Effects of Fe, W and Mo on Kinetics of Discontinuous Precipitation in the Ni–Cr System

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The effects of Fe, W and Mo on the kinetics of discontinuous precipitation in the Ni–Cr system were experimentally examined using a binary Ni–38Cr alloy and ternary Ni–38Cr–0.9Fe, Ni–38Cr–3.2W and Ni–38Cr–1.7Mo alloys. These alloys were homogenized at 1423 K for 3 h, solution treated at 1423 K for 1 h, and then isothermally annealed in the temperature range of 873–1023 K for various times up to 2300 h. Due to the solution heat treatment, all the alloys show the polycrystalline single-phase microstructure of the Ni-rich solid-solution (γ) phase with the face-centered cubic structure. During isothermal annealing, however, 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. At each annealing temperature, the migration distance of the moving cell boundary is proportional to the annealing time. Hence, the growth rate of the cell is constant independent of the annealing time. The growth rate and the interlamellar spacing of the cell almost monotonically increase with increasing annealing temperature at 873–1023 K. The cell growth is decelerated by W and Mo but not by Fe. The deceleration is more remarkable for Mo than for W. A kinetic model for the binary discontinuous precipitation controlled by boundary diffusion was used to analyze quantitatively the experimental result. According to the analysis, W and Mo retard the boundary diffusion of Cr along the moving cell boundary, but Fe slightly hastens that. Such influence of the alloying component on the boundary diffusion is ascribable to the thermodynamic interaction between Cr and the alloying component in the moving cell boundary. As a consequence, it is concluded that the retardation of the Cr boundary diffusion causes the deceleration of the cell growth. [doi:10.2320/matertrans.M2012132]

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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 investigators.^{1–6)} Under usual application conditions, the super alloy indicates the lamellar microstructure composed 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 researchers.^{7–9)} For instance, Kawase *et al.*⁹⁾ observed the crystallographic orientation relationships among the α , γ and γ' phases by transmission electron microscopy (TEM). In this experiment, a polycrystalline Ni–39Cr–3.8Al alloy was homogenized at 1523 K for 1 h and then isothermally annealed at temperatures of 723–1273 K for various times up to 3.8 h. According to their observation, 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 723–1123 K and the parallel orientation relationship of $\{111\}_{\gamma}/\{111\}_{\gamma'}$ and $\langle 110 \rangle_{\gamma}/\langle 110 \rangle_{\gamma'}$ 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 lamella as well as the γ matrix, and the parallel orientation relationship is realized between the γ lamella and the γ' particle. In contrast, the Kurdjumov–Sachs relationship of $\{111\}_{\gamma}/\{110\}_{\alpha}$ and $\langle 110 \rangle_{\gamma}/\langle 111 \rangle_{\alpha}$ 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 discontinuous precipitation with such complex reactions in the Ni–39Cr–3.8Al alloy was experimentally observed by Kawase *et al.*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.

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 observed in a previous study.¹⁰⁾ In this experiment, Ni–38Cr–Al alloys with Al concentrations of 3.8 and 4.2 mass% were isothermally annealed at temperatures of 773–1073 K, and then the microstructure of the alloy was observed by a metallographical technique. According to the observation, the migration distance of the moving cell boundary is proportional to the annealing time at each annealing temperature. 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

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annealing temperature at 773–1073 K. The kinetic model proposed by Aaronson and Liu¹¹⁾ was used to analyze quantitatively the observation. Although the discontinuous precipitation in the ternary Ni–38Cr–Al alloys occurs in a complicated manner as reported by Kawase *et al.*,⁹⁾ the analysis indicates that the growth of the lamellar cell is controlled by the boundary diffusion of Cr along the moving cell boundary and the acceleration effect of Al is attributed to the supersaturation of Cr in the γ matrix enhanced by the continuous precipitation of the γ' phase. In the materials industry, however, slower growth of the cell is more desirable to control accurately the microstructure of the alloy. Thus, the Al effect has to be compensated by addition of other alloying components into the alloy. However, no reliable experimental information is available for such alloying components. In the present study, effects of Fe, W and Mo on the kinetics of the discontinuous precipitation were experimentally examined by the technique used in a previous study.¹⁰⁾ To exclude the influence of the continuous precipitation on the kinetics, however, attention was focused on the growth behavior of the cell in the Ni–Cr–*X* system without Al. In the experiment, ternary Ni–38Cr–0.9Fe, Ni–38Cr–3.2W and Ni–38Cr–1.7Mo alloys as well as a binary Ni–38Cr alloy were isothermally annealed in the temperature range of 873–1023 K. This temperature range is relevant to a practical heat treatment in the materials industry. If a large amount of component *X* is added into the Ni–Cr alloy, the composition dependence of the kinetics can be exaggerated. However, the large-amount addition may deduce formation of different phases and thus change the resultant microstructure. To avoid such a microstructural change, the addition of component *X* was restricted within the solubility ranges of the α and γ phases.^{12,13)} The rate-controlling process for the cell growth was discussed on the basis of the observation.

