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HOMOGENIZATION DURING SOLUTION HEAT TREATMENT OF NI-BASE SINGLE-CRYSTAL SUPERALLOY TMS-238

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ABSTRACT

To maximize the mechanical properties of Ni-base superalloys, solution heat treatment is essential to sufficiently homogenize the dendritic segregations formed during solidification. To investigate the homogenization behavior during solution heat treatment, a Ni-base single crystal superalloy, TMS-238, was heat treated under various conditions; temperatures ranging from 1573 to 1613 K for times ranging from 2 to 100 h. After solution heat treatment, the average concentrations of Re, an element that exhibits the highest degree of segregation, in dendrite core and inter-dendritic regions were analyzed. From these results, apparent diffusion constants, D_{app}, were determined based on a proposed homogenization model. Obtained D_{app} values were significantly smaller than the diffusion constant of Re in Ni, strongly suggesting that the apparent diffusion coefficients should be obtained experimentally when using the target alloy.

INTRODUCTION

Ni-base single-crystal superalloys with γ-γ′ two phases are used in turbine blades for jet engine applications, due to their excellent high-temperature mechanical properties and oxidation resistance. Especially, the latest 6th generation Ni-base single crystal superalloy, TMS-238 [1], which exhibits excellent properties, could be an attractive candidate alloy for next generation jet engine applications. To maximize their properties, solution heat treatment is essential to sufficiently homogenize the dendritic segregations of alloying elements that form during solidification [2-3]. However, the latest superalloys are multi-component alloys containing 10 or more elements, which include heavy elements with low diffusion coefficients, such as Re, Ru, and Ta. Thus, homogenization heat treatment tends to require higher temperatures, longer times, and more complicated heat treatment schedules, which are factors that increase the process costs. For example, a Ni-base single-crystal superalloy, CMSX-4, which contains 3.0 wt.% Re, requires an 8-step solution heat treatment to avoid partial melting and a final heat treatment at maximum temperature of 1594 K or higher for 2 h or more [3]. Furthermore, the optimal condition could vary depending on the degree of microsegregation, which varies with casting conditions. Therefore, there is a need to explore low-cost solution heat treatment conditions, in another words, heat treatment at lower temperatures and shorter holding times, that can maintain the mechanical properties.

The aim of this study is to explore the low-cost solution heat-treatment conditions suitable for TMS-238, which was conducted by investigating the dependence of solution temperature and time on element concentration of dendrite core and inter-dendrite regions. Further, the applicability of homogenization model proposed by Tanzilli *et. al.*[4] to the homogenization behavior in TMS-238 will be discussed. The model predicts homogenization by diffusion of sine functional segregation and was demonstrated to be applicable to the homogenization behaviors of dendritic segregations between secondary arms for Cu alloy [5], steel [6], and some Ni-base superalloys [7]. Using the investigated Re concentration, the apparent diffusion coefficients of the element (D_{app}) in the previously reported homogenization model were experimentally determined, since the D_{app} for multi-component alloy is an unknown parameter. Based on this, the homogenization behaviors for various solution heat treatment conditions for TMS-238 will be discussed.

EXPERIMENTAL PROCEDURE

Ni-base single crystal superalloy, TMS-238, was used in this study. Table 1 shows the nominal composition of TMS-238 and analyzed composition of the alloy used as specimens. Analyzed compositions in at.% are also shown.

Table 1: The nominal and analyzed compositions of TMS-238 (Ni bal.)

	Co	Cr	Mo	W	Al	Ta	Hf	Re	Ru
Nominal /wt.% [1]	6.5	4.6	1.1	4.0	5.9	7.6	0.1	6.4	5.0
ICP-OES /wt.%	6.48	4.57	1.11	3.97	5.88	7.47	0.10	6.50	4.99
ICP-OES /at.%	6.96	5.57	0.73	1.37	13.79	2.61	0.03	2.21	3.13

In directional solidification furnace, alloying elements were melted in an Al_2O_3 crucible at 1873 K in vacuum with the pressure under 6×10^{-2} Pa. After keeping the melt inside the crucible at 1873 K for 5 min, the melt was poured into the mold and held for 10 min. Then, the stage with the mold was lowered from the heating area to the cooling area at 200 mm/h, and eight ϕ11 mm single crystal bars were cast. The mold had a selector and a filter so that single-crystal alloys could be cast without any contamination.

