Surface preparation effect on oxidation kinetics of Ni-base superalloy

Wojciech J Nowak¹, Bartek Wierzba, Jan Sieniawski
Department of Materials Science, Faculty of Mechanical Engineering and Aeronautics, Rzeszow University of Technology, al. Powstancow Warszawy 12, 35-959 Rzeszow, Poland

E-mail: w.nowak@prz.edu.pl

Abstract. In the present study an oxidation behavior of commercially available Ni-base superalloy IN 713C with different surface finishing, namely polished up to 1 μm diamond paste (resulting in Ra=0.023) and ground by SiC paper with 80 grit (Ra=1.23), were investigated at 950°C in air. It was found that ground sample developed very thin, protective α-Al₂O₃ scale. Moreover, locally formation of θ-Al₂O₃ in the forms of spikes was observed. For the sample with polished surface formation of outer chromia scale accompanied with internal oxidation of aluminum was observed. Moreover, for specimen which does not form continuous alumina scale or sub-scale, the GD-OES depth profiles showed an enrichment of boron at the oxide scale/alloy interface. It was proposed that the formation of protective alumina scale on ground samples is caused by introducing the defects into the near-surface region of the material, which are an easy diffusion paths for the elements forming a protective oxide scales.

1. Introduction

Ni-based alloys are optimized to provide a very good strength, also at elevated temperatures. To increase high temperature oxidation resistance an elements like Al and Cr are added to form protective oxide scales (chromia and alumina respectively) during exposures at high temperatures in atmospheres containing oxygen [1, 2]. The alternative method to provide a resistance against environmental reactions (oxidation, nitridation, carburization or sulfidation) is applying a protective coatings such as MCrAlY [3] (where M is mainly Ni or Co) or β-NiAl [4, 5], which are an alumina forming materials. However, coatings production is time consuming, results in additional component costs, and can negatively affect alloy mechanical properties, such as fatigue strength.

Therefore, mechanical surface treatment seems to be an alternative method for promoting protective oxide scales formation without changing the material composition and/or manufacturing methods. The influence of metallic samples preparation, formation was already investigated in literature. Giggins and Pettit [6] investigated the influence of grain size and surface deformation on selective oxidation of chromium in Ni-Cr alloys. The authors observed that oxidation behavior of the samples with deformed surface, due to grit blasting, was similar to that with fine grained structure. This phenomenon was explained by producing fine grains via recrystallization of cold worked layer during sample exposure at elevated temperature. The influence of grain size and deformation on selective oxidation of chromium was observed up to 30 wt.% of Cr. This was found to be correlated with enhanced diffusion of chromium at the grain boundaries of the alloy.

¹ To whom any correspondence should be addressed.
The effect of grain boundaries density, introduced into the material by cold working with subsequent recrystallization, on the oxidation and carburization of Alloy 800 (Fe-base, 35%-Ni, 20%Cr and minor amount of C, Mn, S, Si, Cu, Al and Ti) was already investigated by Leistikow et al. [7]. The authors found that samples containing higher grain boundaries densities showed the smallest mass gain. With decreasing density of grain boundaries the tendency of internal oxidation increased. This observation confirm the role of grain boundaries as an easy diffusion path for oxide forming elements. Therefore, from the crystallographic point of view, the grain boundaries present in the polycrystalline materials are also classified as a defects.

In the recent work of Sudbrack et al. [8] an effect of surface preparation of two single crystal, Ni-based superalloys LDS-1101+HF and CMSX-4+Y on their oxidation behavior was investigated. The samples surface finish includes low-stress ground, polishing up to 9 µm and up to 3 µm as well as electrochemical thinning. The authors observed that the type of the oxide scale formed on samples strongly depends on its surface preparation.

The aim of the present work is to investigate the influence of different surface finishing of commercially based Ni-base superalloy IN 713C on its oxidation behavior at 950°C during air exposure. Moreover, the model for internal oxidation process will be proposed. The model will be based on the generalized Darken method and multiphase approximation. The two-phase zones (internal oxidation) will be mathematically described.

