Influence of Al on Kinetics of Discontinuous Precipitation in Ni–38Cr Alloy

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The influence of Al on the kinetics of discontinuous precipitation in the Ni–Cr system was experimentally examined using ternary Ni–38Cr–Al alloys with Al concentrations of 3.8 mass% and 4.2 mass%. The ternary alloys were homogenized at 1 473 K for 16 h, solution treated at 1 473–1 493 K for 30 min, and then isothermally annealed in the temperature range of 773–1 073 K for various times up to 50 h. Due to the solution heat treatment, both ternary alloys show the polycrystalline single-phase microstructure of the Ni-rich solid-solution (γ) phase with the face-centered cubic structure. In the early stages of isothermal annealing, however, fine particles of the Ni3Al (γ') phase with the L12 structure are formed in the γ matrix by continuous precipitation. On the other hand, the cell of the lamellar microstructure consisting of the γ phase and the Cr-rich solid-solution (α) phase with the body-centered cubic structure is formed along the grain boundary of the γ matrix and then grows into the γ matrix. The fine particles of the γ' phase are dispersed also in the γ phase of the cell. The migration distance of the moving cell boundary is proportional to the annealing time. Thus, the growth rate of the cell is constant independent of the annealing time. The growth rate and the interlamellar spacing of the cell monotonically increase with increasing annealing temperature. A kinetic model was used to analyze quantitatively the relationship between the growth rate and the interlamellar spacing. Although the discontinuous precipitation in the ternary Ni–38Cr–Al alloys occurs in a complicated manner, the analysis indicates that the growth of the lamellar cell is controlled by the boundary diffusion of Cr along the moving cell boundary.

KEY WORDS: Ni-base super alloy; discontinuous precipitation; boundary diffusion; kinetics; cellular reaction.

1. Introduction

Nickel-base super alloys containing around 40 mass% of Cr and around 4 mass% of Al possess superior mechanical properties and heat-resistance at high temperatures and excellent nonmagnetism even at very low temperatures. The capabilities for this type of Ni-base super alloy have been studied by many researchers.1–6) Under usual application conditions, the super alloy indicates the lamellar microstructure consisting of the Ni-rich solid-solution (γ) phase with the face-centered cubic (fcc) structure and the Cr-rich solid-solution (α) phase with the body-centered cubic (bcc) structure. Furthermore, fine particles of the Ni3Al (γ') phase with the L12 structure are dispersed in the lamellar microstructure. The remarkable capabilities of the super alloy are attributed to such a multiphase microstructure. The formation of the multiphase microstructure has been experimentally examined by various investigators.7–9) For instance, Komatsu et al.7) observed the crystallographic orientation relationship between the α and γ lamellae by transmission electron microscopy (TEM). In their experiment, a polycrystalline Ni–38Cr–3.8Al alloy was homogenized at 1 473 K for 2 h and then isothermally annealed at temperatures of 773–1 173 K for various times up to 5 h. According to the observation, the {111}γ//[110]α relationship was recognized between the α and γ lamellae. A more detailed TEM observation of the lamellar microstructure was conducted by Kawase et al.8) using a Ni–39Cr–3.8Al alloy. Their observation shows that fine particles of the γ’ phase are formed in the γ matrix by continuous precipitation in the early stages of isothermal annealing at temperatures of 723–1 123 K and the parallel orientation relationship of {111}γ//{111}α and {110}γ//(110)α holds between the γ and γ’ phases. During isothermal annealing, however, the cell consisting of the α and γ lamellae is produced at the grain boundary of the γ matrix by discontinuous precipitation and grows into the γ matrix. Also in the cell, fine particles of the γ’ phase are dispersed in the γ lamellae as well as the γ matrix, and the parallel orientation relationship is realized between the γ lamella and the γ’ particle. On the other hand, the Kurdjumov–Sachs relationship of {111}γ//(110)α and {110}γ//(111)α is actualized between the γ and α lamellae. Since special crystallographic orientation relationships hardly exist between the adjacent γ lamella and matrix along the moving cell boundary, the γ’ particle in the γ matrix should dissolve in the moving cell boundary to precipitate again in the γ lamella with the parallel orientation relationship. The kinetics of the discontinu-
ous precipitation with such complex reactions in the Ni–39Cr–3.8Al alloy was experimentally observed by Kawase et al.\textsuperscript{9)} Their observation indicates that the addition of Al with 3.8 mass% into the Ni–39Cr alloy diminishes the interlamellar spacing of the cell by one order of magnitude and accelerates the growth of the cell by three orders of magnitude. Unfortunately, however, no quantitative explanation is available for such effects of Al. In order to find the quantitative explanation, the influence of Al on the kinetics of the discontinuous precipitation in the ternary Ni–Cr–Al system was experimentally examined in the present study. In the experiment, Ni–38Cr–Al alloys with Al concentrations of 3.8 mass% and 4.2 mass% were isothermally annealed in the temperature range of 773–1 073 K, and the microstructure of the alloy was observed by a metallographical technique. On the basis of the observation, the kinetics was theoretically analyzed using a diffusion model.

