OXIDE SCALE FORMATION ON IN 792 AT EARLY STAGES OF HIGH TEMPERATURE EXPOSURE

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S u m m a r y

In the present work a commercially available Ni-base superalloy IN 792 was exposed at 1050°C up to 50 hours in $Ar + O_2$ (20%) for investigation of its oxidation kinetics as well as oxide scale formation. It was observed that the alloy formed chromium rich oxide scale. However, detailed analysis, including glow discharge optical emission spectroscopy (GD-OES) and scanning electron microscopy (SEM) showed that the alloy forms multiphase oxide scale consisting of TiO_2, Cr_2O_3, $TiTaO_4$ and Al_2O_3. The latter caused Al-depletion from the bulk material, which resulted in dissolution of the γ' phase and local weakening of the IN 792.

Keywords: high temperature oxidation, Ni-base superalloy IN 792, oxidation kinetic, chromia forming alloys.

Warstwa tlenkowa na podłożu nadstopu IN 792 w początkowym stadium procesu utleniania wysokotemperaturowego

S t r e s z c z e n i e

W pracy przedstawiono analizę wyników próby utleniania wysokotemperaturowego nadstopu niklu IN 792 w temperaturze 1050°C, w czasie 50 h w atmosferze $Ar + O_2$ (20%). Określono kinetykę procesu utleniania oraz scharakteryzowano wytworzoną warstwę tlenków. Analizę składu chemicznego prowadzono metodami emisyjnej spektroskopii optycznej z wyładowaniem jarzeniowym (GD-OES) i elektronowej mikroskopii skaningowej (SEM). Stwierdzono, że na podłożu nadstopu niklu IN 792 tworzy się wielowarstwowa zgorzelina złożona z tlenków TiO_2, Cr_2O_3, $TiTaO_4$ i Al_2O_3. Wykazano również, że tworzenie się wydzieleń Al_2O_3 powoduje lokalne zubożenie ziarn osnowy stopu w aluminium – składnika fazy umacniającej (Ni_3Al). Prowadzi więc do degradacji tego składnika fazowego mikrostruktury i obniżenia stopnia umocnienia nadstopu IN 792.

Słowa kluczowe: korozja wysokotemperaturowa, nadstop niklu IN 792, kinetyka utleniania

1. Introduction

In the stationary gas turbines (SGT) as well as in aircraft engines Ni-based superalloys are commonly used. These alloys can be used in load-bearing

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applications of about 80% of their melting temperature [1]. Moreover the materials used in the hot sections of the gas turbines have to fulfill a number of requirements, such as suitable ductility at low temperature, high creep strength and high oxidation resistance at wide temperature range. The Ni-base superalloys possess an excellent properties due to their microstructure: a fine γ'-Ni_3Al precipitates homogeneously distributed in a γ-Ni matrix. The strengthening phase γ'-Ni_3Al is stabilized by the addition of alloying elements, like Al, Ti, Ta and Nb [1]. However, during exposure at high temperature oxidation products start to form at the interface between metal and the surrounding atmosphere. This fact leads to changes in the local chemical composition in the region below the oxide scale due to the consumption of the alloying elements during reaction with the environment. These changes of chemistry might cause changes in the local alloy microstructure. After formation of a continuous oxide scale the reaction products becomes separated and the oxidation rate is controlled by the solid state diffusion through the oxide according to the mechanism described by Wagner [2].Depending on the Ni-base alloy chemistry, they can be classified as a NiO, Cr_2O_3 or Al_2O_3 forming alloys [3]. The Cr_2O_3 or Al_2O_3 are claimed to be a protective oxide scales due to their relatively slow growth rate, therefore their formation on the alloy surface is desired [4]. It is known from the literature that the alloying elements, like e.g. Ti might increase chromia growth rate [5].

The aim of the present study is to investigate the oxidation kinetics and oxidation products formed during early stages of exposure (50 hours) at 1050°C in Ar-O_2 based atmosphere of commercially available Ni-based superalloy IN 792 and to calculate the reaction constant of such oxidation process.

2. Experimental

From the middle of the rod of Ni-based superalloy IN 792 (Ni-bal., Cr-12.4, Co-9.0, Mo-1.9, W-3.8, Ti-4.5, Al-3.1, Ta-3.9, C-0.12, B-0.015, Zr-0.05 mass %), rectangular specimen was machined with a size of 20 x 10 x 2 mm. The surfaces were ground on SiC papers till 1200 grit finish and then ultrasonically cleaned in ethanol prior to oxidation.

