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Microsegregation behavior of alloying elements in single-crystal nickel-based superalloys with emphasis on dendritic structure

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ABSTRACT

Directionally solidified single crystal of CMSX-4 superalloy was investigated to show the evolution of microsegregation and the effect of crystal orientations on the solute distribution. As the solidification proceeded, Al, Ti, Ta and Mo consistently segregated to the residual liquid, while Co, W and Re segregated to the solidified γ dendrite core. Cr did not exhibit a consistent segregation tendency to either side. Increasing the solid volume fraction resulted in increasing segregation levels of Al, Ti, Ta, Co, W and Re, whereas the segregation levels of Cr and Mo did not consistently change. For most of the alloying elements, the solute profiles of the same element were similar along the [100] and the [110] crystal orientations. For Al, Ti and Ta, the solute contents increased from the dendrite core towards its periphery. Re, W, and Co showed the opposite trend. For Mo and Cr, uniform distribution profiles were shown along the [100] orientation with increasing distance from the γ dendrite core towards its periphery, while a large variation in the solute contents of both elements was observed along the [110] orientation. The solutes across a typical dendrite distributed more homogeneously along the [100] orientation than those along the [110] orientation.

1. Introduction

Substantial additions of dense refractory elements such as Ta, W and Re can significantly improve the high temperature properties of single-crystal nickel-based superalloys. Some researchers [1] reported that Ta not only raises high temperature tensile strength and creep resistance but also obviously improves ductility in high temperature tensile and stress rupture tests. Seo et al. [2] suggested that the addition of W confers considerable solid solution strengthening with simultaneous increases in high temperature creep resistance. A study by Yeh and Tin [3] found that significant increases in the high temperature flow stresses were observed with additions of Re. A similar report [4] showed that an improved creep resistance and a higher alloy temperature capability was observed with the addition of Re. However, some studies [5] showed that these alloying elements highly segregate during solidification, resulting in an inhomogeneous compositional distribution within the microstructure, and some researchers [6] found that this segregation leads to the formation of the highly cored γ/γ′ eutectic pools. Although complicated stepwise solution heat treatments are used to dissolve the non-equilibrium structure [7], completely homogenized microstructures are laborious to obtain because of the elements' sluggish diffusivity in the solid-state γ matrix [8]. For some superalloys, the heat treatment times can become very long and the heat treatment temperatures can exceed 1300 °C, resulting in increased costs [9]. In addition to this, the properties of the alloys are also a function of the degree of homogenization, showing improved properties in alloys exhibiting increased homogeneity [10]. In order to reduce the processing costs by reducing the heat treatment requirements without degrading the properties of the alloys, a reduction in the degree of microsegregation would be required. Consequently, knowledge of the microsegregation behavior of the alloying elements during solidification is essential for optimizing heat treatment cycles.

Over the past few decades, extensive research work into the microsegregation in as-cast single-crystal nickel-based superalloys has shown that the microsegregation behavior of alloying elements is dependent on processing parameters and alloying elements. Wang et al. [11] found that higher thermal gradient ahead of the solidification front significantly reduces the degree of the microsegregation. Some researchers [12] reported that as the cooling rate increases, the degree of the segregation originally is increased, then decreased. A study [13] showed that with increasing withdrawal rate, the degree of the microsegregation is reduced. Some researchers [14] reported that alloying additions also exert a huge influence on the solidification microsegregation. However, the characterization of the microsegregation behavior is only based on the analysis of the final solidified samples, which cannot depict the dynamical development of microsegregation during solidification. Besides this, our previous study [15] showed that the solute distribution of alloying elements along

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the [100] and the [110] orientations differs across a cell. Therefore, the crystal orientation would affect the degree of microsegregation. Dendrites, not cells, are the common microstructures of the single-crystal components in engineering, and the growing mechanism differs between the cells and dendrites. Thus the solute distribution of alloying elements along the two orientations across a typical dendrite needs to be clarified. In the present work, the dynamic evolution of the microsegregation distribution of alloying elements was investigated during solidification. In addition to this, the solute distribution of alloying elements across a typical dendrite was measured to compute the difference in the microsegregation distribution along different crystal orientations.

2. Experimental procedure

A superalloy CMSX-4, possessing the compositions listed in Table 1, was used in the present investigation. The experiments were performed using a vertical Bridgman-type laboratory furnace, as shown in Fig. 1. During the experiments, single-crystal cylindrical specimens of CMSX-4 superalloy (20 mm in diameter) were placed in a ceramic tube and elevated into the furnace chamber, which was preheated to 1673 K. A portion of the specimens remained at this temperature for 15 min. The temperature of the melt, shielded using high-purity argon, was measured separately by lowering a thermocouple into the melt in the ceramic tube. Thermocouple readings were recorded each second during the entire process. Following this, the tube was withdrawn from the chamber using a withdrawal rate (V) of 0.3 mm·min^{-1}. After withdrawing a certain solidification length and on reaching the steady-state directional solidification conditions, the tube was quickly removed from the furnace chamber and quenched in a water bath. To obtain the thermal gradient ahead of the liquid and solid (L/S) interface (G_L), the cooling rate was first calculated from the recorded cooling curve's slope at the liquidus temperature. The G_L was then calculated by dividing the cooling rate by V. The G_L was calculated to be 3.6 K·mm^{-1}.