The specimens (diameter: 11 mm and length: 5 mm) were cut from the single-crystal bar and sealed individually in a quartz tube with Ar gas to prevent oxidation during solution heat treatment. Solution heat treatments were conducted at 1573, 1593, and 1613 K for 2 - 100 h. The heat treatment was conducted as follows; first, 3 specimens were inserted into muffle furnace at temperatures 40 K lower than the objective temperatures, to prevent overshooting after the specimens are inserted. Then, temperatures of the furnace were raised to the objective temperature in 4 min. Afterwards, the specimens were quickly removed from the furnace and quenched in water. After solution heat treatment, as-cast and heat-treated specimens were cut into semi-cylindrical shape and embedded in resin so that the semicircle side (horizontal section) and the cut surface (vertical section) could be analyzed. Yokokawa et al. [2] reported that the segregation of Re was most severe out of all the alloying elements in TMS-238, and that its homogenization rate was the smallest. For this reason, the concentration of Re was used as representative value of homogenization in this study.

Re concentrations at the dendrite core ($C_d(t)$) and in inter-dendritic region ($C_{id}(t)$) at a solution heat treatment time t were obtained by electron probe microanalyzer (EPMA, SHIMADZU EPMA-1610) for each specimen. First, five dendrite cores and five inter-dendrite regions were analyzed. In each area, five points were measured, resulting in the total of 25 analyzed points for both dendrite core and inter-dendrite regions. The average Re concentration of 25 points in dendrite core was used to determine $C_d(t)$, while the average Re concentration of 25 points in inter-dendrite region was used to determine $C_{id}(t)$. The concentrations of both the as-cast and heat-treated specimens were analyzed using this method. For the secondary dendrite arm spacing, 50 points were measured on vertical section of the as-cast specimen, and the average of these results was used.

RESULTS

Figure 1 shows the back-scattered electron (BSE) images after homogenization in solution heat treatment at 1593 K. The value $C_d(t)$ was obtained from the center of dendrite core and $C_{id}(t)$ was obtained from the inter-dendritic region, as shown in the as-cast image (Fig. 1(a)). During solidification, γ phases form in TMS-238, followed by the precipitation of γ′phases. However, due to eutectic solidification, coarse γ′ phases form in TMS-238 during solidification. For simplicity, diffusion was considered only in the γ phases for this study.

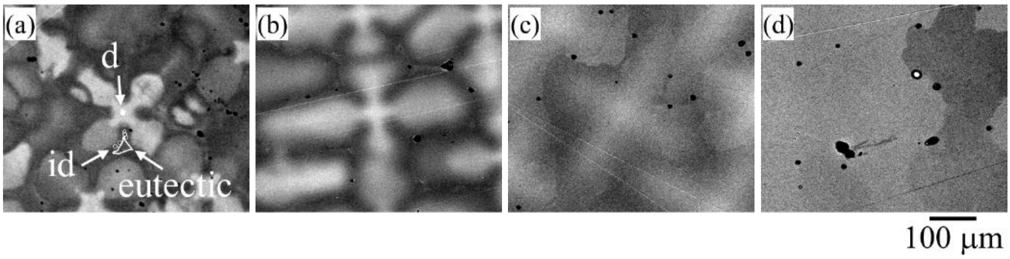

Figure 1: BSE images of horizontal section before and after various stages of homogenization: (a) as-cast specimen, specimens heat treated at 1593 K for (b)2 h, (c) 20 h, and (d) 100 h.

Results obtained from the as-cast specimen, where the solution heat treatment time t = 0, showed that $C_d^0(=C_d(0))$ =3.97 at.% , while $C_{id}^0(=C_{id}(0))$ = 1.23 at.%, respectively. Figure 2 shows the results of the EPMA analysis for C_d(t), shown as a solid line and filled-in plots, and C_{id}(t), shown as dotted lines and outlined plots, in each heat treatment condition. In Fig. 2, blue lines and plots represent the data at 1573 K, while the black represent 1593 K, and the red represent 1613 K. Re enriched in dendritic region, and approached the average concentration of 2.21 at.% (see table 1), with longer homogenization time. The rate in which the concentration of Re approached the average line had increased with higher heat treatment temperatures.