Isothermal oxidation tests was performed using TGA 92-16.18 Setaram thermobalance at 1050°C up to 50 hours in Ar+O_2 (20%). The heating rate was 90 K/min, the cooling rate 10K/min and the gas flow rate 2 dm^3/h.

Prior to cross-sections preparation oxidized specimen were cut in the middle, sputtered with very thin gold layer using cathodic evaporation, electrolithycally coated with nickel and mounted in 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 SiO_2 suspension with 0.25 µm granulation. The cross sections were analyzed using optical microscope and scanning electron microscope (SEM). Also the glow discharge optical emission analysis (GD-OES) was performed on sample after oxidation

prior cross-sectioning. The GD-OES depth profile was quantified using the procedure described in references [6, 7].

3. Results and discussion

IN 792 is the typical, commercially available Ni-based superalloy second generation. Figure 1 shows the microstructure of the etched cross-section of the alloy in the as-cast condition. It is obvious from the Fig. 1, that the material is polycrystalline with the finer and directionally oriented grains in the outer part of the rod and randomly oriented, coarser grain in the centre of the rod. Different colors of the grains indicates different grain orientation. Finer grains in the outer part of the rod is caused by the fact that during casting in these regions the melted alloy had a direct contact with the mold with lower temperature, therefore temperature gradient was high enough to suppress the grain growth. In the middle part of the rod, the temperature gradient was smaller, therefore coarse grains are observed. Similar observation was made by Szeliga et al. [8]. Moreover, within the single grain one can observe a dendritic structure. This structure is visible in more detail on SEM image presented in Fig. 2. It is visible, that the alloy consists of γ'-Ni$_3$Al cubic precipitates distributed within γ-Ni matrix. Also eutectic structure present in the interdendritic regions is shown. Moreover at the grain boundaries coarsening of γ' phase is observed. Such a coarsening of γ' phase was found on another chromia forming Ni-base superalloy Rene 80 with similar chemical composition to studied in present work [9].
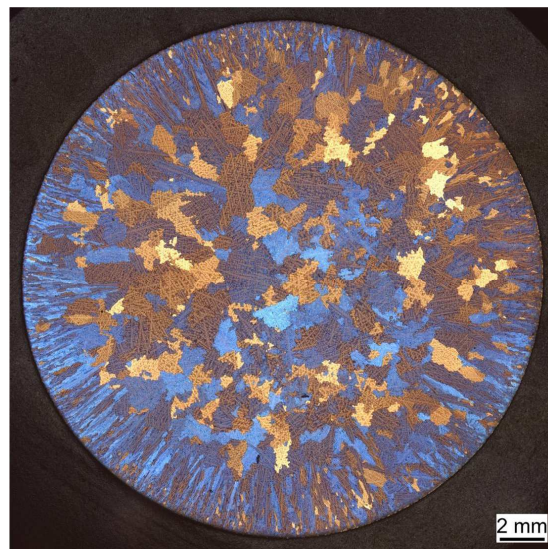

Fig. 1. Light optical microscope image of etched surface of the cross section
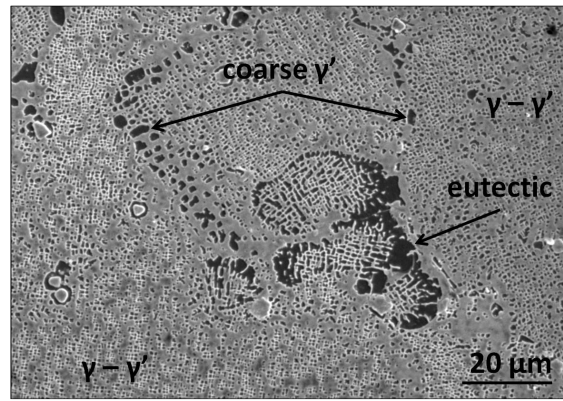of IN 792 in the as-cast conditions showing different grain size and orientation

Fig. 2. SEM backscattered electron image showing cross-section
of IN 792 in the as-cast condition

The sample machined from the material with the microstructure described above was isothermally oxidized at 1050°C in $Ar+O_2$ (20%) for 50 hours. Figure 3 shows the mass gain of IN 792 during the test. One can observe that the sample showed of about 2.5 mg.cm^{-2} mass gain. This value is similar to the mass gain obtained for another typical chromia forming Ni-based superalloy Rene 80 presented elsewhere [9, 10], which showed mass gain of about 3 mg.cm^{-2}. Comparison of mass gains is not very precise way to compare different types of the materials high temperature behavior. Therefore, comparison of the oxidation kinetics using the derived instantaneous apparent oxidation rate constant k'_w. The procedure for k'_w calculation was described by Quadakkers et al. [11]. Most of the alloys shows oxidize according to classical parabolic oxide scale growth kinetics:

$$\Delta m^2 = k_w \times t \tag{1}$$

where Δm – the specific surface weight change in g·cm^{-2}, k_w – the oxidation rate constant and t – the time in s.