2. Experimental

Ternary Ni–38Cr–3.8Al and Ni–38Cr–4.2Al alloys were prepared as 150 kg ingots in a vacuum by an induction melting technique. The former and latter alloys are called alloys A and B, respectively. The chemical compositions of alloys A and B are listed in Table 1. Here, a small amount of carbon contributes to deoxidization, and that of boron improves hot workability. Both ingots were homogenized \textit{in vacuo} at 1 473 K for 16 h (57.6 ks) and then hot forged into columnar bars with a diameter of 20 mm. Disk specimens with a thickness of 10 mm and a diameter of 20 mm were cut from the forged bar and then separately solution treated in evacuated silica capsules for 30 min (1.8 ks), followed by water quenching with breaking the capsules. The temperatures of the solution heat treatment for alloys A and B were 1 473 K and 1 493 K, respectively. Each solution treated specimen was isothermally annealed in an evacuated silica capsule at temperatures of 773–1 073 K for various periods up to 50 h (180 ks), followed by water quenching with breaking the capsule. Hereafter, the annealing temperature and time are denoted by $T$ and $t$, respectively.

Cross-sections of the annealed specimen were mechanically polished on 800–4 000 emery papers and then finished using diamond with a diameter of 1 $\mu$m. The finished cross-section was electrolytically etched with an etchant consisting of 10 vol% of oxalic acid and 90 vol% of distilled water at room temperature. The microstructure of the cross-section was observed by optical microscopy (OM) and scanning electron microscopy (SEM). After the microstructure observation, the Vickers hardness was determined on the cross-section.

3. Results and Discussion

3.1. Microstructure

Typical OM photographs of the cross-section for the solution treated specimens are shown in Fig. 1. Figure 1(a) and 1(b) indicates the photographs for alloys A and B, respectively. As can be seen, the polycrystalline single-phase microstructure of the $\gamma$ phase is realized for both alloys by the solution heat treatment. On the other hand, small dark particles are slightly distributed in the $\gamma$ matrix.

Since the concentration of Cr is very large for both alloys, the small dark particle may be a chromium oxide formed during induction melting. The mean grain size of the $\gamma$ matrix is about 400 $\mu$m for both alloys. A vertical section with a constant Cr concentration of 38 mass% for the phase diagram in the ternary Ni–Cr–Al system was calculated by a Calphad technique in a previous study.\textsuperscript{10)} Here, Calphad is the abbreviation of calculation of phase diagram. The vertical section is represented in Fig. 2. In this figure, the ordinate shows the absolute temperature $T$, and the abscissa indicates the concentration of Al measured in mass%. According to the vertical section, the temperature $T_a$ of the $\gamma/(\gamma + \alpha)$ phase boundary is 1 436 K and 1 467 K for alloys A and B, respectively, and that $T_g$ of the $(\gamma + \alpha)/(\gamma + \gamma' + \alpha)$ phase boundary is 1 173 K and 1 197 K for alloys A and B, respectively. On the other hand, the temperatures of the solution heat treatment for alloys A and B are 1 473 K and 1 493 K, respectively, and hence sufficiently higher than $T_a$=1 436 K and 1 467 K, respectively.

