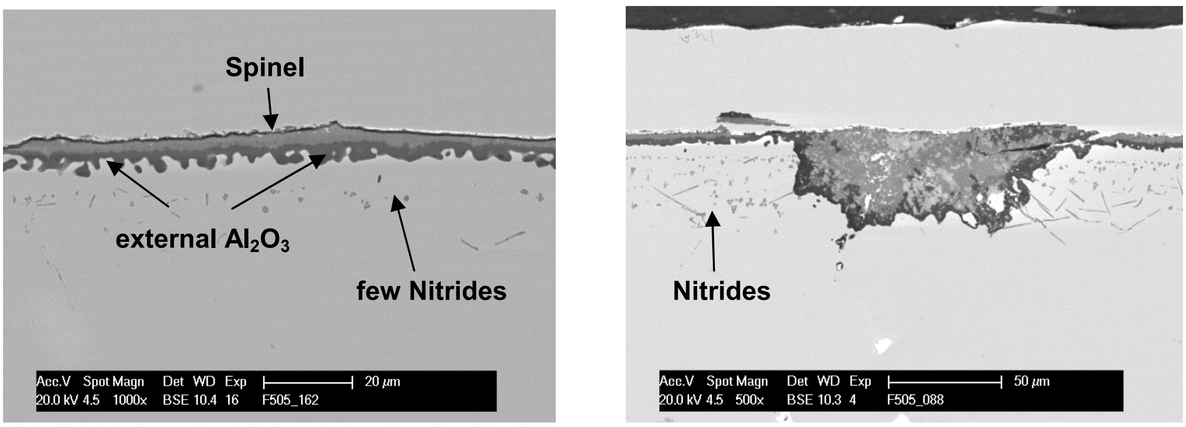
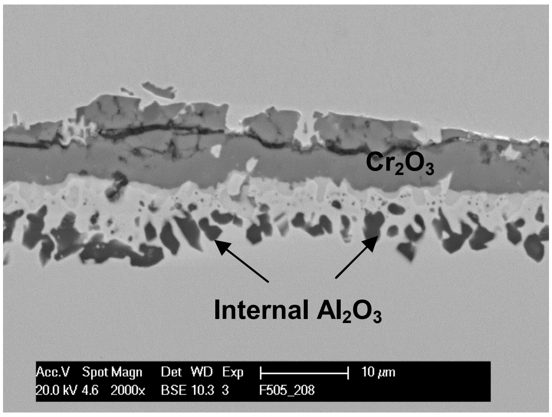


Fig. 6: Left micrograph: Metallographic cross-section of an implanted sample of IN738 (5 x 10^{16} F cm^{-2} / 38 keV) after oxidation (1000h/1050°C/air). Right micrograph: Unimplanted sample of IN738 after oxidation (1000h/1050°C/air). The outer chromia scale has been spalled.



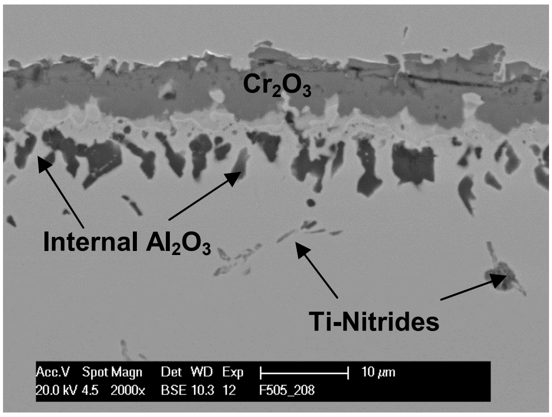


Fig. 7: Left micrograph: Metallographic cross-section of an implanted sample of IN939 (4 x 10^{17} F cm^{-2} / 38 keV) after oxidation (72h/1050°C/air). Right micrograph: Untreated side.

Despite the prediction of a positive F-effect for IN939 the results show no difference between implanted and untreated sample (fig. 7). Beneath the chromia scale an internal growing alumina scale was formed. Nitrides are visible only on the untreated side, whereas no nitrides were found on the implanted side. Obviously the Al-content is too low to establish a protective alumina scale.

Summary

Following Wagner's theory of oxidation the artificial increase of the Al-activity allows the formation of a dense protective alumina scale even for Ni-base alloys with a low Al-content. The F-effect was proposed for increasing the Al-activity on the metal surface. From thermodynamic calculations the existence of a positive F-effect was predicted for the alloys IN738 and IN939. By using F-ion implantation a screening was done to determine the optimal F-concentration. After oxidation at 1050°C a dense and protective external alumina scale was formed on IN738. No F-effect was found for IN939 due to its low Al-content.

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