Solidification Process and Behavior of Alloying Elements in Ni-Based Superalloy Inconel718*1

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The thermal and metallographic analysis of Inconel718 alloy revealed that the solidification proceeds in the order of primary γ at 1615 K, (γ + NbC) eutectic at 1561 K, and (γ + Ni3Nb) eutectic at 1452 K. Additional equilibrium evaluation performed using Thermo-Calc predicts the following solidification sequences: primary γ at 1633 K, followed by (γ + NbC) eutectic at 1555 K. The (γ + Ni3Nb) phase does not appear in the equilibrium calculation, indicating that the (γ + Ni3Nb) phase crystallizes as a non-equilibrium eutectic phase. The partition coefficients of alloying elements in the primary γ and eutectic phases were also determined experimentally (k(T-C)) and compared with the values calculated using Thermo-Calc (k(T,C)). The behaviors of alloying elements during solidification were estimated using k(T,C) in various solidification models. It was found that the results of the experiments are in agreement with the calculations obtained using the Clyne-Kurz model.

1. Introduction

Ni-based superalloy Inconel718[2, 1] 718 exhibits superior corrosion and oxidation resistance in addition to good creep and fatigue properties at moderate temperatures. However, it is highly susceptible to hot cracking in the heat affected zone (HAZ) during arc welding.[3] This micro-fissuring could be attributed to its coarse grain structure and an increased presence of low-melting-point phases that are the result of heavy inter-dendritic segregation.[3, 2] The elucidation of the behavior of alloying elements during the solidification of Inconel718 is vital to control both its structure and properties and thus enhance the weldability of this alloy.

Moreover, the thermodynamic software, Thermo-Calc,[5] enables us to make predictions regarding the phase behavior of multi-component alloys through calculations of the phase diagrams (CALPHAD). This method of analyses is based on the thermodynamic database. However, with regard to the highly alloyed multi-component materials, particularly Ni-based superalloys, little is known about the accuracy and validity of the estimated results using the Thermo-Calc in terms of the behavior of alloying elements and its application to non-equilibrium solidification.

The main purpose of this study is to investigate the accuracy of the estimated results (i.e., solidification sequence, partition coefficient, and phase diagram) using Thermo-Calc against the experimentally determined ones. First, in order to elucidate the behavior of the alloying elements of Inconel718, the thermal and microstructure analyses were performed on a series of alloy specimens quenched during solidification, and the partition coefficients of the alloying elements between the liquid and the primary γ as well as between the liquid and the eutectic phase were determined experimentally (k(Exp)). The values hence obtained were compared with the calculated values using Thermo-Calc (k(T,C)). The behaviors of the alloying elements during solidification were estimated by using k(T,C) in Scheil’s model (except for C in the equilibrium model).

2. Experimental Procedure

The chemical composition of Inconel718 is shown in Table 1.[5]

Using 30 g specimens, the samples were melted in a siliconit furnace by heating them to 1700 K under a pure Ar atmosphere. They were kept at 1700 K for 600 s and then cooled at 0.16 K/s through the solidification temperature range. The specimens were then polished with diamond paste and electro-etched in 10% oxalic acid. The microstructure was observed by light optical microscopy, and the chemical composition of alloying elements for each phase was quantitatively measured using an electron probe micro analyzer (EPMA).

Moreover, the equilibrium partition coefficients of the alloying elements in the primary γ phase were determined by using specimens held for 3.6 ks at the beginning of solidification and were calculated using Thermo-Calc. The behaviors of the alloying elements in the liquid phase during solidification were estimated using several models. The equilibrium phase diagram was calculated by using the Thermotech Ni superalloy Database 11 of Thermo-Calc and the calculated result was compared with the experimental one.

Table 1 Chemical composition (mass%).[5]

<table>
<thead>
<tr>
<th></th>
<th>Ni</th>
<th>Cr</th>
<th>Fe</th>
<th>Ct(Nb)</th>
<th>Mo</th>
<th>Ti</th>
<th>Al</th>
<th>C</th>
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<tr>
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<td>0.002</td>
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<td>0.01</td>
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<td></td>
<td>&lt;0.01</td>
</tr>
<tr>
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</table>

*1This Paper was Originally Published in Japanese in J. Japan Inst. Metals 67 (2003) 675–680.
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Results and Discussion

3.1 Solidification sequence of Inconel718

A carbide and a Ni$_2$Nb intermetallic phase solidify in the inter-dendritic spaces. The composition and microstructure of each phase are shown in Fig. 1. Phase(I) crystallized as MC and contains 76.5 mass% Nb, 12.4 mass% C, and 8.13 mass% Ti; and phase(II) crystallized as Ni$_2$Nb and contains 39.2 mass% Ni, 28.1 mass% Nb, 13.8 mass% Cr, and 11.3 mass% Fe.

