MATERIALS CHARACTERIZATION 89 (2014) 43–55

Available online at www.sciencedirect.com

ScienceDirect

www.elsevier.com/locate/matchar

A comparative study of quantitative microsegregation analyses performed during the solidification of the Ni-base superalloy CMSX-10

Seong-Moon Seo[a,*], Hi-Won Jeong[a], Young-Keun Ahn[a], Dae Won Yun[a], Je-Hyun Lee[b], Young-Soo Yoo[a]

[a]High Temperature Materials Group, Korea Institute of Materials Science, Changwon 642-831, Republic of Korea
[b]Department of Metallurgy & Materials Engineering, Changwon National University, Changwon 641-773, Republic of Korea

ARTICLE DATA

Article history:
Received 4 September 2013
Received in revised form
9 December 2013
Accepted 17 December 2013

Keywords:
Superalloy
Microsegregation
Solidification
CMSX-10

ABSTRACT

Quantitative microsegregation analyses were systematically carried out during the solidification of the Ni-base superalloy CMSX-10 to clarify the methodological effect on the quantification of microsegregation and to fully understand the solidification microstructure. Three experimental techniques, namely, mushy zone quenching (MZQ), planar directional solidification followed by quenching (PDSQ), and random sampling (RS), were implemented for the analysis of microsegregation tendency and the magnitude of solute elements by electron probe microanalysis. The microprobe data and the calculation results of the diffusion field ahead of the solid/liquid (S/L) interface of PDSQ samples revealed that the liquid composition at the S/L interface is significantly influenced by quenching. By applying the PDSQ technique, it was also found that the partition coefficients of all solute elements do not change appreciably during the solidification of primary γ. All three techniques could reasonably predict the segregation behavior of most solute elements. Nevertheless, the RS approach has a tendency to overestimate the magnitude of segregation for most solute elements when compared to the MZQ and PDSQ techniques. Moreover, the segregation direction of Cr and Mo predicted by the RS approach was found to be opposite from the results obtained by the MZQ and PDSQ techniques. This conflicting segregation behavior of Cr and Mo was discussed intensively. It was shown that the formation of Cr-rich areas near the γ/γ′ eutectic in various Ni-base superalloys, including the CMSX-10 alloy, could be successfully explained by the results of microprobe analysis performed on a sample quenched during the planar directional solidification of γ/γ′ eutectic.

1. Introduction

As a structural material with high-temperature applications, such as in turbine blades and vanes in aero engines and industrial gas turbines, Ni-base superalloys have been extensively alloyed with various solute elements for enhanced creep strength, oxidation, and hot-corrosion resistance at elevated temperatures. In recent years, advanced single-crystal (SC) Ni-base superalloys containing many dense refractory elements, such as Re, W, and Ta, have been developed for the solid-solution strengthening of fcc matrix γ and ordered γ′ (Ni_3Al, $L1_2$ structure) precipitates [1]. However, these refractory elements are known to segregate strongly during the solidification of Ni-base superalloys, resulting in an inhomogeneous chemical distribution within the alloy microstructure [2–6]. This, in turn, leads to a number of problems, such as freckle defect formation during the SC casting process [7,8], increased level of coarse γ/γ′ eutectic

* *Corresponding author*. Tel.: +82 55 280 3325; fax: +82 55 280 3599.
E-mail address: castme@kims.re.kr (S.-M. Seo).

1044-5803/$ – see front matter.
http://dx.doi.org/10.1016/j.matchar.2013.12.009

pools in the as-cast microstructure [9,10], and the formation of refractory-rich topologically close-packed (TCP) phases during thermal exposure at elevated temperatures [11–13]. Although advanced SC Ni-base superalloys are generally subjected to complicated stepwise solution heat treatments to dissolve γ/γ′ eutectic and reduce the chemical segregation of elements [14], it is still difficult to obtain fully homogenized microstructures via practical heat treatment because dense refractory elements have not only a strong segregation tendency during solidification but also a very low diffusion coefficient in matrix γ. Therefore, an understanding of the microsegregation during solidification is essential for controlling the solidification microstructures and optimizing the solution heat treatment cycles when new alloy chemistries are evaluated and/or numerical models are developed for the prediction of local compositions of alloy castings.

