High Temperature Materials

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

H.-E. Zschau , M.C. Galetz, M. Schütze
e-mail: zschau@dechema.de

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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 (fig. 1). In contrast their oxidation behaviour is insufficient at temperatures above 1000°C. Ni-base alloys do not form a dense Al_2O_3 protective scale on the surface when oxidized in air at temperatures above 1000°C but rather a complex layered structure as shown in fig. 2. The formed alumina scale is characterized by internal oxidation, i. e. it grows into the metal showing a discontinuous structure.

Fig. 1: The turbine blades for aircraft engines and gas fired power stations are manufactured with an Al-rich bond coat and a TBC.

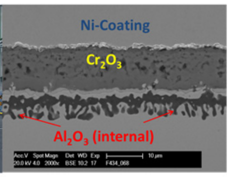


Fig. 2: Oxide scale of IN738 after isothermal oxidation of 24h/1050°C/air.

In the manufacturing process the oxidation protection can be achieved by covering the Ni-base alloy with Al-rich coatings (bond coat). An alternative method to form a protective alumina scale is proposed by using the halogen effect.

Principle of the F-Effect for Ni-base Alloys

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.

The **halogen effect** „artificially" increases the Al-amount on the surface forming a dense protective alumina scale. This concept - which works successfully in the case of TiAl-alloys – is now applied to Ni-base alloys. After doping the alloy surface with F, possible reactions can occur within pores and microcracks at the metal/oxide interface at high temperatures (fig. 3). The Al-amount on the F-doped metal surface can be increased by a selective formation of gaseous Al-fluorides and their transport to 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.

Thermodynamical calculations using FactSage for the alloy IN 738 show a corridor for the F-effect within a temperature range of 900-1200°C (fig. 4).

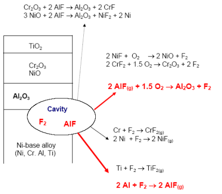


Fig. 3: Possible reactions for the formation of gaseous metal fluorides in a cavity. The dominance of gaseous Al-fluorides is key for the halogen effect.

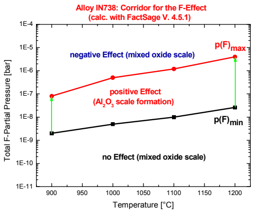


Fig. 4: The corridor between $p(F)_{min}$ and $p(F)_{max}$ predicts the fluorine effect for the alloy IN 738 within the temperature range of 900 - 1200°C. Calc. with FactSage V. 4.5.1.

Ion Implantation and Oxidation of Ni-Al-Cr Model Alloys

Small ingots of Ni-Al-Cr model alloys of nominal compositions given in tab. 1 were prepared by Ar arc-melting at MPC, Iowa State University, followed by drop-casting to form 10 mm diameter rods. The positions of model alloys 1-4 in the Ni-Al-Cr oxide map under dry oxidizing conditions at 1000°C are shown in fig. 5. The borderline characterizes the critical Al-concentration required for the formation of a continuous protective alumina scale during oxidation in dry air. Alloys 2 and 3 are situated close to the borderline (borderline alloys) between the region corresponding to the formation of internal oxidation of Al and the region corresponding to protective Al_2O_3 – scale formation. Sub-critical alloy 1 lies beneath the borderline while alloy 4 lies above the borderline and is able to form a continuous protective alumina scale.

Alloy	Ni [at.%]	Al [at.%]	Cr [at.%]	Ni [wt.%]	Al [wt.%]	Cr [wt.%]
Alloy 1	90	6	4	93.46	2.86	3.68
Alloy 2	88	6	6	91.60	2.87	5.53
Alloy 3	88	8	4	92.42	3.86	3.72
Alloy 4	86	8	6	90.53	3.87	5.60

Tab. 1: Composition of the model alloys 1 – 4 (in at.% and wt.%).

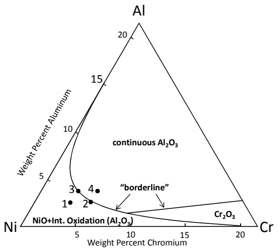


Fig. 5: Location of alloys 1-4 in the oxide map for Ni-Al-Cr alloys with the "Al_2O_3" - border line for 1000°C/dry air.