OM photographs of the cross-section for the specimens annealed at $T=873$ K are indicated in Fig. 3. Figure 3(a) and 3(b) shows the photographs of alloy A with $t=8$ h (28.8 ks) and 16 h (57.6 ks), respectively, and Fig. 3(c) and 3(d) indicates the photographs of alloy B with $t=8$ h (28.8 ks) and 16 h (57.6 ks), respectively. Two regions with bright and dark contrasts are recognized in Fig. 3(a). The area of the

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<th>Table 1. Chemical compositions of alloys in mass%.</th>
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Fig. 1. OM photographs of cross-section after solution heat treatment for (a) alloy A and (b) alloy B.
3.2. Growth Behavior of Cell

From the OM photographs like Fig. 3(a), the distance \( l_i \) between the stationary grain boundary of the \( \gamma \) matrix and the moving cell boundary was determined for forty different moving cell boundaries, and then the mean value \( l \) of \( l_i \) was evaluated by the following equation.

\[
l = \frac{1}{N} \sum_{i=1}^{N} l_i \quad \text{(1)}
\]

Here, \( N = 40 \). The value \( l \) indicates the mean migration distance of the moving cell boundary.\(^{11}\) The evaluation is shown in Figs. 5 and 6. Figure 5(a) and 5(b) indicates the results of alloy A at \( T = 773–873 \) K and \( T = 923–1073 \) K, respectively, and Fig. 6(a) and 6(b) shows the results of alloy B at \( T = 773–873 \) K and \( T = 923–973 \) K, respectively. In these figures, the ordinate and the abscissa indicate the migration distance \( l \) and the annealing time \( t \), respectively, and various open symbols show the results at different annealing temperatures. As can be seen, most of the open symbols are located well on the corresponding straight line, though only one plotted point is available at \( T = 1023–1073 \) K in Fig. 5(b) and at \( T = 923–973 \) K in Fig. 6(b). Thus, the migration distance \( l \) of the moving cell boundary is proportional to the annealing time \( t \) as follows.

\[
l = vt \quad \text{..............................}(2)
\]

In Eq. (2), the proportionality coefficient \( v \) corresponds to the migration rate of the moving cell boundary. The mean value of \( v \) was estimated from the open symbols in Figs. 5 and 6 by the least-squares method. The values of \( v \) estimated for alloys A and B are plotted as open circles and squares, respectively, against the annealing temperature \( T \) in Fig. 7. In this figure, the corresponding result of the Ni–39Cr–3.8Al alloy reported by Kawase \textit{et al.}\(^9\) is shown as open double-circles. On the other hand, the results of the binary Ni–39Cr, Ni–42Cr and Ni–45Cr alloys reported by Gust \textit{et al.}\(^{11}\) are indicated as open triangles, inverse-triangles and rhombuses, respectively, in Fig. 7. The Ni–39Cr–3.8Al, Ni–39Cr, Ni–42Cr and Ni–45Cr alloys are hereafter called alloys C, D, E and F, respectively. As to alloys A and B, the migration rate \( v \) monotonically increases with increasing annealing temperature \( T \). Although \( v \) is rather close to one another among alloys A–C, it is slightly greater for alloy B than for alloy A. However, for alloy C, \( v \) reaches to the maximum value at \( T = 123 \) K and then slightly decreases at \( T = 173 \) K. In contrast, \( v \) is about three orders of magnitude smaller for alloy D than for alloys A–C. Among alloys D–F, \( v \) gradually increases with increasing concentration of Cr. Hence, both Al and Cr accelerate the growth of the cell. However, the acceleration effect is more remark-
able for Al than for Cr. In the case of alloys D–F, the cell is merely composed of the $\gamma'$ and $\alpha$ phases. On the other hand, for alloys A–C, the fine $\gamma'$ particles are dispersed in the $\gamma$ matrix and the $\gamma$ lamella in the cell. Consequently, the acceleration effect of Al on the growth of the cell should be attributed to the continuous precipitation of the $\gamma'$ phase.