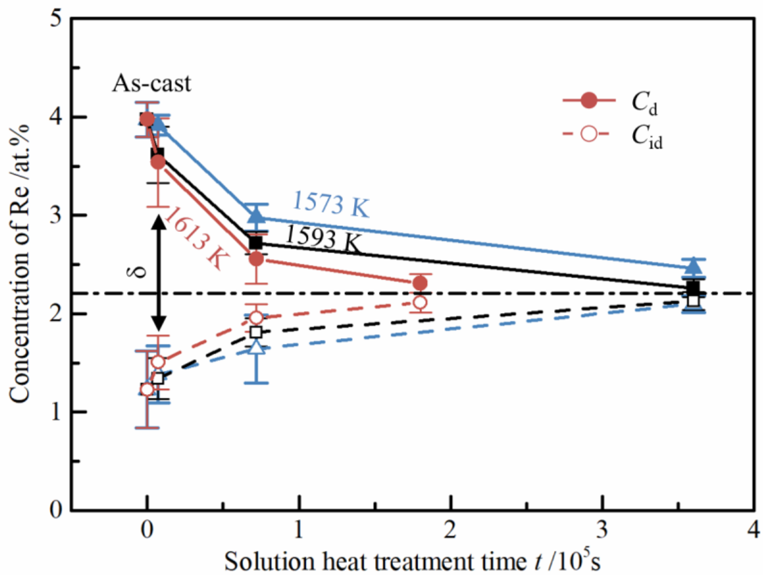

Figure 2 The solution heat treatment time dependence of (a) $C_d(t)$ (b)$C_{id}(t)$ for each testing temperature. The definition of residual segregation index δ is shown in a black arrow.

DISCUSSION

Homogenization behavior of element segregation can be estimated with the initial segregation condition and the diffusion coefficient as illustrated in Fig. 3(a) [4] . Further, a degree of element segregation is expressed as residual segregation index δ defined by Kattamis et al. [8], and its time and temperature dependence are as show below;

$$\delta=\frac{C_d(t)-C_{id}(t)}{C_d^0-C_{id}^0}=\exp\left\{-\frac{4\pi^2}{\lambda_2{}^2}D_{app}t\right\} \quad (1) \text{ and}$$

$$D_{app}=D_{app}^o\exp\left(-\frac{Q_{app}}{RT}\right) \quad (2).$$

Here, D_{app} is an apparent diffusion coefficient, λ_2 is secondary dendrite arm spacing (μm), D_{app}^o is apparent frequency factor (m^2/s), Q_{app} is an apparent activation energy (kJ/mol), R is the gas constant (8.31 J/(molK)) and t is time (s). Thus, in this study, the obtained C_d(t) and C_{id}(t) of Re were analyzed based on the model. Here, the secondary dendrite arm spacings in as-cast TMS-238 were observed by the BSE shown in Fig. 3(b), which was measured as λ_2= 46.3 ± 10.6 μm. Further, this model is usually applied for homogenization between secondary arms of the dendrites. However, it is difficult to analyze the most Re-rich point in the secondary dendrite arm, since the most enriched locations may not appear in the analyzed surface. Therefore, in this study, the homogenization behavior of TMS-238 was analyzed by using the concentration obtained from the primary dendrite core, where the most Re-rich point can be measured with certainty.

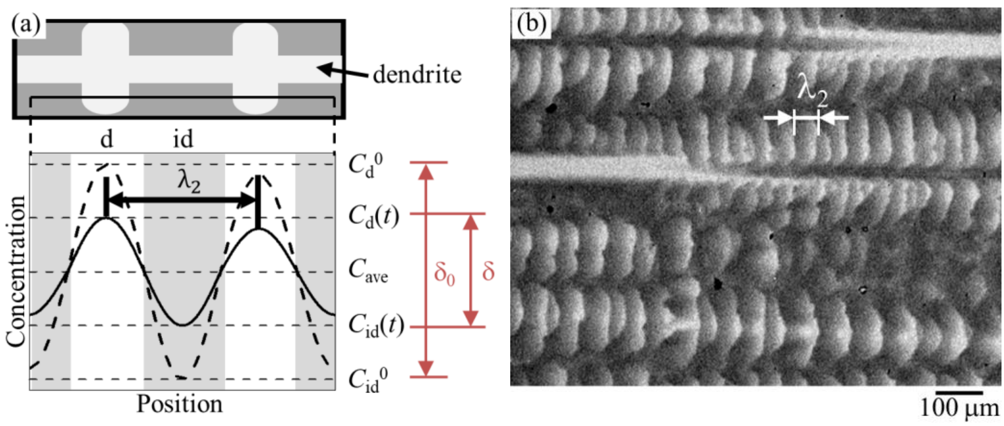

Figure 3: (a) Schematic diagram depicting the changes in dendritic and inter-dendritic concentrations of elements in the homogenization model and (b) BSE image of vertical section of the as-cast specimen.

