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Effect of thermal cycling on protective properties of alumina scale grown on thin Haynes 214 foil

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ABSTRACT

The isothermal and cyclic oxidation of a thin alloy 214 foil (130 μm thick) has been studied in air at 1200 °C for up to 720 h. Haynes 214 forms a duplex oxide scale consisting of pure, columnar alumina overlaid by mixed $Ni(Al,Cr)_2O_4$ spinel with minor inclusions of $(Al,Cr)_2O_3$. A transition from external alumina to chromia scaling (abbreviated as TACS) occurs at the oxide-alloy interface after the Al reservoir of the foil is exhausted due to oxidation. The tensile cracking of the oxide scale upon thermal cycling is shown to promote the early transition from protective to accelerated breakaway oxidation.

1. Introduction

The construction materials envisaged for clean power generation technologies such as solid oxide fuel cells [1], high efficiency gas and steam turbines [2], jet engines [3], and also for numerous applications in the heat processing industry such as heat exchangers [4,5] and gas burners [6] are usually exposed to highly corrosive environments at high temperatures. The heat-resistant high temperature metallic materials for the aforementioned applications are generally based on the Ni/Fe–Cr, Ni–Cr–Al, and Fe–Cr–Al alloy systems [7]. Their good oxidation resistance relies on the formation of dense, adherent, slow growing chromia or alumina scales [8–10]. The wrought Ni-base alloys such as alloy 602CA [11], Haynes 214 [12,13] and Haynes 224 [13] containing 16–25 wt.% Cr and 2.5–4.5 wt.% Al demonstrate excellent oxidation resistance and adequate creep strength up to 1100 °C. The outstanding oxidation resistance at high temperatures of Ni/Fe–Cr–Al alloys is provided by alumina scales forming during high temperature exposure [14,15]. The continuous growth of alumina at the alloy surface is associated with a selective depletion of Al from the alloy [16–21]. In a number of high temperature applications the mentioned alloys are used as construction materials in extremely thin components (some tenths of a mm), e.g., foils, tubes, wires or rods. Due to the limited Al reservoir [22] such thin-walled components may after a certain time suffer from a critical Al depletion and eventually breakaway oxidation [19,23–25], i.e., rapid oxidation of a less noble base element such as iron or nickel. The time to occurrence of breakaway is generally considered to be the lifetime limit for such thin-walled components. Theoretical approaches were developed to predict the oxidation-limited lifetime as a function of temperature, alloy chemistry and specimen thickness and geometry [23,25–27].

HAYNES® alloy HR-214™ [12] is a solid-solution strengthened Ni-base alloy which has the highest aluminum content (4.5 wt.%) among the commercially available wrought Ni-base alloys and is one of the most suitable materials for thin-section heat-exchangers [4], catalyst carriers [28–31], and aircraft engine honeycomb seals [32]. The alloy exhibits good forming and welding characteristics and is developed to have the highest oxidation resistance in oxidizing environments among the wrought austenitic metallic FCC materials [13,14].

The oxidation behavior of Ni/Fe–Cr–Al alloys has been investigated in a number of publications [13–15]. In our previous work [15], the transition from protective to breakaway oxidation of thin foils of alloy HR-214 was studied in the temperature range 1100–1200 °C. It has been shown that during air oxidation the alloy initially forms an outer $Ni(Al,Cr)_2O_4$ spinel layer which is then isolated from the metal by formation of an inner, slowly growing alumina scale. After approximately 700 h of air oxidation at 1150 °C,

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Table 1
Chemical composition in weight percent of alloy HR-214 analyzed by ICP-OES.

Element	Ni	Cr	Al	Fe	Mn	Si
wt.%	Bal.	16.0	4.4	3.6	0.17	0.26

the 130 μm thick HR-214 foil was found to be completely depleted of Al and therefore no longer able to retain alumina growth. The oxygen partial pressure at the scale-alloy interface dramatically increases and the formation of chromia in the innermost part the scale becomes possible. After this transition from alumina to chromia scaling, the alumina layer is no longer in equilibrium with the underlying alloy and becomes dissolved by the chromia growing underneath [15]. Hereafter the abbreviation TACS (transition from alumina to chromia scaling) will be used to avoid the confusion with the well-established term “breakaway oxidation”, i.e., the formation of rapidly growing nickel- or iron-rich oxides.

Depth profiles through the oxide scales measured before and after occurrence of TACS suggested an outward transport of Cr and Ni after aluminum was completely removed from the foil [15]. It was assumed that after TACS Cr diffuses outwards through the alumina grain boundaries, however, it was not clear how nickel can oxidize at the chromia–alloy interface and further migrate outwards contributing thus to the thickening of the outer spinel after the occurrence of TACS. The latter phenomenon was nonetheless confirmed by several analytical techniques.