From the SEM photographs like Fig. 4, the interlamellar spacing $s_i$ between the neighboring $\alpha$ lamellae in the cell on the cross-section was determined for forty different cells, and then the mean value $s_m$ of $s_i$ was evaluated by the following equation.

$$s_m = \frac{1}{N} \sum_{i=1}^{N} s_i$$ ...............................(3)

Like Eq. (1), $N=40$. If the interlamellar spacing $s$ takes an identical value for all the cells, $s$ is estimated from $s_m$ as follows.12)

$$s = 0.5s_m$$ ...............................(4)

The estimated values of $s$ for alloys A and B are plotted as open circles and squares, respectively, against the annealing temperature $T$ in Fig. 8. In this figure, the corresponding results of alloys C,9) D, E and F11) are shown as open double-circles, triangles, inverse-triangles and rhombuses, respectively. As can be seen, $s$ is almost one order of magnitude smaller for alloys A–C than for alloys D–F. Among alloys D–F, $s$ monotonically decreases with increasing Cr concentration. On the other hand, $s$ is smaller for alloy B than for
alloy A but greater for alloy C than for alloy A. Between alloys A and B, s slightly decreases with increasing Al concentration.

The Vickers hardness $H_V$ of the γ matrix was determined with a load of 0.98 N using the same specimen as the microstructure observation. The results of alloy A for $T=773–873$ K and $T=923–1 073$ K are shown in Fig. 9(a) and 9(b), respectively. On the other hand, Fig. 10 indicates the results of alloy B for $T=773–923$ K. In these figures, the ordinate and the abscissa show the Vickers hardness $H_V$ and the annealing time $t$, respectively. As can be seen, the Vickers hardness $H_V$ monotonically increases with increasing annealing time $t$. According to the TEM observation by Kawase et al.,9) the size of the γ′ particle is usually smaller than 10 nm under the present annealing conditions as previously mentioned. Thus, the γ′ particle is invisible in Figs. 3 and 4. Nevertheless, the dependence of $H_V$ on $t$ in Figs. 9 and 10 suggests that the continuous precipitation of the γ′ phase occurs in the γ matrix.9,10)

3.3. Kinetic Analysis

Various kinetic models for discontinuous precipitation have been proposed by many investigators.13–24) However, these models are restricted to binary alloy systems and thus cannot be applicable to the ternary Ni–Cr–Al system in a straightforward manner. In alloys A and B, fine particles of the γ′ phase are dispersed in the γ matrix as well as the γ lamella of the cell as mentioned earlier. Here, the cell consists of the γ, γ′ and α phases, but the matrix is composed of only the γ and γ′ phases. If most of Al is consumed by the continuous precipitation of the γ′ phase, the concentration of Al in the γ matrix becomes very small. When the γ′ particle is not an obstacle against the migration of the cell boundary, the discontinuous precipitation in alloys A and B occurs like that in the binary Ni–Cr system. A kinetic model for the discontinuous precipitation controlled by boundary diffusion was proposed by Aaronson and Liu.19) In this section, their model was used to analyze quantitatively the kinetics of the discontinuous precipitation in the ternary Ni–Cr–Al system. The moving cell boundary for the cell consisting of the γ and α lamellae is schematically shown in Fig. 11. According to the Aaronson and Liu model,19) the migration rate $v$ of the moving cell boundary for the discontinuous precipitation in the binary Ni–Cr system is related with s by the following equation.