Fluence	Oxidation in dry air		Oxidation in wet air	
	900°C/20h	1000°C/20h	900°C/20h	1000°C/20h
5 x 10^{16} F cm^{-2}	+	+	+	+
1 x 10^{17} F cm^{-2}	+	+	+	+
2 x 10^{17} F cm^{-2}	+	+	+	+

Table 2: Test matrix for each of the alloys 1-4.

F-ion implantation was performed on one side of the samples with fluences of 5 x 10^{16}, 1 x 10^{17} and 2 x 10^{17} F cm^{-2} / 38 keV. The PIGE-technique was used to verify the implantation profiles. The implanted alloys were isothermally oxidized for 20 hours at 900°C and 1000°C in dry air and in wet air (air+30% H_2O), resp. The test matrix for each of the alloys 1-4 is presented in table 2 revealing a total number of 48 samples.

Promotion of Al_2O_3-Scale Formation and shift of Borderlines

Results for the alloys 1-4 are summarized in tab. 3 and illustrated selectively in fig. 6-10. For **dry oxidation conditions** and a fluence of 5 x 10^{16} F cm^{-2} alloys 1 and 3 showed the formation of a protective alumina scale at 900 and 1000°C, whereas the protective alumina scale on alloy 4 showed a higher quality (no inclusions) than in the unimplanted case. For 1 x 10^{17} F cm^{-2} a protective alumina scale was observed for alloy 3 at 900°C and 1000°C, whereas alloys 1 and 2 remained unprotected. No protective scale was formed at 2 x 10^{17} F cm^{-2}. To summarize, for the **implanted** alloys the best results were obtained with a fluence of 5 x 10^{16} F cm^{-2}. No protective alumina scale was formed on alloy 2. For **wet oxidation conditions** alloy 4 formed a protective alumina scale for 1 x 10^{17} F cm^{-2} / 900°C.

		dry	dry	wet	wet
Alloy	F-Fluence	900°C	1000°C	900°C	1000°C
Alloy 1	without	-	-	-	-
	5 x 10^{16}	+	+	-	-
	1 x 10^{17}	-	-	-	-
	2 x 10^{17}	-	-	-	-
Alloy 2	without	-	-	-	-
	5 x 10^{16}	-	-	-	-
	1 x 10^{17}	-	-	-	-
	2 x 10^{17}	-	-	-	-
Alloy 3	without	-	-	-	-
	5 x 10^{16}	+	+	-	-
	1 x 10^{17}	+	+	-	-
	2 x 10^{17}	-	-	-	-
Alloy 4	without	+	+	-	-
	5 x 10^{16}	++	+	-	-
	1 x 10^{17}	-	+	+	-
	2 x 10^{17}	-	-	-	-

Table 3: Results for model alloys 1-4. The formation of a protective alumina scale is denoted by +, while - denotes internal oxidation.

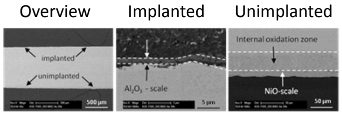


Fig. 6: Alloy 1 with 5 x 10^{16} F cm^{-2} after oxidation (900°C/20h/dry air).

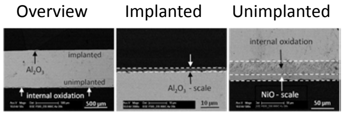


Fig. 7: Alloy 3 with 5 x 10^{16} F cm^{-2} after oxidation (900°C/20h/dry air).

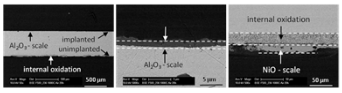


Fig. 8: Alloy 3 with 1 x 10^{17} F cm^{-2} after oxidation (1000°C/20h/dry air).

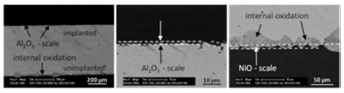
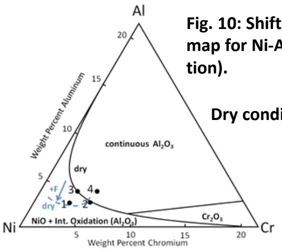
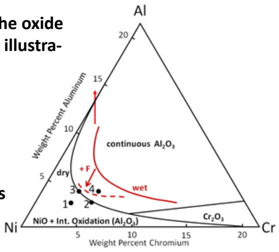


Fig. 9: Alloy 4 with 1 x 10^{17} F cm^{-2} after oxidation (900°C/20h/wet air).



Dry conditions



Wet conditions

Fig. 10: Shift of the borderline in the oxide map for Ni-Al-Cr alloys (schematic illustration).