2. Experimental

From the rod of conventionally cast Ni-based superalloy IN 713 C (Ni-bal., Cr-14, Ta-2, Mo-4, Nb-5.1, Al-6, Ti-1, C-0.2, B-0.01 given in wt. %) a coupons with 20 mm diameter and 2 mm height were cut. The surfaces of the samples were prepared with three different surface finishing: polishing up to 1 µm and grinding using 80 grit SiC paper. Surface of such prepared samples were investigated by the profilometer HOMMEL to determine the roughness parameters and using scanning electron microscopy Hitachi S3400N (SEM) to investigate the surface topography. Such prepared samples were oxidized for 48 hours in laboratory air at 950°C using tube furnace Carbolite STF 16/450. The samples were balanced before and after oxidation tests using microbalance RADWAG WAA 100/C/1 for oxidation kinetics determination. After exposure samples were investigated using glow discharge optical emission spectrometry (GD-OES). The GD-OES depth profiles were quantified using the procedure described in references [9, 10, 11]. After GD-OES depth-profiling, all samples were sputtered with very thin gold layer using cathodic evaporation, electrolitically coated with nickel and mounted in epoxy resin. Metallographic cross section of the alloy after oxidation as well as in the as-cast condition were prepared by series of grinding and polishing steps, finishing with a fine polishing in SiO₂ suspension with 0.25 µm granulation. The cross sections were analyzed using optical microscope Nikon Epiphot 300 and scanning electron microscope Hitachi S3400N (SEM).

3. Oxidation modeling

In this chapter the internal oxidation model will be proposed. The model will be based on the generalized Darken method with drift determination and multiphase approximation of components during the diffusion process. The main law is the mass conservation for average component of the ternary diffusion couple, e.g. Ni-Cr-O.

\[
\frac{\partial \bar{c}_i}{\partial t} = - \frac{\partial \bar{J}_i}{\partial x}, \quad i = 1, 2, 3
\]  

The average concentration can be defined from the Gibbs concentration triangle, when the values of the phase ratio \( f^\alpha \) and \( f^\beta \) are known (\( f^\alpha + f^\beta = 1 \)):

\[
\bar{c}_i = f^\alpha c_i^\alpha + f^\beta c_i^\beta
\]

where \( \bar{J}_i \) is the average flux of the component, \( c_i^\alpha \) and \( c_i^\beta \) are the concentration in \( \alpha \) and \( \beta \) phase, respectively.
\[ J_i = f^\alpha J_i^\alpha + f^\beta J_i^\beta, \quad i = 1, 2, 3 \]  
(3)

The fluxes in \( \alpha \) and \( \beta \) phase are defined after Darken [12]:

\[ J_i^\alpha = -D_i^\alpha \frac{\partial c_i^\alpha}{\partial x} + c_i^\alpha v^\alpha, \quad i = 1, 2, 3 \]  
(4)

and

\[ J_i^\beta = -D_i^\beta \frac{\partial c_i^\beta}{\partial x} + c_i^\beta v^\beta, \quad i = 1, 2, 3 \]  
(5)

\( D_i^\alpha \) and \( D_i^\beta \) are the intrinsic diffusion coefficients of the components. The drift velocity can be calculated from the volume continuity equation in each phase:

\[ v^\alpha = \frac{1}{c_i^\alpha} \sum_{i=1}^{\alpha} D_i^\alpha \frac{\partial c_i^\alpha}{\partial x} \quad \text{and} \quad v^\beta = \frac{1}{c_i^\beta} \sum_{i=1}^{\beta} D_i^\beta \frac{\partial c_i^\beta}{\partial x} \]  
(6)

Finally, the mass conservation for average concentration in ternary system can be rewritten in the following form:

\[ \frac{\partial \bar{c}_i}{\partial t} = -\frac{\partial}{\partial x} \left( -f^\alpha D_i^\alpha \frac{\partial c_i^\alpha}{\partial x} - f^\beta D_i^\beta \frac{\partial c_i^\beta}{\partial x} + f^\alpha c_i^\alpha v^\alpha + f^\beta c_i^\beta v^\beta \right), \quad i = 1, 2, 3 \]  
(7)

when the phase diagram is known, the tie-lines and thermodynamic properties, the reactive diffusion can be calculated.