$$v = C(s, t)$$
Due to the continuous precipitation of the $\gamma'$ phase in the $\gamma$ matrix, Ni as well as Al is consumed in the $\gamma$ matrix. The consumption of Ni and Al causes the increase in the concentration of Cr in the $\gamma$ matrix, $x_0$ is the mol fraction of Cr in the untransformed $\gamma$ matrix, $x_p$ is that in the $\gamma'$ lamella, and $x_m$ is that in the untransformed $\gamma$ matrix just ahead the $\alpha$ lamella. In order to emphasize the boundary diffusion rate-controlling process, the thickness of the moving cell boundary is exaggerated in Fig. 11. Equation (5) is expressed in a different manner as follows.

$$D^b = \frac{s^2 \delta (x_p - x_m)}{4 \delta (x_p - x_m)} \quad \text{(6)}$$

Here, $D^b$ is the boundary diffusion coefficient of Cr along the moving cell boundary, $\delta$ is the thickness of the moving cell boundary, $x_0$ is the mol fraction of Cr in the untransformed $\gamma$ matrix, $x_p$ is that in the $\gamma'$ lamella, and $x_m$ is that in the untransformed $\gamma$ matrix just ahead the $\alpha$ lamella. The boundary diffusion coefficient $D^b$ was calculated from Eq. (7) using $4.2\,$Al, $2.83 \times 10^{-2} \,$Al, and $5.69 \times 10^{-2} \,$Al. The corresponding results of the Ni–39Cr, Ni–42Cr and Ni–45Cr alloys are also represented as solid, dashed and dotted thin lines, respectively.

$$D^b = D_0^b \exp \left( -\frac{Q}{RT} \right) \quad \text{(7)}$$

Here, $D_0^b$ is the pre-exponential factor, $Q$ is the activation enthalpy, and $R$ is the gas constant. From the plotted points in Fig. 13, $D_0^b$ and $Q$ were estimated by the least-squares method. The estimated values are shown in Fig. 13. The dependence of $D^b$ on $T$ was calculated from Eq. (7) using these values of $D_0^b$ and $Q$. The calculations of alloys A and B are indicated as solid and dashed bold lines, respectively. The corresponding results of the Ni–39Cr, Ni–42Cr and Ni–45Cr alloys are also represented as solid, dashed and dotted thin lines, respectively.

$$v = 4 \delta D^b (x_p - x_m) \quad \text{and} \quad 1 \times 10^{-4} \text{m/s}$$

**Fig. 11.** Schematic drawing of the moving cell boundary for the cell consisting of the $\gamma$ and $\alpha$ lamellae.

**Fig. 12.** The dependencies of $x_p$ and $x_m$ on $x_0$ for alloys A and B calculated by the Calphad technique in a manner similar to a previous study.10)

**Fig. 13.** The boundary diffusion coefficient $D^b$ versus the reciprocal of the annealing temperature $T$ for alloys A and B shown as open circles and squares, respectively. Solid and dashed bold lines indicate the calculations from Eq. (7) for alloys A and B, respectively. The corresponding results of the Ni–39Cr, Ni–42Cr and Ni–45Cr alloys are also represented as solid, dashed and dotted thin lines, respectively.
other between alloys A and B in Fig. 13, though \( Q \) is slightly smaller for alloy A than for alloy B. In this figure, the corresponding results of alloys D, E and F reported by Gust et al.\(^{11,12}\) are also represented as solid, dashed and dotted thin-lines, respectively. For alloys D–F, \( D^b \) increases by 3 and 10 times at \( T=823 \) K and 1073 K, respectively, with increasing Cr concentration from 39 to 45 mass%. Although the Cr concentration is close to each other between alloys A–B and alloy D, \( D^b \) is nearly equal to each other between alloys A–B and alloy F. Thus, as to the influence of alloying on \( D^b \), the addition of Al with 4 mass% into the Ni–39Cr alloy is almost equivalent to that of Cr with 6 mass%. As reported by Kawase et al.,\(^6\) the fine \( \gamma' \) particle in the \( \gamma \) matrix dissolves in the moving cell boundary and then precipitates again in the \( \gamma \) lamella of the cell. Such a dissolution–precipitation reaction can work as a drag force against the migration of the cell boundary. The drag force may yield underestimation of \( D^b \). Nevertheless, as shown in Fig. 13, \( D^b \) is not smaller for alloys A–B than for alloys D–F. Consequently, the dissolution–precipitation reaction is not the obstacle against the growth of the cell, and hence the kinetic model of binary alloy system is valid for the quantitative analysis of the discontinuous precipitation in the ternary Ni–Cr–Al system. On the other hand, the continuous precipitation of the \( \gamma' \) phase in the \( \gamma \) matrix enhances the supersaturation of Cr in the \( \gamma \) matrix as shown in Fig. 12. According to the schematic drawing in Fig. 11, the cell possesses the excess energy \( G^a \) due to the interface energy \( \sigma \) of the \( \alpha'\gamma \) interface as follows, even if the equilibrium composition is realized in the \( \gamma \) and \( \alpha \) lamellae.

