Journal of Alloys and Compounds 582 (2014) 299–304

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

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

Synergistic effect of rhenium and ruthenium in nickel-based single-crystal superalloys

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ARTICLE INFO

Article history:
Received 17 December 2012
Received in revised form 31 July 2013
Accepted 31 July 2013
Available online 9 August 2013

Keywords:
Nickel-base single crystal superalloy
Scanning electron microscopy
Transmission electron microscopy
Density functional theory

ABSTRACT

The microstructures of ternary Ni–Al–Re and quaternary Ni–Al–Re–Ru single-crystal alloys were investigated at atomic and electronic levels to clarify the synergistic effect of Re and Ru in nickel-based single-crystal superalloys. In the Ni–Al–Re alloy, it was directly observed that Re atom occupied the Al site of γ' phase. In the Ni–Al–Re–Ru alloy, the mechanisms of Re repartition between γ and γ' phases were proposed. In the dendritic cores, high concentrations of Re exceeded the solubility limit of γ' phase and partitioned to γ phase, which led to the homogenization. In the interdendritic regions, Ru resulted in the repartitioning of Re to γ phase which was proved by transmission electron microscopy and first-principles calculations.

1. Introduction

Ni-based single-crystal superalloys with excellent high-temperature (above 1000 °C) mechanical properties are critical for the blade applications in aero engines [1,2]. The typical microstructure of these alloys involves the γ'-Ni_3Al phase with $L1_2$ structure coherently embedded in a solid solution matrix of the γ-Ni phase. Alloying elements, such as Co, Cr, Mo, Re, Ru, Ta, Ti, W and so forth are added to enhance the high-temperature properties. Among these alloying elements, Re mainly partitions into the γ phase of multicomponent superalloys and remarkably improves the strength and creep resistance [3,4]. Nevertheless, excessive Re will deteriorate the properties by promoting the precipitation of brittle topologically close-packed (TCP) phases in γ phase [5]. The interactions between Re and other alloy elements will influence the phase stability of superalloys. Recent experiments reported that the addition of Re increased the W content and decreased the Cr content in the γ phase, which was the reason that Re promoted the precipitation of TCP phase [6]. Ru was reported to stabilize the γ/γ' microstructure during high-temperature exposures, and effectively improve the creep performance [7,8]. Re and Ru, when combined, will contribute to the excellent mechanical properties of superalloys. This cooperative mechanism of multiple elements was referred as synergistic effect [9,10]. Earlier studies on Ru-containing nickel-based single-crystal superalloys suggested a 'reverse partitioning' mechanism, by which Ru led to less partitioning of Re to the γ phase, thus making Re unavailable for TCP phase formation in the γ matrix [11,12]. Other studies doubted this mechanism because no strong influence of Ru on the partitioning of Re was found in some alloy systems [13,14]. Furthermore, experimental results [15] showed that a large amount of Ru increased the solubility of Re in the γ phase with high Cr content. Unlike the previous reports, this study showed that the addition of Ru significantly promoted the precipitation of TCP phases at both 1000 °C and 1100 °C. Since the synergistic effect of alloy elements is very complicated, there is still lacking of deep understanding of the fundamental interaction between Re and Ru.

Besides, the directional solidification introduces the large-scale solute segregation between the dendritic cores and the interdendritic regions [16–19]. The chemical inhomogeneity of the dendritic microstructure cannot be completely eliminated by the subsequent heat treatment [20]. Although previous researchers have explored the effects of Ru on the distribution of Re between the γ and γ' phases [11–14], they did not clearly distinguish the dendritic cores and interdendritic regions.

In the present study, the synergistic effect of Re and Ru at the atomic and electronic levels was investigated in the ternary and quaternary model alloys in order to exclude the interactions from

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http://dx.doi.org/10.1016/j.jallcom.2013.07.201

other alloying elements. It is well known that the high-resolution electron microscopy in combination with the composition analysis is a powerful tool to reveal small precipitates and clarify the atomic structure of the interface, chemical bonding and dislocation in superalloys [21]. In our study, high-resolution scanning transmission electron microscope (HRSTEM) with spherical aberration correctors [22–27] were used to obtain direct experimental evidence of element partitioning and site preference at atomic scale resolution. The dual-beam focused ion-beam (FIB) was used to select specimens from the dendritic cores and interdendritic regions. Meanwhile, electronic structure calculation based on density functional theory (DFT) [28,29] was used to explain the experimental phenomena.

2. Experimental details, results and discussion

2.1. Materials and experimental techniques

Three kinds of alloys, including Ni–Al, Ni–Al–Re and Ni–Al–Re–Ru were directionally solidified using the Bridgman technique (2 mm/min withdrawal rate) to form a⟨100⟩-oriented single-crystal. The chemical compositions of the alloys are listed in Table 1. The single-crystal bars were subjected to solid solution treatment at 1330 °C for 20 h under flowing argon followed by the water quenching and aged at 870 °C for 32 h.

Table 1
The compositions of the model alloys investigated in this work.

