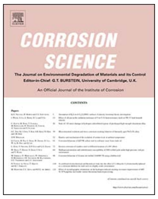
Corrosion Science 135 (2018) 78–86

Contents lists available at ScienceDirect

Corrosion Science

journal homepage: www.elsevier.com/locate/corsci



Early stages of scale formation during oxidation of γ/γ' strengthened single crystal ternary Co-base superalloy at 900 °C

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ARTICLE INFO

Keywords:
Oxidation
Cobalt
Superalloys
STEM
Internal oxidation

ABSTRACT

A study on the individual role of γ and γ'-phase during the scale formation on Co-9Al-9W (at.%) at 900 °C was conducted. High-accuracy thermogravimetric analysis was used to locate changes in the kinetics of scale growth. Compositions of three separated layers within the scale have been elucidated in detail. The results demonstrate the substantial impact of the two-phase microstructure on the initiation of oxidation for the appearance of the scale. Examination of STEM-EDX elemental mappings of the internal oxidation front during the early stages of scale growth can explain the origin of isolated Al_2O_3 precipitates instead of a closed protective layer.

1. Introduction

Since the discovery of a stable $L1_2$ phase in the ternary Co-Al-W system by Sato et al. in 2006 [1], the investigation of this new class of high temperature material has substantially expanded. The microstructure of these Co-base superalloys, cuboidal γ' precipitates coherently embedded in a γ matrix, is similar to those of well-known Ni-base superalloys [2]. In recent years mechanical properties, such as creep resistance and yield strength at elevated temperature, could be improved by widening the range of considered alloying elements [3–6]. Nevertheless, the oxidation properties above 800 °C remained relatively poor. Extensive studies on the oxidation behaviour of Co-base superalloys between 800 and 900 °C were conducted since 2010 [7–12]. Hardly any of the investigated alloy compositions based on the ternary system showed a continuous, protective Al_2O_3-layer after oxidation for up to 500 h at 900 °C [8,11]. Interestingly, however, growth of a protective layer on Cr-free Co-based alloys during the oxidation in laboratory air at 800 °C could be demonstrated [9].

The above described oxidation behaviour stands in contrast to that of Ni-base superalloys already in use for high temperature application over decades. In oxidation resistant high temperature superalloys an advantageous balance between the progress of internal oxidation and diffusion velocity of alloying elements, such as Al or Cr, results in the formation of a protective Cr_2O_3 or Al_2O_3-layer after a relative short duration of exposure at 900 °C and above [13,14]. Due to the consumption of Al, the region below the protective oxide layer is depleted in γ'. Driven by high diffusion velocities of alloying elements, this depletion is particularly pronounced for oxidation at elevated temperatures. Several studies on the role of γ' phase on the formation of protective oxides in fourth generation Ni-base superalloys at 700 °C can be found in literature [15,16]. *In situ* oxidation experiments of a second generation Ni-base superalloy in a TEM were conducted to learn more about the oxygen diffusion paths at 850 °C [17].

During high temperature oxidation of Al-containing alloys, the formation of transient oxides is another interesting phenomenon. Even though only few groups addressed these questions, the potential for analytical TEM investigations to provide new microstructural insights in the reaction mechanisms during the early stages of scale formation was already demonstrated [18,19]. The long transient phase as well as the absence of a distinct γ' depleted zone below the internal oxidation front (IOF) makes ternary Co-base superalloys an outstanding model system to investigate transient oxidation processes as well as the role of a two-phase microstructure on the progress of scale formation at high temperatures. Elucidation and understanding of elementary oxidation mechanisms can be an essential contribution in the community to find more oxidation resistant composition for this new class of alloys.

In the present work, classical experimental techniques such as thermogravimetry and subsequent evaluation of cross-sections are combined with high-resolution analytical scanning transmission electron microscopy (STEM). Elemental mappings of relevant regions in the complex multilayered oxide scale are attributed to changes measured in the oxidation kinetics. The ternary composition reported by Sato et al. [1] was chosen as a model system to gain detailed insights in elementary mechanisms occurring during oxidation in synthetic air at 900 °C.

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https://doi.org/10.1016/j.corsci.2018.02.020
Received 21 November 2017; Received in revised form 26 January 2018; Accepted 16 February 2018

Table 1
Chemical composition in atom percent of the investigated ternary Co-base superalloy.

Element	Co	Al	W
at.%	Bal.	9.6	9.0

2. Experimental procedures

2.1. Materials

A rod-shaped single-crystalline ternary Co-base superalloy with a nominal composition of Co-9Al-9W was casted in a Bridgman investment casting facility by a project in the framework of the collaborative research center SFB-TR103 at the Institute of Metals Science and Technology (WTM, University of Erlangen-Nürnberg (FAU), Germany). To determine the chemical composition after heat treatment part of the alloy was dissolved and subsequently investigated by ICP-OES. Results are given in Table 1.

The heat treatment consisted of a 12 h homogenisation step at 1300 °C followed by a 200 h aging step at 900 °C. Discs with approximately 0.8 mm height and 11 mm diameter were cut from the rod. Subsequently all samples were ground and polished down to 1 µm surface finish.

