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Effect of ruthenium on the precipitation of topologically close packed phases in Ni-based superalloys of 3rd and 4th generation

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ABSTRACT

The precipitation of topologically close packed (TCP) phases is detrimental for the high temperature strength of high refractory Ni-based superalloys. The beneficial influence of Ru with respect to this so called instability is nowadays well accepted. In the present paper the precipitation of topologically close packed (TCP) phases is studied quantitatively in two experimental alloys (one Ru-free and one with addition of Ru) to clarify the mechanism of the Ru effect. It is confirmed that the TCP phase precipitates undergo sequential phase transformation with the tetragonal σ-phase precipitating first. Ru retards the phase transformation and leads to decreased equilibrium volume fraction of TCP phases. The results clearly indicate that Ru decreases the driving force for TCP phase precipitation. Investigations of crystallography and chemistry of the TCP/matrix interface point to an additional effect by increase of misfit strain energy.

1. Introduction

High-temperature strength of nickel based superalloys is strongly dependent on the content of refractory elements, particularly Re. The beneficial characteristic of Re is attributed to its high solid solution strengthening effect [1–3], high melting point and a very low diffusion coefficient [4,5]. Quantitatively, the effect of Re depends on the alloy composition. As reported by Heckl, addition of 1 at.% Re can improve the high-temperature capability by up to 87 K [6]. However, beside the beneficial effect, the very low diffusion coefficient of Re also brings about some disadvantages. Considering the as cast microstructure, strong segregation of Re to the dendrite core demands the application of expensive homogenization heat-treatments [7,8]. Moreover, Re induces precipitation of topologically close packed (TCP) phases during long-term high-temperature exposition [9–14]. TCP phases are very detrimental because of two main factors. At first, when they nucleate and grow, they deplete the γ-matrix phase from solid solution strengtheners. This leads to decreased creep resistance of the material [10,14]. Further, TCP phases are brittle and exhibit a complex lath- or plate-like morphology [15], which evolves with time [16]. Thus, cracks are easily nucleated. As a consequence the fatigue life-time and tensile ductility of the material will be decreased [14].

It is widely accepted that precipitation of TCP phases can be suppressed by an addition of ruthenium. Several possible mechanisms for this effect were proposed based on experiments [10,17–20] and simulations [21,22]. Among the solubility related mechanisms, 'reverse partitioning' [18–20] or increased solubility of Re and W within the γ-matrix phase [10,17] was suggested. Alternatively, a change in TCP/matrix interface energy [21,22] was considered as a potent factor influenced by Ru. However, as TCP phases exhibit very small sizes in the early stages of precipitation and are very sensitive to alloy chemistry, it was difficult to draw the final conclusions without advanced high-resolution characterization and quantitative description of phase transformation.

Recently the present authors [16] used the Johnson–Mehl–Avrami equation to describe the precipitation of TCP phases [23]. It was found that ruthenium influences both nucleation and growth rate of TCP phases. This observation indicates that Ru affects the interface energy or the chemical driving force for TCP phase

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formation. The TCP phases undergo a precipitation sequence [9,11,16] and thus it is most relevant to understand the Ru influence on the nucleation of the first TCP particles. Nevertheless, the mechanism of TCP phase growth also needs to be studied.

In the present paper we describe the precipitation process of TCP phases by combining crystallographic and compositional data obtained by transmission electron microscopy (TEM) and atom probe tomography (APT), respectively. We complement these results with the standard two-dimensional (2D) and advanced three-dimensional (3D) microscopic observations. Based on the results, conclusions on the influence of Ru on the precipitation of TCP phases are drawn.

2. Experimental

2.1. Material

Astra 1–20 and Astra 1–21, two experimental nickel based superalloys of the 3rd and 4th generation, respectively, were used to investigate the influence of Ru on the early stages of TCP phase precipitation. The detailed chemical compositions of the two alloys are given in Table 1. The designation Astra refers to a series of experimental alloys developed in our laboratory based vaguely on the commercial alloy CMSX-4 [6,7]. Both alloys studied here, Astra 1–20 and Astra 1–21, contain 2 at.% of Re. The two alloys differ only in Ru content. While Astra 1–20 has no additional Ru, Astra 1–21 contains 1 at.% Ru. Ru is being added at the expense of Ni. The definition of the alloys in at.% allows to keep the content of all other alloying elements constant, i.e. avoids unintended additional compositional changes.