Alloy	Al	Re	Ru	Ni	
Ni–Al	8.77	–	–	Bal.	wt.%
	17.29	–	–	Bal.	at.%
Ni–Al–Re	7.95	4.94	–	Bal.	wt.%
	16.32	1.47	–	Bal.	at.%
Ni–Al–Re–Ru	7.96	4.96	2.86	Bal.	wt.%
	16.53	1.49	1.58	Bal.	at.%

The element segregation behaviors of the Ni–Al–Re and Ni–Al–Re–Ru alloys were studied via energy dispersive spectrum (EDS) in FEI Quanta 600 scanning electron microscope (SEM) at the voltage of 15 kV. The SEM specimens were prepared by mechanical polishing and electrochemical corrosion. The etchant consisted of 48% (volume fraction) H_2SO_4, 40% HNO_3 and 12% H_3PO_4. The data of element concentration were collected from at least ten areas in the dendritic and interdendritic regions for each experimental alloy. Besides, the average γ' volume fractions of the two regions were analyzed by the image statistical software *ImageJ*. The area fractions of γ' phases in three SEM images for each region were counted to estimate the γ' volume fractions.

The element partitioning behaviors between the γ and γ' phases were analyzed by TEM experiments. The TEM specimens were prepared employing the dual-beam FIB microscope (FEI Quanta 3D FEG). Samples were selected from the dendritic cores and interdendritic regions respectively and milled by Ga ions at the voltage of 2–30 kV. The EDS mapping was conducted on the Titan-G2 80-200 STEM at 200 kV, equipped with a probe Cs corrector and energy dispersive spectrum. The Z contrast imaging through high-angle annular dark field (HAADF) technique was operated on the JEM-ARM200F STEM at 200 kV, with a spherical aberration corrector for electron optical system.

2.2. Element segregation between the dendritic and interdendritic regions

During the process of directional solidification, several solute elements partition to the solid dendritic cores and others partition to the liquid interdendritic regions. For the Ni–Al–Re alloy, there are average 2.22 ± 0.13 at.% Re in the dendritic cores versus 1.38 ± 0.15 at.% Re in the interdendritic regions. While for Ni–Al–Re–Ru alloy, there are average 2.57 ± 0.20 at.% Re in the dendritic cores of the Ni–Al–Re–Ru alloy versus 1.13 ± 0.05 at.% Re in the interdendritic regions. Because of the low diffusion rate in the Ni matrix [30–32], the segregation of Re between dendritic and interdendritic regions can hardly be completely eliminated. The segregation parameter K_i is employed to characterize the partitioning behavior of the alloying element between these two regions, where $K_i = \frac{c^i_{\text{dendritic}}}{c^i_{\text{interdendritic}}}$ is the ratio of the concentration of the element i in the dendritic cores to its concentration in the interdendritic regions. In the Ni–Al–Re alloy, the average K_{Re}, K_{Al} and K_{Ni} are 1.61 ± 0.23, 0.96 ± 0.01 and 0.99 ± 0.01, respectively; and in the Ni–Al–Re–Ru alloy the average K_{Re}, K_{Ru}, K_{Al} and K_{Ni} are 2.27 ± 0.24, 1.11 ± 0.08, 0.94 ± 0.04, 0.99 ± 0.01. The results show that after solid solution treatment at 1330 °C for 20 h, the segregation parameters of Ni, Al and Ru are close to 1. That means these three elements tend to homogenization across the dendritic structures. However, the element Re

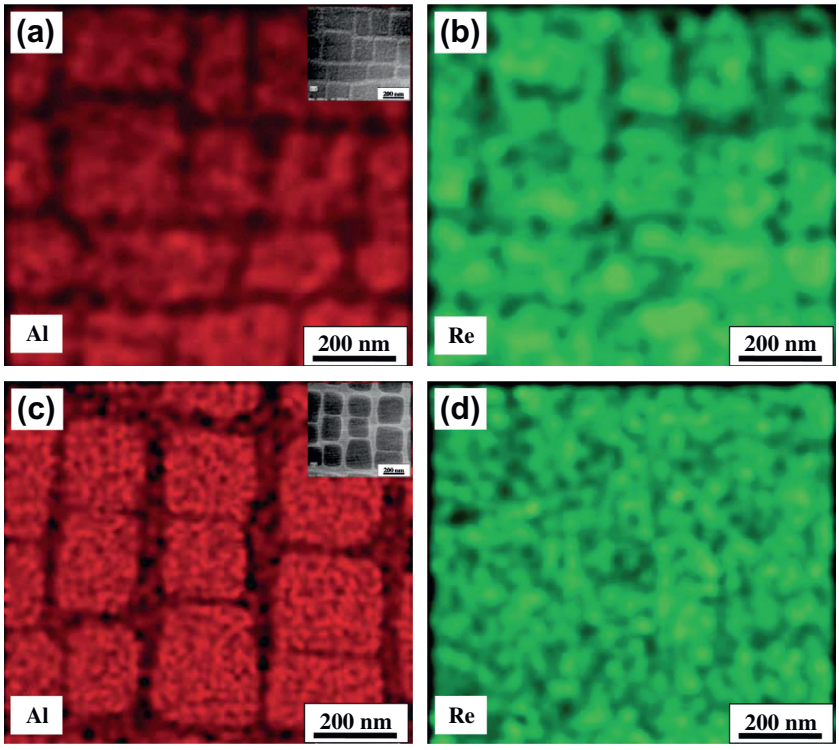

Fig. 1. The HRSTEM-EDS mapping of (a) Al in the interdendritic region; (b) Re in the interdendritic region; (c) Al in the dendritic core; (d) Re in the dendritic core of the Ni–Al–Re alloy. Insets are the topography images.