Microsegregation results from the solute redistribution that occurs on a microscopic level during solidification at the solid/liquid (S/L) interface. The magnitude of microsegregation can generally be estimated by determining the partition coefficient of solute elements. When equilibrium exists at the S/L interface, the partition coefficient is defined as the ratio of the solid concentration to the liquid concentration at the S/L interface [15]. One of the techniques used to measure the composition at the S/L interface involves the planar directional solidification of the alloy, followed by quenching (PDSQ) [16]. In the PDSQ technique, the partition coefficient can be measured by microprobe analysis of the solid and liquid at the planar S/L interface, allowing the extent of segregation to be estimated. As Sung and Poirier [17] noted, this technique results in an equilibrium partition coefficient because the planar S/L interface is usually obtained at an extremely low solidification rate, and there are no effects of interfacial kinetics. Another direct method to measure the partition coefficient is using the mushy zone quenching (MZQ) technique [18]. In the MZQ technique, the alloy is heated above its liquidus temperature and then cooled to a temperature at which the liquid and solid co-exist, i.e., the mushy zone. The alloy maintained at this temperature is subsequently quenched, and microprobe analyses of the solid and the quenched liquid yield the partition coefficient.

In addition to these direct techniques, the random sampling (RS) approach developed by Flemings et al. [19] has been widely used for characterizing microsegregation in Ni-base superalloys because the RS approach does not require a controlled solidification experiment to obtain the appropriate microstructure for measurement [5–7,14,20–22]. The RS approach is based on the statistical analysis of the microprobe data obtained on the as-cast alloy sample. Compositional measurements by microprobe analysis are carried out along arbitrarily selected lines or a square/rectangle grid on the sample prepared by the conventional solidification process. It should be noted that the measuring area must be large enough to represent the entire solidification microstructure for the application of RS approach to quantify the microsegregation. The compositions from all of the sampling points are sorted, and continuous solute profiles can then be obtained with respect to the solid fraction (f_s) formed during solidification. Various sorting schemes for the RS approach have been proposed, and a detailed description of these sorting schemes can be found in Reference [6]. The partition coefficient of each solute element can be determined by fitting the solute profile with a Scheil-type equation [23] from the sorted data.

Although several experimental techniques have been implemented to quantify the microsegregation during the solidification of Ni-base superalloys, few comparative works have been reported on any differences in the elemental partitioning behavior determined by different experimental techniques. Therefore, in the present work, the methodological effect on the quantification of microsegregation was investigated in detail for the advanced SC Ni-base superalloy CMSX-10. Three representative experimental techniques, namely, MZQ, PDSQ, and RS, were implemented for the analyses of the microsegregation tendency and the magnitude of solute elements. Particular attention was paid to clarifying the microsegregation behavior of Cr and Mo, whose segregation direction is still subject to debate [4,6].

2. Experimental Details

2.1. Materials and DSC Measurements

The CMSX-10 master ingot used in the present work was provided by Cannon-Muskegon Co. (heat no. 3V2038). The chemical composition of this alloy is listed in Table 1. To analyze the thermo-physical properties of CMSX-10, differential scanning calorimetry (DSC) was carried out using a Netzsch model DSC 404C instrument. Prior to the experiment, the thermocouple of the DSC instrument was calibrated at a scanning rate of 10 °C/min with the melting point of high-purity Ni (99.99%) and Au (99.9999%). By performing DSC runs of one heating and cooling cycle, several important phase transformation temperatures, including the liquidus (T_l), solidus (T_s), primary γ formation ($T\gamma$) from liquid, and end of solidification (T_f) temperatures, were determined by analyzing the corresponding thermograms.

2.2. Sample Preparation and Analysis Method

To quantify the microsegregation of solute elements during the solidification of CMSX-10, specimens for compositional measurement were prepared by (1) quenching the specimen after maintaining it at the temperature at which the liquid and solid co-exist, (2) quenching the specimen at the designated solid fraction during planar directional solidification, and (3) conventional directional solidification with the dendritic S/L interface.

The mushy zone quenching (MZQ) specimen was prepared using a vertical tube furnace, as described elsewhere [2]. Approximately 30 g of the alloy sample was placed in a mullite crucible and remelted by heating to 1500 °C under a purged Ar gas atmosphere. After holding at this temperature

Table 1 – Chemical composition of CMSX-10 alloy (wt.%).

	Co	Cr	Mo	W	Al	Ti	Ta	Hf	Nb	Re	Ni
CMSX-10	3.2	2.2	0.39	5.5	5.72	0.23	8.3	0.04	0.1	6.3	Bal.