Materials were produced in a vacuum arc furnace. Subsequently directional solidification in a lab-scale Bridgman vacuum induction melting furnace was used to convert them into columnar grained structures. A cluster of three cylindrical rods with a diameter of 12 mm and a height of 180 mm was cast with a withdrawal rate of 9 mm min^{-1}. This resulted in a primary dendrite arm (PDA) spacing of 180 μm. All details of the casting process can be found in [7].

A three step heat-treatment was applied after the casting process. In the first step the alloys were homogenized at 1340 °C for 16 h to reduce the segregation of refractory elements. Two subsequent aging steps were conducted to precipitate γ′ particles and stabilize their morphology. The detailed parameters of the heat-treatment procedure are given in Table 2. Experimental evidence suggested that the same heat-treatment conditions can be used for both alloys with and without addition of Ru [7].

Specimens of 10 mm in height and 12 mm in diameter were cut from heat-treated samples. The small specimens were then annealed at various time–temperature conditions. The present paper focuses on the materials annealed at 950 °C between 500 and 2000 h with 500 h intervals. All the steps of standard heat-treatment as well as high-temperature exposition were conducted in Ar atmosphere.

The annealed samples were prepared for microscopic observations via standard metallographic operations, i.e. gradual grinding and polishing.

Table 1
Chemical compositions of investigated alloys (at.% and wt.%). The designation Astra refers to a series of in-house experimental alloys approximately based on commercial second generation superalloy CMSX-4. The two alloys investigated here, Astra 1–20 and 1–21, differ only in Ru-content (0 vs. 1 at.% Ru, resp.).

	Astra 1–20		Astra 1–21	
	at.%	wt.%	at.%	wt.%
Al	13.50	5.88	13.50	5.84
Co	9.00	8.56	9.00	8.50
Cr	6.00	5.03	6.00	5.00
Mo	0.60	0.93	0.60	0.92
Re	2.00	6.01	2.00	5.97
Ru	0.00	–	1.00	1.62
Ta	2.20	6.42	2.20	6.38
W	2.00	5.93	2.00	5.89
Ni (bal.)	64.70	61.24	63.70	59.88

Table 2
Heat-treatment process parameters.

Step	Heating rate [K/min]	Temperature [°C]	Holding time [h]	Cooling
Solutioning	4	1340	16	In air
1st annealing	4	1140	2	In air
2nd annealing	4	870	24	In air

2.2. Focused Ion Beam (FIB) – scanning electron microscopy (SEM) investigations

SEM-FIB investigations were conducted on a Helios NanoLab 600i instrument. The (0 0 1) planes of the γ/γ′ microstructure were observed with the use of a concentric backscattered (CBS) detector operating in an in-lens mode, accelerating voltage of 5 keV and a beam current of 0.69 nA. This method allowed for ultra-high resolution (UHR) imaging of TCP phases.

The three-dimensional (3D) inspection of the microstructure was possible by employing automated FIB sectioning and subsequent imaging with the use of backscattered detector (BSE) in UHR mode. A stack of 400 slices with the thickness of 20 nm each were collected by thinning the material with an ion beam current of 0.79 nA. The area of a single slice covered 100 μm^2, resulting in a total scanned volume of 800 μm^3 obtained in a reasonable time for ion thinning.

2.3. Image processing and analysis

The images obtained in SEM were binarized to reveal TCP phases only. The area fraction of TCP phases was calculated by counting the corresponding area of TCP phases and dividing it by the full imaged area. Each single value was obtained by analyzing 3–5 images.

The real 3D morphology of TCP phases was obtained with the use of FEI SAS AvizoFire software. The slices were added one by one to reconstruct the full scanned volume. Algorithms for alignment were applied to eliminate problems with drift and bring the slices to the same x, y coordinates (z varies with the slice number). The morphology of TCP phases was extracted from the γ/γ′/TCP microstructure by applying grayscale thresholding algorithms.

2.4. Transmission electron microscopy investigations

The Astra 1–20 TEM sample was prepared by grinding and polishing disks to a thickness of about 80 μm followed by a dimple grinding step to a thickness of only a few μm. To obtain high quality samples for HRTEM investigations the sample was thinned to electron transparency by using Ar^+ ions with a final polishing step at −20 °C and ion energy of 700 eV.

The sample of Astra 1–21 was prepared in a FEI Helios NanoLab 600i dual beam instrument by employing a standard TEM lamella lift out technique. For a final milling step, both sides of the lamella were polished using a voltage of 2 kV to obtain a sample with a thickness below 50 nm.