As shown in Fig. 3 after of about 20 hours of exposure the mass gain curve slope drops which means that the oxidation rate slow down and establish. The oxidation kinetics at this stage might me described by the following equation [11]:

$$\Delta m = \Delta m_0 + k_w^{1/2} \times t^{1/2} \tag{2}$$

where Δm_0 is an offset value derived from the transient stage of oxidation.

The instantaneous apparent oxidation rate $k'_w(t)$ is obtained when plot the k_w as a function of time with the slope described by the following equation [11]:

$$\left[\frac{\mathrm{d}(\Delta m)}{\mathrm{d}(t^{1/2})}\right] = k'_w \tag{3}$$

The instantaneous apparent rate constant k'_w obtained for oxidation test of IN 792 is shown in Fig. 4. The plot shows that the k'_w dropped rapidly at the beginning of the oxidation (up to of about 1 hour of exposure). This period is so called transient stage of oxidation, during which all elements present in the alloy becomes oxidized. After this period the k'_w established and after 50 hours of exposure showed the value of about $7 \cdot 10^{-10}$ $g^2 \cdot cm^{-4} \cdot s^{-1}$. Such a value of k'_w is typical for a chromia forming alloys containing Ti and it is comparable to k'_w obtained for Rene 80 [9, 10].
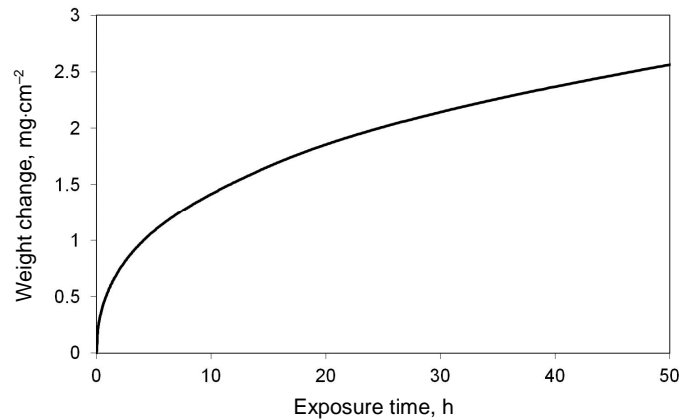
Fig. 3. Mass change obtained for IN 792 during isothermal exposure
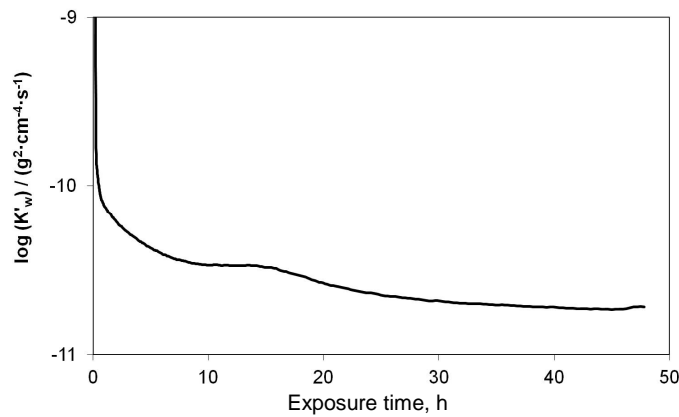at 1050°C in Ar+O$_2$ (20%) for 50 h

Fig. 4. Instantaneous apparent parabolic rate constant k'_w obtained for IN 792
during isothermal exposure at 1050°C in Ar+O$_2$ (20%) for 50 h. The k'_w was
calculated using data from Fig. 3. in according to procedure described in Ref. [11]