After quenching, four transverse sections (perpendicular to the growth direction, that is the [001] crystal orientation) within the mushy zone were cut at distances of 0.22 mm, 0.61 mm, 1.15 mm and 3.82 mm from the dendrite tip, which corresponds to different solid volume fractions (f_s). The samples were prepared by standard metallographic procedures and etched in a solution of 60 ml ethanol + 40 ml HCl + 2 g (Cu_2Cl. $2H_2O$). The microstructures were examined using an Axioplan 2 optical microscope (OM). The solute distribution was measured using a Zeiss 1540 XB cross beam scanning electron microscope equipped with an energy-dispersive X-ray spectroscope (EDX). Within the respective transverse sections, the alloying elements' concentrations were measured at a minimum of ten points in the dendrite cores and the residual liquid. The average values of the measured data were used to calculate the segregation coefficients. Within the cross-section 3.82 mm from the dendrite tip, the solute profiles were obtained along the [100] and [110] crystal orientations (Fig. 2) on three typical dendrites to obtain the average solute distributions. The individual data acquisition points along the [100] and [110] orientations were spaced 5 μm and 2 μm apart using an average length of about 265 μm and 90 μm, respectively.

3. Results

Fig. 2 depicts the characteristic transverse sections showing an array of adjacent γ dendrites. The corresponding f_s for (a), (b), (c) and (d) is about 10.57%, 40.56%, 55.74%, and 83.92%, respectively. Since the preferred orientation for the crystal growth in cubic metals is [001], the cross-section of the dendrites is cruciform with orthogonal secondary arms pointing in the [100] and [010] directions. As the solidification proceeds, the secondary dendrite arms gradually coarsen.

Table 1
The compositions (wt%) of the superalloy CMSX-4.

Al	Co	Cr	Re	Ta	Ti	W	Hf	Mo	Ni
5.0	10.02	6.32	2.78	6.04	1.0	5.83	0.51	0.36	Balance

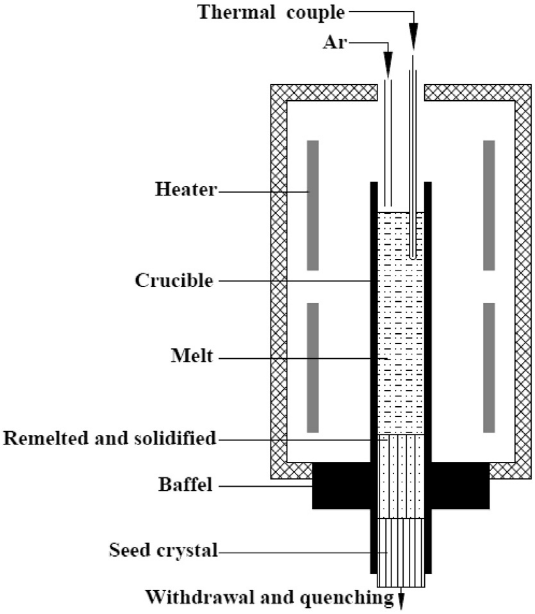

Fig. 1. Schematic diagram of the vertical Bridgman-type laboratory furnace.

Microsegregation behavior can be characterized by the segregation coefficient k', defined as the ratio of the alloying elements' concentration in the dendrite core to that in the residual liquid [16]. k' values less than unity indicate segregation to the residual liquid, while k' values greater than unity indicate segregation to the dendrite core. Table 2 shows the average concentrations of the alloying elements in the dendrite core and the residual liquid measured in the transverse sections. Based on the concentrations, the segregation coefficients of the alloying elements are calculated, and their evolution with increasing f_s is plotted in Fig. 3.

The alloying elements Al, Ta, Ti and Mo segregate to the residual liquid, while W, Re and Co segregate to the dendrite core. With increasing f_s, the segregation coefficients of Al, Ta and Ti gradually decrease and increasingly deviate from unity. The segregation coefficient of Mo doesn't significantly vary and remains smaller and close to unity. It is conspicuous that the degree of segregation of Al, Ti and Ta to the residual liquid becomes stronger during solidification, whereas little variation in the degree of segregation of Mo can be found. On the other hand, as the solidification proceeds, the segregation coefficients of W, Re and Co gradually become greater and increasingly deviate from unity. This suggests that with increasing f_s, the degree of segregation of these elements increases to the dendrite core. The segregation coefficient of Cr fluctuates around unity, indicating that Cr doesn't exhibit a great tendency to segregate either to the dendrite core or to the residual liquid. As the solidification proceeds, a small variation in the segregation coefficient of Cr is observed which suggests that Cr homogeneously distributes between the γ dendrite and the residual liquid. Of all the elements that segregated to the residual liquid, Ta and Ti exhibit the largest degree of segregation followed by Al. However, of the elements that segregated to the dendrite core, Re exhibits the most pronounced tendency followed by W.

In Fig. 4, the measured solute profiles are plotted versus the distance from the dendrite's core to its periphery along the [100] and the [110] orientations. For most alloying elements, the variation in tendency is similar for the solute profiles of the same element along both crystal orientations. For Al, Ti and Ta, the solute contents increase from the core of the γ dendrite towards its periphery. Re, W, and Co show the opposite trend. For Mo and Cr, a significant difference is found between the solute