4. Results and discussion

Figure 1 shows the SEM/BSE image of IN 713C in the as-received conditions. The alloys shows the microstructure based on the \( \gamma \)-Ni matrix strengthened by the \( \gamma' \)-Ni3Al precipitates [13]. Due to the high Nb content an relatively high carbon content the Nb-carbides formation is observed (see Fig. 1). The Nb-carbides formation is also one of the strengthening mechanisms [13]. A similar microstructure of IN 713C has been observed by Binczyk and Śleziona [14] or Matysiak et al. [15]. Moreover the surface topography captured using SEM/BSE 3D mode revealed that the surface of the sample prepared with 1 \( \mu \)m polishing differs substantially from the sample with ground surface. This observation is strongly supported by the roughness profiles presented in Fig. 2. The average \( R_a \) value based on five measurement is presented in Table 1. The measurements results reveal that the \( R_a \) values differ of about two orders of magnitude between the 1 \( \mu \)m and 80 grit SiC-paper.

![Figure 1](image-url)  
**Figure 1.** SEM/BSE images showing surface of IN 713C after: a) polishing up to 1 \( \mu \)m polishing and b) grinding using 80 grit SiC paper
Figure 2. Roughness profiles of IN 713C after: a) polishing up to 1 μm polishing and b) grinding using 80 grit SiC paper

Table 1 The average values of the $R_a$ values measured on polished and ground IN 713C

| Average measured value | 1 um | 80 grit |
|------------------------|------|---------|
| $R_a$                  | 0.023| 1.240   |
| Standard deviation     | 0.002| 0.212   |

Figure 3. Mass change plot of ground and polished IN 713C after air exposure at 950°C for 48 hours.

The GD-OES depth profile of polished IN 713C (Fig. 4 a) showed that the outer part of the oxide scale is enriched in Ni. Below outer Ni-peak a co-enrichment in Cr and Nb is present. Moreover whole outer oxide scale is slightly enriched in Ti. Also an enrichment in boron is observed at the oxide scale/alloy interface. Below the boron peak a zone of boron depletion is present. An enrichment of aluminum accompanied with decreasing oxygen profile suggests presence of zone of internal Al-oxidation. The GD-OES depth profile of ground specimen revealed an enrichment of aluminum in the outer part of the oxide scale accompanied with slight enrichment in Ti and Nb (Fig. 4 b). For ground specimen no boron peak is found. A similar effect of hampering boron diffusion through alumina scale was observed by Nowak et al. [16].

Considering the SEM images of the cross-sections (Fig. 5 a and b) one can observe that on polished specimen non uniform oxide scale is formed, i.e. regions with an outer Cr-rich oxide scale and internally oxidized aluminum and regions with relatively thin oxide scale without internal oxidation zone are present. Contrary, polished sample developed thin, aluminum rich oxide scale. However, as shown if Fig. 5 b, two types of oxides morphology are present: a dense and flat oxide scale and oxides
in the form of spikes. The first one are typical for the $\alpha$-$\text{Al}_2\text{O}_3$ while the spikes are characteristic for $\theta$-$\text{Al}_2\text{O}_3$. It is known from the literature that at 950°C a metastable $\theta$-$\text{Al}_2\text{O}_3$ can form [17]. An nodules observed on the surface of oxidized ground IN 713C might be correlated with the presence of $\theta$-$\text{Al}_2\text{O}_3$. Formation of $\theta$-$\text{Al}_2\text{O}_3$ might be supported by the larger zone of $\gamma'$-depletion below the spiky oxides, which in turn is correlated with higher growth rate of $\theta$-$\text{Al}_2\text{O}_3$ as compared with $\alpha$-$\text{Al}_2\text{O}_3$ and the same consumption of Al from its in the $\gamma'$ is larger.

Figure 4. The GD-OES depth profiles obtained for: a) polished and b) ground IN 713C exposed in air for 48 hours at 950°C.

Figure 5. SEM/SE images showing surface and cross sections of polished (a) and b)) and ground (c) and d)) IN 792 after isothermal oxidation test at 950°C for 48 hours in air. The dashed line indicates the zone of $\gamma'$ depletion

Figure 6. Arrhenius plot of parabolic rate constant ($k_p$) for the oxidation of pure NiAl [17]
5. Summary and conclusions
As shown in the present work, the type of formed oxide scale can be affected by different surface treatment. When the surface was ground (R_a=1.23), the alloy formed a protective, continuous alumina layer at all tested temperatures, since polished specimens (R_a=0.02) developed outer Ni/Cr-mixed oxide and internally oxidized aluminium. Therefore, one can conclude that increasing of R_a value by two orders of magnitude forced material to form a protective alumina scale. It is known that at lower temperatures the grain boundary diffusion plays bigger role than lattice diffusion. The reason for that is lower activation energy of the boundary process caused by more disordered structures in the boundaries [18]. Considering the latter, the hypothesis is that with different surface preparation different amount and type of defects are introduced which also lowers an activation energy of the elements forming a protective oxide scales. It was observed in the present work, that the different surface treatment alters the type of the oxide scale formed on nominally alumina forming alloy.