Considering Ni, Cr and Al content, IN 792 can be classified as a marginal alumina forming alloy according to the oxidation map by Giggins and Pettit [3] (Fig. 5). However, due to increased chromia growth rate by Ti doping described by Jałowicka et al. [5] the boundary between the field II and III on Fig. 5 shifts up and IN 792 become a chromia forming alloy. A detailed analysis using glow discharge optical emission spectroscopy (GD-OES) showed that IN 792 formed not pure chromia, but multiphase oxide scale. Figures 6a and 6b show the GD-OES depth profiles of oxidized IN 792. The GD-OES depth profiles were quantified using relative sensitivity factors (RSF's) according to the procedure described in references [6, 7].
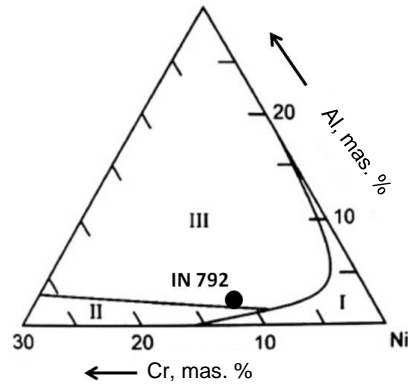

Fig. 5. Oxidation map for Ni-Cr-Al alloys [3] showing fields of various types of oxide scale formation as function of alloy Cr and Al-contents at 1000-1100°C: I – NiO forming alloys, II – Cr$_2$O$_3$ forming alloys, III – Al$_2$O$_3$ forming alloys. Superimposed are Cr and Al contents of IN 792

On GD-OES depth profiles illustrated in Fig. 6 a and b one can observe enrichment of Ti below which Cr is enriched. The zone of Cr enrichment is relatively wide which suggests that the majority of the oxide scale consists of Cr$_2$O$_3$. Following Al profile one can observe enrichment of Al in the inner part of the oxide scale which corresponds to the internal precipitates of Al$_2$O$_3$. Below the zone of internal oxidation of aluminum, the zone of Al-depletion is observed on Al-profile. Considering the latter, the dissolution of the γ' phase is expected. Between the peaks of Cr and Al a peak of B is found above which enrichments of Ti and Ta is observed. The maximum enrichment of the B profile is less than 2 atomic %. Co-enrichment of Ti and Ta profiles suggests formation of TiTaO$_4$ phase. Formation of TiTaO$_4$ phase was already observed by Jalowicka et al. [5] on another Ni-base superalloy PWA 1483 after air exposure at 1050°C. The SEM/BSE image of the cross-sections of IN 792 after isothermal oxidation test at 1050°C for 50 hours (Fig. 7) and SEM elemental mapping (Fig. 8) confirms
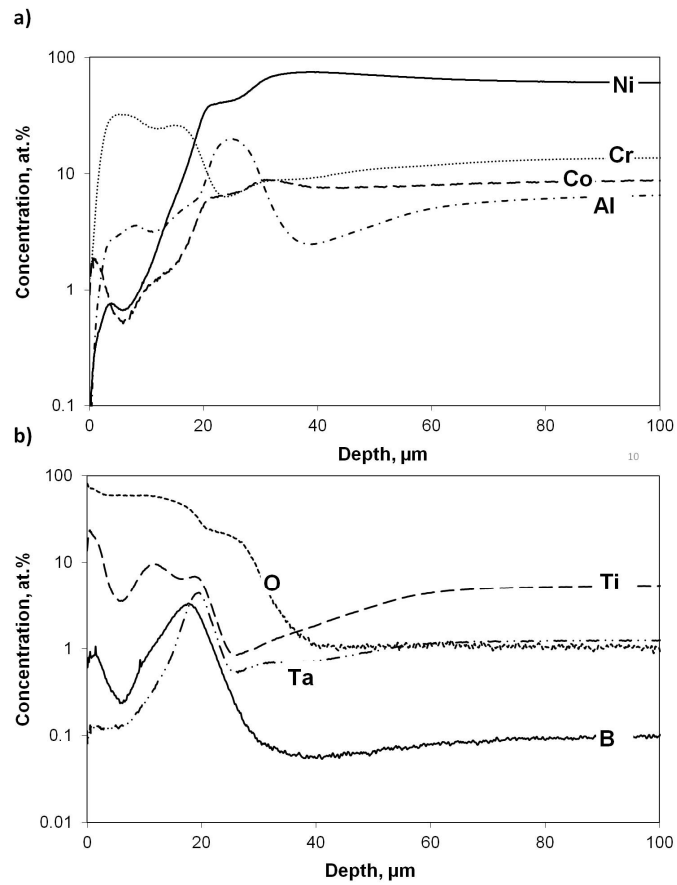
Fig. 6. GD–OES depth profiles of IN 792 after oxidation at 1050°C in Ar+O_2 (20%) for 50 h showing depth profiles of: a) major and b) minor alloying elements
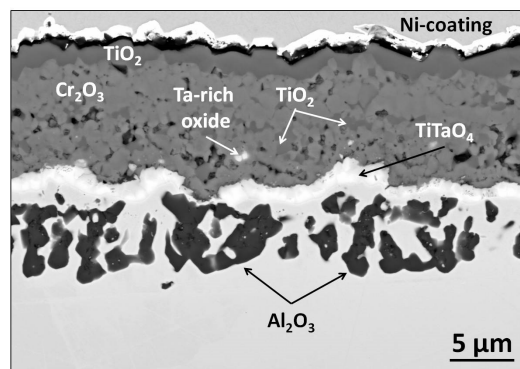