Three phase transformations were observed during cooling as shown in Fig. 2: primary $\gamma$ at 1615 K, followed by ($\gamma +$ NbC) eutectic at 1561 K, and finally ($\gamma +$ Ni$_2$Nb) eutectic at 1452 K.

On the other hand, Thermo-Calc evaluation shows the following equilibrium solidification sequences: primary $\gamma$ at 1633 K, followed by ($\gamma +$ NbC) eutectic at 1555 K, as shown in Fig. 3. The ($\gamma +$ Ni$_2$Nb) eutectic phase cannot be seen in the equilibrium calculation, indicating that the ($\gamma +$ Ni$_2$Nb) phase crystallizes as a non-equilibrium eutectic phase.
3.2 Behavior of alloying elements during solidification

The behavior of the alloying elements during solidification is determined by the partition coefficient at the interface between the liquid and solid phases. The specimens weighing 30 g were remelted in a 99.99% Ar atmosphere at approximately 100 K above the liquidus and were then cooled to just below liquidus. Following this, they were held for 3.6 ks and quenched in water.

The alloying contents in the dendrite γ and liquid phase just before quenching were measured by EPMA, and the partition coefficients of the alloying elements (k) were determined by the ratio of the composition in the γ phase (Cγ) to the one in the liquid phase (CL). The microstructure of the quenched specimen was composed of the coarsened primary γ dendrite and the mixture of fine dendrites and eutectic phases. Since the line analysis barely revealed microsegregation in the intra-dendritic region in comparison to that in the inter-dendritic region (rapid solidification structure), the average alloying contents of the primary γ were analyzed with a finely focused beam at several dendrites cores and those of quenched liquid were measured by a scanning electron beam at several regions.6)

The partition coefficients of alloying elements in eutectic carbide (kE/NbC) and γ (kγ/γ) were determined by CE/NbC/CE/L and CE/γ/CE/L, respectively, by the same method.

By using Thermo-Calc, the equilibrium partition coefficients of the alloying elements in the primary γ and eutectic phase were evaluated.

The experimental equilibrium partition coefficients of the alloying elements in the primary γ phase are shown in Table 2, which were compared to the values calculated by Thermo-Calc. No significant difference was observed between the calculated and experimental k values. Ni, Cr, and Fe values were larger than unity and are consequently distributed in the solid phase. On the other hand, Nb, Mo, Ti, Al, and C are segregated in the liquid phase. EPMA analysis gives C concentration is much larger than expected one because of the contamination caused by the EPMA electron beam. Therefore, the partition coefficient calculated by Thermo-Calc was applied to the following calculations for C.

The experimental partition coefficients of the alloying elements in the (γ + NbC) eutectic phase were calculated by the following equation, using the specimen quenched just below the beginning of the (γ + NbC) solidification, which are shown in Table 3.

\[
k_E = f_E/k_E + f_E/NbC k_{E/NbC}
\]

where, kE is the partition coefficient of the (γ + NbC) eutectic phase, fE/γ is the fraction of the eutectic γ phase in the (γ + NbC) eutectic phase (0.93), kE/γ is the partition coefficient of the eutectic γ phase, fE/NbC is the fraction of the eutectic NbC phase in the (γ + NbC) eutectic phase (0.07), and kE/NbC is the partition coefficient of the eutectic NbC phase. These values are close to the ones obtained using Thermo-Calc.

Moreover, the variation in concentrations of the residual liquid during solidification was calculated by using the experimental partition coefficients with Scheil’s solidification equation (eq. (2)).7) This equation is used with the assumption that the alloying contents are homogeneous in the residual liquid, and that there is no back-diffusion in the solid phase.

\[
C_L = C_{L0}(1 - f_s)^{N-1}
\]

(The equilibrium equation and kT/C were applied for the estimation of the concentration of C that completely diffuses in the solid).

Where CL is the alloy composition in residual liquid (mass%), CL0 is the initial alloy composition (mass%), fS is the fraction of the solid phase, and k is the partition coefficient in the primary γ or (γ + NbC) eutectic phase.

