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Reasons for the enhanced phase stability of Ru-containing nickel-based superalloys

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Abstract

Improvements in phase stability on the addition of Ru are well known in the field of nickel-based superalloy development. However, the key mechanism of this benefit remains unclear. A new alloy series with stepwise increased additions of Ru was used to systematically investigate the impact of Ru on yopologically close-packed (TCP) phase inhibition. In addition, the investigation was carried out on a less known type of TCP formation, the so-called discontinuous precipitation. This type of TCP phase formation offers two major advantages compared with commonly investigated TCP plates in dendritic regions. First, the microstructure is much coarser than fine TCP plates, allowing reliable and less time consuming investigations. Second, discontinuous precipitation transforms the supersaturated and unstable γ/γ' microstructure in a condition close to equilibrium, permitting a meaningful insight into the stable alloy constitution. The experimental results for alloy phase stability dependence on Ru are evaluated with respect to all possible effects of TCP phase inhibition by Ru. Furthermore, experimental evidence for increased Re solubility in the γ matrix was found on addition of Ru, which is not seen in corresponding ThermoCalc calculations. This finding is probably the dominant reason for the increased TCP phase capability of Ru-containing alloys. A ternary phase diagram model has been developed to describe the new approach.

Keywords: Phase stability; Discontinuous precipitation; Topologically close-packed phase inhibition; ThermoCalc; Ruthenium

1. Introduction

Due to the demand for increasing material temperature capabilities, the development of nickel-based superalloys has led to continuously rising levels of refractory elements. In particular, the addition of Re has proved to significantly increase high temperature creep resistance, which is one of the major demands in the application of nickel-based superalloys as turbine blade materials. As a result, the latest generation of single crystal nickel-based superalloys permit operation at temperatures up to 1100 °C, which represents a temperature increase of 100 °C in the past 30 years [1–7]. However, the increasing content of refractory elements, in particular Re, also significantly decreases the long-term phase stability of the alloys by promoting the formation of brittle and harmful topologically close-packed (TCP) phases [3,7–16]. To overcome this concern about long-term phase stability recent alloy developments have included the addition of Ru, which appears to be beneficial in suppressing TCP phase formation. The key mechanism of this effect has been attributed to the so-called reverse partitioning of Re, reduced supersaturation of the γ matrix due to an increased Re concentration in the γ' phase [7–10]. However, this approach remains controversial, since evidence for reverse partitioning is not consistently found for each nickel-based superalloy system, indicating a dependence on the alloy composition [11,12,17–19]. Furthermore, a study by Pyczak et al. showed that an increased content

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of Re in the γ' precipitates due to the presence of Ru does not lead to a significantly decreased concentration of Re in the γ matrix [20]. As a consequence, other correlations must exist besides reverse partitioning of Re. One possible suggestion is a reduction in the γ' volume content on addition of Ru, accompanied by decreased γ supersaturation due to a higher γ volume content [10]. However, this effect also has not been found consistently [19,22]. Further possibilities for TCP phase inhibition effect have been ascribed to an influence on lattice parameters [8,9,13,23,24]. However, a fundamental verification of the different possible approaches is still not available, since experimental analysis of typically a few nanometers wide TCP plates is challenging.

The present paper focuses on a less well-known type of TCP phase formation, which is referred to as discontinuous precipitation (DP). This type of TCP phase precipitation occurs at high angle grain boundaries as a phase transformation of the unstable and supersaturated γ/γ' microstructure to a stable condition including coarse TCP columns several microns in size. The reaction can be summarized by the transition (SS, supersaturated):

$$(\gamma^{SS}_{matrix} + \gamma'_{precipitates}) = (\gamma'_{matrix} + \gamma_{precipitates}) + TCP$$