\[
G^a = \frac{2\sigma}{s} \quad \text{..........................}(8)
\]

Here, \( G^a \) and \( \sigma \) have dimensions of energy per unit volume and energy per unit area, respectively. As the supersaturation of Cr in the \( \gamma \) matrix increases, \( G^a \) may increase, and thus \( s \) will decrease through Eq. (8). As can be seen in Fig. 8, \( s \) is actually one order of magnitude smaller for alloys A–B than for alloy F. In contrast, \( D^b \) is close to each other between alloys A–B and alloy F and the ratio \( (x_p-x_o)/\sqrt{(x_p-x_o)^2+(x_o-x_p)^2} \) in Eq. (5) is not so dissimilar in alloys A–B and alloy F. Hence, Eq. (5) deduces that \( v \) increases in inverse proportion to the square of \( s \). As a result, \( v \) becomes two orders of magnitude greater for alloys A–B than for alloy F in Fig. 7. Although \( D^b \) slightly increases with increasing Cr concentration \( x_o \) for alloys D–F in Fig. 13, the dependencies of \( v \) and \( s \) on \( x_o \) in Figs. 7 and 8, respectively, for these alloys can be also explained in a similar manner.

### 4. Conclusions

The kinetics of the discontinuous precipitation in the ternary Ni–Cr–Al system was experimentally observed using the Ni–38Cr–Al alloys with Al concentrations of 3.8 mass% and 4.2 mass%. The ternary alloys with the single-phase microstructure of the fcc-\( \gamma \) phase were isothermally annealed at temperatures of 773–1073 K for various periods up to 50 h. During isothermal annealing, the continuous precipitation of the L12-\( \gamma' \) phase occurs in the \( \gamma \) matrix, and then the discontinuous precipitation of the bcc-\( \alpha \) phase takes place in the \( \gamma \) matrix dispersed with the \( \gamma' \) phase. Owing to the discontinuous precipitation, the cell consisting of the \( \gamma \) and \( \alpha \) lamellae is formed along the grain boundary of the \( \gamma \) matrix and then grows into the \( \gamma \) matrix under steady-state conditions. Here, the \( \gamma' \) phase is dispersed also in the \( \gamma \) lamella of the cell. The growth rate and the interlamellar spacing of the cell monotonically increase with increasing annealing temperature. The addition of Al with around 4 mass% into the Ni–38Cr alloy accelerates the growth of the cell by three orders of magnitude. The observation was quantitatively analyzed using the kinetic model proposed by Aaronson and Liu.\(^{19}\) The analysis shows that the growth of the cell is controlled by the boundary diffusion of Cr along the moving cell boundary. The acceleration effect of Al is attributed to the supersaturation of Cr in the \( \gamma \) matrix enhanced by the continuous precipitation of the \( \gamma' \) phase.

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