The changes in alloying contents were calculated by using the experimental partition coefficients, which were assumed to be constant values during solidification aimed at easy calculation, and are shown in Fig. 4 with the experimental concentrations at fS = 0.71 and fS = 0.92 measured by EPMA analysis. Regarding Nb concentration, when it reached a value of approximately 12 mass% at fS = 0.71, (γ + NbC) eutectic solidification began. Since the partition

<table>
<thead>
<tr>
<th>Table 2</th>
<th>Partition coefficient of alloying element in the primary γ phase.</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(N/γ)(mass%)</td>
<td>Ni</td>
</tr>
<tr>
<td>C(N/γ)(mass%)</td>
<td>51.7</td>
</tr>
<tr>
<td>C(N/γ)(mass%)</td>
<td>50.2</td>
</tr>
<tr>
<td>kE(Exp)</td>
<td>1.03</td>
</tr>
<tr>
<td>kE(T/C)</td>
<td>1.02</td>
</tr>
</tbody>
</table>

Fig. 4 The changes estimated using kE(Exp) of the alloying elements in residual liquid during the solidification of Inconel718.
coefficient of Nb was 0.61 for eutectic solidification, Nb concentration shows a higher increase to approximately 20 mass% at $f_s = 0.92$. The calculated plots and the experimental data for both of the alloying contents and the fraction of each solid phase are in agreement.

To investigate the effect of the variation of the partition coefficient, $k_{NP}$, was changed continuously with the changes in alloying contents in the liquid phase during solidification. In the case of the partition coefficient of primary $\gamma$ calculated using Thermo-Calc, it changed from an initial value of 0.20 just after the beginning of solidification to 0.25 just before the ($\gamma$ + NbC) eutectic crystallization. The change in Nb concentration estimated using variable $k_{NP}$ was almost the same as that calculated by using constant $k$. (just as shown in Fig. 4.

In order to evaluate the influence of diffusion in a freezing crystal on the redistribution of alloying elements during solidification, Brody-Flemings\(^8\) and Clyne-Kurz\(^9\) models were applied on back-diffusion in solids as follows:

$$C_L = C_{L0} [1 - (1 - Bk)t_s]^{k-1}/C_{13}$$  \hspace{0.5cm} (3)

$$\alpha = 4D_tD_s/\lambda_2^2$$  \hspace{0.5cm} (4)

where, $D_s$ is the diffusion coefficient in solid (m\(^2\)/s), $t_s$ is the local solidification time (s), and $\lambda_2$ is the secondary dendrite arm spacing (m).

The diffusion coefficient was expressed as Arrhenius’ equation as follows:

$$D_s = D_0 \exp(-Q/RT)$$  \hspace{0.5cm} (5)

where, $D_0$ is the diffusion constant (m\(^2\)/s), $Q$ is the molar activation energy (J/mol), $R$ is the molar gas constant (8.31 J/(mol·K)), and $T$ is the absolute temperature (K).

In this study, $t_s = 1011$ s, $\lambda_2 = 62.9 \times 10^{-6}$ m. For eq. (3), $B = 0$ in the Scheil model, $B = 2\alpha$ in the Brody-Flemings model, $B = 2\alpha(1 - \exp(-1/\alpha)) - \exp(-1/2\alpha)$ in the Clyne-Kurz model, and $B = 1$ in the equilibrium model. When $D_0^{(NB)} = 5.6 \times 10^{-4}$ (m\(^2\)/s) and $Q = 28.6 \times 10^4$ (1433~1616 K) (J/mol)\(^{11}\) are selected for the distribution of Nb in $\gamma$-Fe, for example at the melting point, $\alpha$(Nb) = 0.32 could be calculated by using eqs. (4) and (5).

When $D_0^{(C)} = 1.2 \times 10^{-5}$ (m\(^2\)/s) and $Q = 14.2 \times 10^4$ (873~1673 K) (J/mol)\(^{11}\) are chosen for the distribution of C in Ni for example, $\alpha$(C) = 313.21 at the melting point. The changes in Nb and C concentrations were calculated using these data, under the assumption that these are constant in the temperature interval from 1561 to 1615 K. The results are shown in Fig. 5 and Fig. 6. The experimental Nb concentration is in agreement with the results calculated by using the Scheil, Brody-Flemings, and Clyne-Kurz models, and this result shows that the diffusion of Nb in primary $\gamma$ is very limited.

On the other hand, for the behavior of C, there is an agreement between the results calculated by the Clyne-Kurz and equilibrium models. Here, the measurements of C were much higher than expected ones because of the contaminations in the electron beam of EPMA; hence, these results are not seen in Fig. 6. The Brody-Flemings model shows that it is impossible to obtain a value that is in agreement with the experimental result when $\alpha$ is larger than 0.5. To solve this problem, Clyne-Kurz subsequently developed their modified model\(^9\) as a first approximation, which can be used for the evaluation when $\alpha$ is larger than 0.5. Since $\alpha$(C) = 313.21, this model is applicable to this case.