6. Acknowledgment
This work has been supported by the National Science Centre (NCN) in Poland, decision number 2015/19/P/ST8/03995 in the frame of grant “POLONEZ 1”.

7. Literature

[1] R. Prescott and M. J. Graham, “The Formation of Aluminum Oxide Scales on High-Temperature Alloys”, Oxidation of Metals, Vol. 38, Nos. 3/4, 1992
[2] C. S. Giggins, F. S. Pettit, “Oxidation of Ni-Cr-Al Alloys Between 1100° and 1200°C”, Solid State Science Vol. 118, No. 11, pp 1782-1790, (1971)
[3] K. Yuan, R. Eriksson, R. L. Peng, X.-H. Li, S. Johansson, Y.-D. Wang, “Modelling of microstructural evolution and lifetime prediction of MCrAlY coatings on nickel based superalloys during high temperature oxidation”, Surface and Coating Technology, Volume 232, pp 204-215, (2013)
[4] M.J. Pomeroy, “Coatings for gas turbine materials and long term stability issues”, Materials and Design 26, 223-231, (2005)
[5] K. H. Stern, “Metallurgical and Ceramic Protective Coatings”, Chapman and Hall, 2-6 Boundary Row, London SE1 8HN, UK, (1996)
[6] C. S. Giggins and F. S. Pettit, “The effect of Alloy Grain-Size and Surface Deformation on the selective Oxidation of Chromium in Ni-Cr Alloys at temperatures of 900°C and 1100°C”, Transactions of the Metallurgical Society of AIME, Vol. 245, 2509-2514, 1969
[7] S. Leistikow, I. Wolf and H. J. Grabke, “Effect of cold work on the oxidation behavior and carburization resistance of Alloy 800”, Werkstoffe und Korrosion 38, 556-562 (1987)
[8] C. K. Sudbrack, D. L. Beckett, R. A. Mackay, “Effect of Surface Preparation on the 815°C Oxidation of Single Crystal Ni-Based Superalloys”, JOM, Vol. 67, No. 11, 2015
[9] J.P. Pfeifer, H. Holzbrecher, W.J. Quadakkers, J. Speier: Quantitative analysis of oxide films on ODS*-alloys using MCs+SIMS and e-beam SNMS**, J. Anal.Chem., 346, 1993, 186 – 191.
[10] W.J Quadakkers, A. Elschner, W. Speier, H. Nickel: Composition and growth mechanisms of alumina scales on FeCrAl-based alloys determined by SNMS, App. Surf. Sci., 52, 1991, 271 – 287
[11] Wojciech J. Nowak: Characterization of oxidized Ni-base superalloys by GD-OES, JAAS, 2017, DOI: 10.1039/C7JA00069C
[12] Danielewski M., Wierzba B., "Thermodynamically consistent bi-velocity mass transport phenomenology", Acta Materialia 58, 2010, 6717
[13] J.R. Davis: ASM Specialty Handbook, Heat Resistant Materials. ASM International - Materials Park, Ohio, 1997
[14] F. Binczyk, J. Ślezioma: Phase transformations and microstructure of IN-713C nickel superalloy, ARCHIVES OF FOUNDRY ENGINEERING 9, 2009, 109-112
[15] H. Matysiak, M. Zagorska, A. Balkowiec, B. Adamczyk-Cieslak, R. Cygan, J. Cwajna, J. Nawrocki, and K. J. Kurzydlowski: The Microstructure Degradation of the IN 713C Nickel-Based Superalloy After the Stress Rupture Tests, *Journal of Materials Engineering and Performance* **23**, 2014, 3305-3313

[16] W.J. Nowak, D. Naumenko, A. Jałowicka, D.J. Young, V. Nischwitz and W.J. Quadakkers: Effect of alloy composition on the oxidation-induced boron depletion in cast Ni-base superalloy components, *Mat. Corr. 68* No. 2, 2017, 171-185

[17] H.J. Grabke, Oxidation of NiAl and FeAl, *Intermetallics, 7* (10), 1999, 1153-1158

[18] D. Young, High Temperature Oxidation and Corrosion of Metals, Second ed., Elsevier, 2016