2.2. Isothermal oxidation

Isothermal oxidation experiments were conducted in a Setaram Evolution 1650 thermogravimetric analyser under constant gas flow of 20 $cm^3 min^{-1}$. Prior to oxidation, the atmosphere inside the device was changed to Ar. After reaching the target temperature of 900 °C, the chamber was evacuated and subsequently filled with dry synthetic air (80%N_2 20%O_2). Several oxidation experiments with a maximum duration of 100 h were carried out. Prior to further metallographic preparation, the oxidised samples were protected by an electrochemically deposited Ni-layer.

2.3. Electron microscopy

Samples were cut approximately in the middle. A representative region along the cut edge was polished with a Hitachi IM4000 ion milling system. Morphologies of cross-sections were subsequently investigated in a scanning electron microscope (Hitachi FE-SEM S-4800). Distances were directly determined from the backscattered SEM micrographs with the imaging software ImageJ.

The preparation of the oxide layers as TEM samples was rather complex, due to the brittleness of the oxide layer itself. Two small pieces of the oxidised bulk sample were extracted along the ⟨100⟩ direction, using a wire saw. On top of the oxidised layer, a slice of superalloy base material was glued to protect the scale during the mechanical preparation. The whole stack was clamped into a Titanium TEM sample plate carrier for subsequent one-sided grinding and polishing. After reaching a common height with the plate carrier, a wedge grinding and polishing method (wedge angle of 5–7°) was applied to the opposite side. By then, the scale on tip of the sample had a thickness of about 20 µm. The final thinning was performed in different steps by ion milling. In the last step an acceleration voltage of 1 kV at 5° was used for 30 min to reach electron transparency.

Annular dark field scanning TEM (ADF-STEM) was performed on a double-aberration-corrected Titan Themis[3] 300 operating at an acceleration voltage of 300 kV. In order to reveal the different oxides and phases, ADF-STEM was performed under conditions of *Z*-contrast using a small camera length of 115 mm. The high-resolution STEM-EDX mappings at 300 kV were carried out using a Super-X detector incorporating the Bruker ChemiSTEM™ system. The Super-X detector comprises four silicon drift detectors (SDD) symmetrically placed around the optical axis, close to the sample area. All four signals are combined into one spectrum to improve the collection efficiency. More details explaining this system can be found in the literature [20–22].

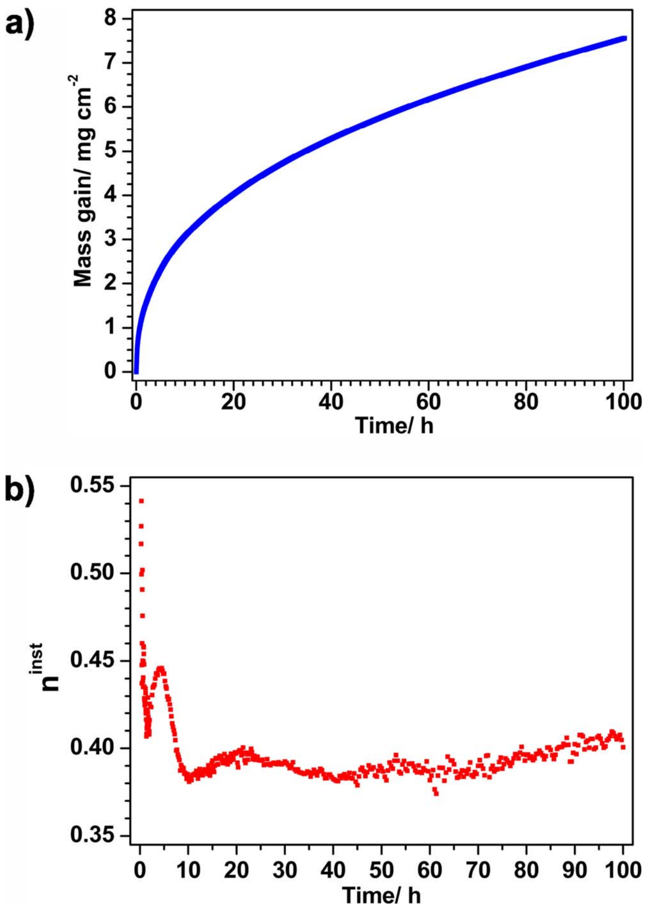

Fig. 1. (a) Mass gain of Co-9Al-9W at 900 °C during 100 h oxidation and (b) instantaneous time exponent n^{inst} for the duration of exposure.

Part of the EDX results are shown as colour coded element distribution maps. For each investigated sample, mappings of the four relevant elements (Co, Al, W and O) are combined to one figure. Due to varying maximum concentrations, the colour coding is individually adjusted, with dark blue representing a low and red a high amount (at.%) of the corresponding element.

3. Results

3.1. Mass gain and multilayered scale growth at 900 °C

Mass gain of the ternary Co-base superalloy was continuously measured during 100 h isothermal oxidation in artificial air at 900 °C. Results are given in Fig. 1a. Prevailing kinetics are subjected to a first examination. A power rate law for mass gain was assumed for the whole duration of the oxidation experiment to draw first conclusions.

$$\Delta m = kt^n \tag{1}$$

The instantaneous time exponent n^{inst} is equal to the deviation of the double-logarithmic plot of mass gain over time. To reduce the noise, increments between the considered data points are increased with ongoing progress of oxidation. The instantaneous time exponent is plotted for the whole range of performed oxidation experiments in Fig. 1b.

As noted by several authors, interpretation of instantaneous time exponents is not always straightforward. Nevertheless, this way of treating kinetic data can help to locate and isolate changes in the overall kinetics of the scale growth reactions. Scale growth processes at