The purpose of the present paper is to elucidate the mechanism of accelerated oxidation of the thin HR-214 foils by means of Transmission electron microscopy (TEM). Since the exposures performed in the previous study [15] were cyclic (100 h cycles), stress initiation may have resulted in a repeated crack formation in the oxide upon repeated cooling and re-heating and thus affecting the overall oxidation process. Therefore a set of isothermal exposures was carried out to eliminate the effect of thermal cycling. The present study is focused on exposures at 1200 °C because all previously observed [15] microstructural effects in the oxide scale were qualitatively very similar in the entire temperature range of 1100-1200 °C and occurred at the shortest test time at the highest test temperature.

2. Experimental

2.1. Material

Rolled HR-214 foil of 0.13 mm thickness was supplied by Haynes International. The chemical composition of the alloy batch used in the present study is given in Table 1. Test coupons measuring $12 \times 12 \times 0.13\,\mathrm{mm}^3$ in size were cut from the foil. The edges were ground with 1200 grit SiC paper. The surfaces of the foils were used in the as-rolled condition. For hanging the specimen on a Pt wire in the furnace, an orifice 2 mm in diameter was drilled in each specimen at least 2 mm away from the foil edge.

2.2. Oxidation exposures

The oxidation tests were carried out in a horizontal resistance-heated furnace. The heating and cooling rates were approximately $10\,\mathrm{K\,min^{-1}}$. All exposures were performed in static laboratory air at 1200 °C. The cyclic exposures were interrupted every 100 h for weight measurements (see Ref. [15]). At each time interval one specimen was removed from the furnace for microstructural analyses. The longest exposure time during the thermal cycling was 600 h, i.e. 6 cycles. The isothermal tests were run separately for 300, 500 and 720 h, respectively, without intermediate weight measurements.

2.3. Metallographic preparations

Before preparing the metallographic cross sections the samples were sputter coated with a thin gold layer to impart the oxidized foil surfaces electrical conductivity. The specimens were subsequently electroplated with nickel to obtain a 10–20 μm thick Ni-layer between the oxide scale and the mounting resin. The plane of the cross section was aligned perpendicular to the broad surface of the specimen. The mounted samples were ground to 1200 grit with SiC grinding papers and polished with diamond pastes to 1 μm surface finish. The final polishing step was made using colloidal SiO_2 slurry.

2.4. Analytical techniques

2.4.1. Scanning electron microscopy, SEM

Backscattered electron (BSE) and secondary electron (SE) images were taken from the cross-sectioned foil specimens using a Zeiss SUPRA 50 VP FEG-SEM equipped with an EDX (Energy Dispersive X-ray analysis) system by Oxford Instruments.

2.4.2. Focused ion beam/scanning electron microscopy, FIB/SEM

An FEI Versa 3D combined Focused ion beam/SEM (FIB/SEM) workstation was used to produce cross-section thin foils from the oxide scale and subjacent metal. In order to protect the oxidized surface during the subsequent ion milling, a thin Pt layer was first deposited with the aid of electrons on the surface ($25 \times 5\,\mu\mathrm{m}^2$) and then a thicker Pt layer (with a thickness of ~2 μm) was deposited on top using Ga-ions. At the initial stages of the milling, higher ion currents were used, while lower currents were chosen at the final stages to produce finer milled surfaces. Lower ion energies (2 and 5 kV with ion currents of 49 and 27 nA, respectively) were selected in the final stages of polishing in order to minimize the potential artifacts from FIB milling.

2.4.3. Scanning transmission electron microscopy, STEM

Scanning transmission electron microscopy (STEM) was performed using an FEI Titan 80-300 TEM/STEM equipped with an Oxford Instruments EDX detector and a Field Emission Gun (FEG) to acquire STEM micrographs in High Angle Annular Dark Field (HAADF) and Bright Field (BF) modes as well as to obtain chemical composition and EDX concentration maps.

2.4.4. Transmission Kikuchi diffraction, TKD

Transmission Kikuchi diffraction (TKD) investigations were carried out using a LEO Ultra 55 FEG-SEM equipped with an HKL Channel 5 EBSD system with a Nordlys II detector on thin-foil specimens extracted by the FIB/SEM technique for STEM analyses. The analyses were performed using parameters described in reference [33].

3. Results

The NiCrAl-base alloy HR-214 is known to form a duplex oxide scale upon air oxidation at 1100–1200 °C [15,34]. The outer layer is mainly a mixed $Ni(Al,Cr)_2O_4$ spinel formed during the transient oxidation stage whereas the innermost layer consists of columnar alumina [14,15]. This type of oxide scale microstructure was also observed after the present 100 h isothermal air exposure at 1200 °C as shown in HAADF and BF STEM images in Fig. 1. The BF image of the oxide scale (Fig. 1b) demonstrates the columnar conical morphology of the alumina grains. The grains in the spinel part of the oxide scale are more equiaxial. The STEM results revealed that the outer oxide layer, regarded as outer spinel in previous studies, is not single-phase. A few grains showing a darker contrast in the HAADF image were found mainly close to the spinel–alumina interface.