### 3.3 Validation of the solidification diagram by Thermo-Calc

To validate the calculation by Thermo-Calc, the changes in the alloying contents were calculated using calculated partition coefficients and are shown in Fig. 7 with the experiments. As can be seen in Tables 2 and 3, the experimental and calculated partition coefficient values are similar. Thus, the behavior of the alloying elements calculated using $k_{(T-C)}$ also does not differ widely from the measurements.

The changes in Nb and C concentrations on the pseudoternary liquidus surface diagram calculated using Thermo-Calc are shown in Fig. 8, where the behaviors of Nb and C influence the crystallization process of the secondary phases.

Moreover, specimens with these compositions were systematically altered from 4.88 to 20.0 mass% of Nb and from 0.06 to 0.50 mass% of C. The microstructures, thus produced, were investigated to clarify which phase is the first to crystallize, as shown in Fig. 8. Specimen No. 2, containing...
9.81 mass% of Nb and 0.13 mass% of C shows that primary NbC crystallizes in a plate shape at the middle of the γ dendrite. The (γ + NbC) eutectic line that depends on the existence of primary NbC can be seen as a broken line in Fig. 8 and it is also close to that of the calculated one by Thermo-Calc, except that it is on the lower side of the C concentration.

In this diagram, the changes of alloying contents calculated by using the calculated partition coefficients shown in Fig. 7 are plotted using the dashed and a dotted line. As soon as the primary γ crystallization was completed, the solidification of the (γ + NbC) eutectic phase began at 10.11 mass% Nb and 0.12 mass% C. The concentration of Nb increased and that of C decreased with the progress of eutectic solidification until the completion of solidification. In fact, since microsegregation can be seen during solidification, the Nb concentration in the liquid increases to a higher value at the end of solidification; therefore, (γ + Ni2Nb) eutectic crystallizes as a non-equilibrium phase.

As a result, especially during the final solidification
process, there exists a large difference between the equilibrium diagram calculated by Thermo-Calc and the experimental one for this kind of alloy. This is because the diagram calculated by Thermo-Calc is for the initial composition of this alloy, even though the alloying contents may change with the progress of solidification. As can be seen by the dashed and two-dot line in Fig. 8, the diagram for the composition at the end of primary γ crystallization was calculated by Thermo-Calc and, following this, the (γ + NbC) eutectic line shifted to the lower Nb side. The effect of some elements and microsegregation should be taken into account for the estimation of the overall solidification process in this alloy.

4. Conclusions

The analysis of the solidification process was carried out to study the behavior of the alloying elements of Inconel718, and the results were then evaluated using the Thermo-Calc software. The following conclusions were obtained.

1) The solidification sequence of Inconel718 shows the primary γ at 1615 K, followed by (γ + NbC) eutectic at 1561 K, and finally (γ + Ni$_2$Nb) eutectic at 1452 K. On the other hand, the Thermo-Calc evaluation shows the primary γ at 1633 K, followed by the (γ + NbC) eutectic at 1555 K.

2) The experimental partition coefficients of primary γ and (γ + NbC) eutectic of alloying elements are not significantly different from the calculated ones.

3) The experimental and calculated partition coefficients in the Clyne-Kurz solidification model provide a good description the behavior of alloying elements during solidification.

4) There exists a small difference between the (γ + NbC) eutectic line on the equilibrium diagram by Thermo-Calc and the one on the experimental diagram. The behavior of alloying elements in this alloy during solidification can be estimated by using the pseudobinary liquidus surface diagram calculated using Thermo-Calc.

5) The (γ + Ni$_2$Nb) eutectic was not identified on the equilibrium diagram calculated by Thermo-Calc, because (γ + Ni$_2$Nb) eutectic crystallizes as a non-equilibrium phase. The effect of some elements and microsegregation should be taken into account for the estimation of the overall solidification process in this alloy.

Acknowledgements

This research was supported by the Japan Aerospace Exploration Agency. The authors would also like to thank Dr. D. M. Stefanescu and Dr. F. R. Juretzko (Department of Metallurgical & Materials Engineering, University of Alabama, U.S.A.) for their helpful discussions on this paper.

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5) Ishikawajima Precision Castings Co., Ltd.
12) Inconel is a trademark of INCO Alloys International, Inc., Huntington, WV.