The influence of time on obtained δ according to Eq. 1 is shown in Fig. 4 (a). In Fig. 4 (a), δ = 1 is the as-cast condition, while δ =4.74×10^{-2} is heat treated at 1593 K for 100 h, which is the most homogenized specimen. Meanwhile, the dotted lines were obtained using weighted least squares fitting. For all temperatures, the values of δ quickly approaches 0 at the beginning of the heat treatment, however, slows down as time goes on..
If the natural logarithm of δ is taken in Eq. 1, then the obtained lnδ exhibits a liner relation with solution heat treatment time, t, as shown in Eq. 3.

$$\ln\delta=-\frac{4\pi^2}{\lambda_2{}^2}D_{app}^o\exp\left(-\frac{Q_{app}}{RT}\right)t \quad (3)$$

Using this equation, the time dependence of ln*δ* is shown in Fig. 4 (b). The obtained ln*δ* shows a linear relation with solution heat treatment time, t, as expected. As shown in the Fig. 4(b), time gradient of ln*δ* increases with heat treatment temperature. Further, the time gradient of ln*δ* for each homogenization temperature, dln*δ*/d*t* (Eq. 4), were determined from the slopes of dotted lines obtained using weighted least squares fitting.

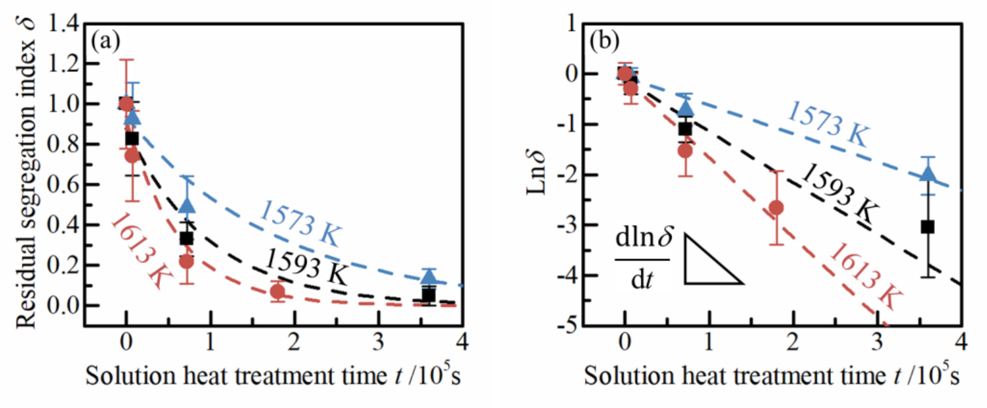

Figure 4: The solution heat treatment time dependence of (a) residual segregation index δ (b)lnδ for each testing temperature

$$\frac{\mathrm{d}}{\mathrm{dt}}\ln\delta=-\frac{4\pi^2}{\lambda_2{}^2}D^{\mathrm{o}}_{\mathrm{app}}\exp\left(-\frac{Q_{\mathrm{app}}}{\mathrm{R}T}\right) \tag{4}$$

By taking the natural logarithm of dln*δ*/d*t* in Eq.4, the obtained ln(dln*δ*/d*t*) will exhibit a liner relation with the reciprocal of solution heat treatment temperature, 1/*T*, which can be written out as the following Arrhenius-type equation:

$$\ln\left(-\frac{\mathrm{d}\ln\delta}{\mathrm{d}t}\right)=\ln\left(\frac{4\pi^2}{\lambda_2{}^2}D^{\mathrm{o}}_{\mathrm{app}}\right)-\frac{Q_{\mathrm{app}}}{\mathrm{R}T} \tag{5}$$

Figure 5(a) shows the temperature dependence of the natural logarithm of -dln*δ*/d*t*. The dotted line in Fig. 5(a) is obtained using weighted least squares fitting. As expected from Eq. 5, ln(-dln*δ*/d*t*) showed a linear relation with the reciprocal of heat treatment temperature, 1/*T*. Meanwhile, the slope and intercept of the fitted line correspond to $-Q_{app}$/R and $4\pi^2 D^{\mathrm{o}}_{\mathrm{app}}/\lambda_2{}^2$, respectively, based on Eq. 5. Thus, the apparent activation energy Q_{app} and the apparent frequency factor $D^{\mathrm{o}}_{\mathrm{app}}$ of Re diffusion in TMS-238 can be determined from the values of slope and intercept, respectively, by substituting the values of R and l_2. As a result, in this study we can determine the values as follows; Q_{app}=549.5±164.8 (kJ/mol) and $D^{\mathrm{o}}_{\mathrm{app}}$ = $5.57\times10^2\pm6.95\times10^3$ (m^2/s).