Fig. 7. SEM/BSE images of the cross-section of IN 792 after isothermal oxidation test at 1050°C for 50 hours in Ar+O_2 (20%)

the findings by GD-OES. In Fig. 8 the elemental map for B shows its uniform distribution, however due to the relatively small atomic number of boron, this element is very difficult for analysis using SEM/EDX. Based on GD-OES depth profile, the maximum enrichment of boron was less than 2 atomic %, therefore no boron enrichment is observed on elemental map. As expected, oxidation of aluminum and its depletion caused dissolution of γ' precipitates which results in presence γ'-depleted zone below the oxide scale (Fig. 9).
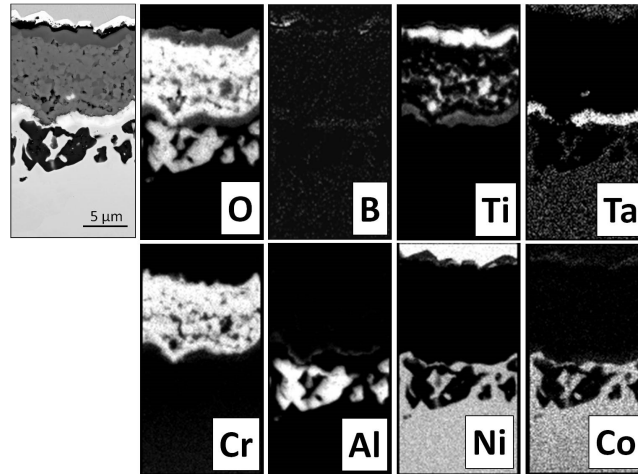

Fig. 8. SEM/EDX elemental maps of IN 792 after isothermal
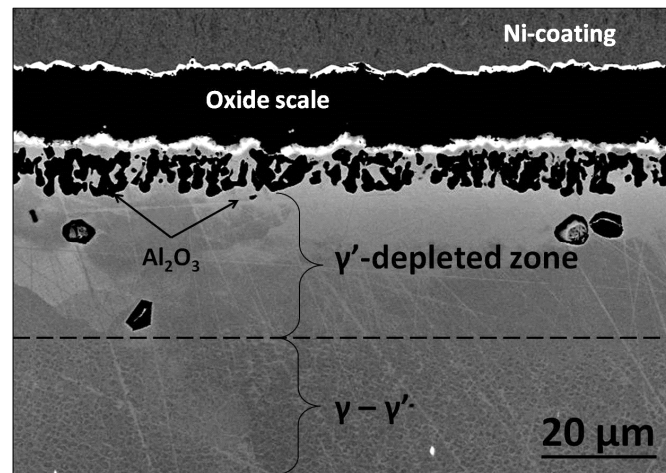oxidation test at 1050°C for 50 hours in Ar+O_2 (20%)

Fig. 9. SEM/BSE images of the cross-section of IN 792 after isothermal oxidation test
at 1050°C for 50 hours in Ar+O_2 (20%) showing the γ' depletion. The contrast
of the image was intentionally changed for better visibility of the γ-γ' microstructure

4. Summary and conclusions

The results obtained in the present work showed, that despite the fact that IN 792 is classified as an alumina forming alloy it formed a chromia rich scale. Moreover, the alloy showed the oxidation kinetics comparable to another Ni-based superalloy with similar composition, namely Rene 80, which was claimed to be a chromia forming alloy due to Ti doping effect as described in the literature. The exposure at 1050°C in $Ar+O_2$ (20%) up to 50 hours leads to formation of multiphase oxide scale consisting of TiO_2 in the outer part of the oxide scale, below which chromia scale is visible. In the inner part of the chromia scale Ti-rich oxide precipitates are present. At the oxide/alloy interface formation of $TiTaO_4$ is observed, below which internally oxidized alumina precipitates are present. Formation of the latter caused aluminum depletion, which is clearly visible on GD-OES depth profiles, which in turn caused dissolution of the γ' precipitates.

Acknowledgment

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