Details of the DP colony growth mechanism in nickel-based superalloys based on the same alloy series have been investigated and published in a related article [25]. Although the mechanism of DP has been the focus of studies of other alloy systems, there is only sparse literature in the field of nickel-based superalloys, since these alloys are commonly used as single crystals lacking the necessary grain boundaries for DP colony growth [25–30]. The absence of DP colony growth in bulk single crystals might also be the reason for the lack of information. However, compared with investigations on nano-scaled intragranular TCP plates, DP colonies offer a unique opportunity to obtain meaningful insights into the stable alloy condition due to full transition of the microstructure. Furthermore, the much coarser microstructure of DP colonies allows reliable microstructure analysis by less time-consuming techniques than transmission electron microscopy (TEM). Hence, these TCP phase-containing DP colonies were used as a new approach in the present work to investigate the phase stability of Ru-containing nickel-based superalloys. The TCP volume content and equilibrium γ/γ' compositions, as well as lattice parameters, dependence on the Ru content have been experimentally analysed. The results are compared with calculated data obtained from ThermoCalc simulations. All possible inhibition effects of Ru are evaluated from a general point of view and with respect to experimental correlations. As an outcome of the newly developed TCP phase in DP colonies approach evidence for a new mechanism of TCP phase inhibition was found. Using the experimental data a model illustration in the form of a ternary phase diagram has been established and verified.

2. Experimental

A newly designed Astra1 alloy series, based on the commercial nickel-based superalloy CMSX-4, was investigated. A major difference to CMSX-4 is that the minor concentrations of Ti and Hf have been removed and the alloy series is set as based on at.%. The atomic concentrations of all alloying elements besides Re and Ru were kept constant. Compared with alloy series based on wt.%, this approach allows a systematic investigation of element additions, since each alloy composition is adjusted individually, instead of rather than modifying atomic ratios by simple weight additions. Re and Ru were added stepwise in the range 0–2 at.% at the expense of Ni. A full table of all Astra1 compositions have been previously published [22,25,31–33]. The compositions given in Table 1 represent the TCP-prone alloys of this series which were selected for the investigations in this work.

The alloys were investigated as directionally solidified samples. Full details of the in-house casting process, casting conditions and quality control have been reported [31,32]. Heat treatment of the Astra1 alloy series was developed based on the standard procedure for CMSX-4 with the objective of obtaining comparable remaining Re segregation as in CMSX-4. Further procedure details and heat treatment results can be found in Heckl et al. [33].

For the investigation of alloy phase stability fully heat treated samples were aged in a batch furnace (LT9/13, Nabertherm GmbH, Lilienthal, Germany) at 950 °C and 1050 °C for 500, 1000 and 2000 h each. To avoid oxidation the samples were encapsulated in dense alumina rubalit tubes placed in weld sealed stainless steel containers with Ti and Zr chippings as oxygen getters. Sample preparation was performed using the polishing steps 6 μm Allegro, 3 μm DP-Mol, both with lubricant green, and 0.25 μm MD-Chem with OP-U/H_2O 1:5 suspension. A V2A etchant (100 ml H_2O, 100 ml HCl (32%), 10 ml HNO_3 (65%) and 0.3 ml Vogels Sparbeize) at 60 °C was used to obtain lightly etched microstructures.

For microstructural analysis a scanning electron microscope (SEM XL30, Phillips, Eindhoven, The Netherlands) was used to document the original γ/γ'- and TCP-containing DP colonies. A SEM image (Fig. 1) illustrates the striking transition of the original and supersaturated γ/γ'- to a TCP-containing DP colony. Evaluation of the TCP phase area fraction within the DP colony was performed with the software Image C, version 5.0 (Aquinto AG, Berlin, Germany). For this purpose the surrounding γ/γ' areas have been excluded by separating the DP colony as a reference surface. Within the separated DP colonies the TCP phase content has been experimentally determined as the area fraction in statistically sufficient numbers. The generated mean values have been compared with calculated TCP phase volume contents using ThermoCalc, version R (ThermoCalc Software, Stockholm, Sweden) with the database TTNi7 (ThermoTech Ltd., Guildford, UK).