To compare the Re diffusion in TMS-238 with Re diffusion in Ni, the D_{app} in TMS-238 calculated from Q_{app} and $D^{\mathrm{o}}_{\mathrm{app}}$ was replotted in Fig. 5(b). Meanwhile, reported coefficients of Re in Ni [9], are also plotted as a blue dotted line. As shown in Fig. 5(b), the calculated D_{app} values are significantly smaller than the diffusion coefficients of Re in Ni. Even though direct comparison of D_{app} and the diffusion coefficients of Re in Ni are inadequate, the large difference strongly suggests that the apparent diffusion coefficients should be obtained experimentally for multi-component alloys like TMS-238.

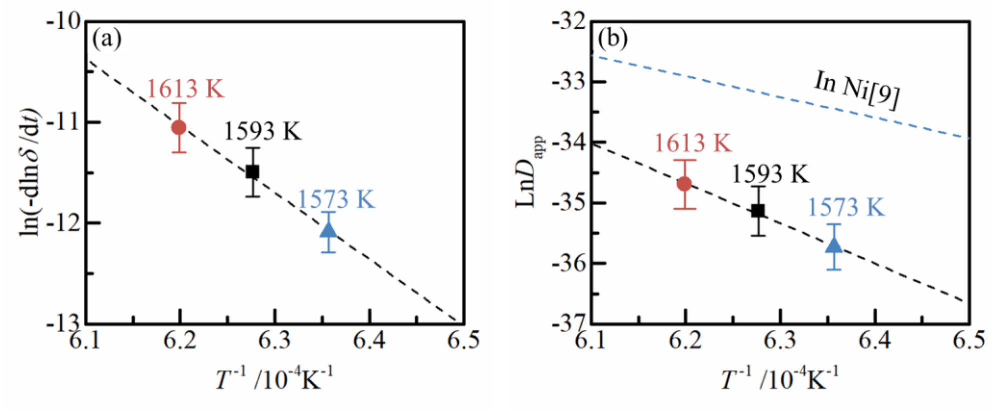

Figure 5: Comparison of solution heat treatment temperature dependence of (a) ln(-dlnδ/dt) and (b) apparent diffusion coefficients

By substituting the D_{app} obtained here into Eq. 1 and Eq. 2, the residual segregation index δ during homogenization of TMS-238 with various l_2 can be estimated. This will be useful to explore the low-cost process condition without much degradation of mechanical properties. Yokokawa *et al.* [2] reported that homogenization of TMS-238 prepared by the same casting process can be fully achieved by solution heat treatment at 1608 K for 20 h. When calculating δ under this condition using Eq. 1 and Eq. 2, δ for the acceptable degree of segregation is 0.35. To achieve this homogeneity, for example, solution heat treatment at low temperatures such as at 1523 K would take about 204 h, while at high temperatures such as 1623 K would take about 14 h. However, it is necessary to determine the heat treatment conditions by taking into consideration other factors such as the possibility of being outside the single-phase region at low temperatures, and partial melting due to segregation at high temperatures.

CONCLUSIONS

Aiming to explore the low-cost solution heat treatment conditions suitable for TMS-238, the dependence of solution heat treatment temperature and time on element concentration of dendrite core and inter-dendrite area were investigated. Further, the applicability of the proposed homogenization model to the homogenization behavior in TMS-238 has been discussed. The following has been made clear:

(1) Based on proposed homogenization model, apparent diffusion coefficients of Re in TMS-238 were experimentally obtained from concentrations of Re after heat treatment. That value was significantly lower than the diffusion coefficient of Re in Ni. Therefore, it is necessary to experimentally determine the apparent diffusion coefficient for estimating the degree of homogenization δ for multi-component alloys.

(2) Using the obtained apparent diffusion coefficients, it can be estimated that to fully homogenize the alloy, solution heat treatment is required for 204 h at 1523 K, or 14 h at 1623 K.

In future works, the effects of eutectic γ' phases and partial melting will be considered, to conduct a more precise prediction of the homogenization behavior for Ni-base single crystal superalloys.

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