2. Experimental

A binary Ni–38Cr alloy and ternary Ni–38Cr–0.9Fe, Ni–38Cr–3.2W and Ni–38Cr–1.7Mo alloys were prepared as 150 kg ingots in a vacuum by an induction melting technique. The Ni–Cr, Ni–Cr–Fe, Ni–Cr–W and Ni–Cr–Mo alloys are called alloys A1, A2, A3 and A4, respectively. The chemical compositions of these alloys were measured by chemical analysis. The raw result is listed in Table 1. In this table, the concentration of each component is shown in mass%. Here, a small amount of C contributes to deoxidization, and that of B improves hot workability. The ingots were homogenized in an ambient atmosphere at 1423 K for 3 h (10.8 ks) and then hot forged into columnar bars with a diameter of 18 mm. Due to the high Cr concentration, the alloy is protected from internal oxidation by a thin surface layer of Cr₂O₃. Disk specimens with a thickness of 10 mm and a diameter of 18 mm were cut from the forged bar and then solution treated in an ambient atmosphere at 1423 K for 1 h (3.6 ks), followed by water quenching. Each solution treated specimen was isothermally annealed in an ambient atmosphere at temperatures of 873–1023 K for various periods up to 2300 h (8.28 Ms), followed by water quenching. Hereafter, the annealing temperature and time are denoted by *T* and *t*, respectively.

Table 1 Chemical compositions of alloys A1–A4 in mass%.

Alloy	Ni	Cr	Fe	W	Mo	C	B
A1	61.17	38.78	0.02	<0.01	<0.01	0.007	0.003
A2	60.31	38.75	0.91	<0.01	<0.01	0.010	0.003
A3	58.38	38.33	0.02	3.23	0.03	0.005	0.004
A4	59.72	38.58	0.02	<0.01	1.66	0.006	0.003

Fig. 1 OM photograph of cross-section for alloy A1 after solution heat treatment.

Cross-sections of the annealed specimen were mechanically polished on #800–4000 emery papers and then finished using diamond with a diameter of 1 μ 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).

3. Results and Discussion

3.1 Microstructure

A typical OM photograph of the cross-section for the solution treated specimen of alloy A1 is shown in Fig. 1. As can be seen, the polycrystalline single-phase microstructure of the γ phase is realized for alloy A1 by the solution heat treatment. Such a single-phase microstructure was actualized also for alloys A2–A4. On the other hand, small dark particles are slightly distributed in the γ matrix. Since the concentration of Cr is very high for alloys A1–A4, the small dark particle may be a chromium oxide formed during induction melting. The mean grain size of the γ matrix is about 150 μ m for these alloys.

OM photographs of the cross-section for the specimens annealed at $T = 923$ K for $t = 1000$ h (3.6 Ms) are indicated in Fig. 2. Figure 2(a)–2(d) shows the photographs of alloys A1–A4, respectively. Two regions with bright and dark contrasts are recognized in Fig. 2. The area of the dark region is smaller for Fig. 2(c) and 2(d) than for Fig. 2(a) and 2(b) but slightly greater for Fig. 2(c) than for Fig. 2(d). A typical SEM photograph of cells in alloy A2 with $T = 973$ K and $t = 1000$ h (3.6 Ms) is shown in Fig. 3. In this figure, the

Fig. 2 OM photographs of cross-section after isothermal annealing at $T = 923$ K for $t = 1000$ h (3.6 Ms): (a) alloy A1, (b) alloy A2, (c) alloy A3 and (d) alloy A4.

Fig. 3 SEM photograph of the cell in alloy A2 annealed at $T = 973$ K for $t = 1000$ h (3.6 Ms).

bright and dark lamellae are the α and γ phases, respectively, and the α and γ lamellae in each cell are almost parallel to each other. Such cells were formed by discontinuous precipitation according to the following reaction: $\gamma_0 \rightarrow \gamma + \alpha$, where γ_0 is an untransformed matrix phase supersaturated with a solute, γ is the matrix phase depleted with the solute, and α is a precipitate phase. Discontinuous

Fig. 4 Schematic drawing of cross-sectional microstructure of isolated cell.

precipitation is known to occur in many alloy systems. The mechanism of discontinuous precipitation is discussed in detail by Manna *et al.*¹⁴⁾ and thus not repeatedly described in the present article.

3.2 Growth behavior of cell

A cross-sectional microstructure of an isolated cell is schematically depicted in Fig. 4. From OM photographs like Fig. 2, the maximum distance l_i between the stationary grain boundary of the γ matrix and the moving cell boundary for

Fig. 5 The migration distance l of the moving cell boundary versus the annealing time t at $T = 873\text{--}1023 \text{ K}$: (a) alloy A1, (b) alloy A2, (c) alloy A3 and (d) alloy A4. Straight lines indicate the calculations from eq. (2).

each isolated cell was determined for forty different moving cell boundaries, and then the mean value l of l_i was evaluated by the following equation.

$$l = \frac{1}{N} \sum_{i=1}^N l_i \quad (1)$$

Here, $N = 40$. The distance l_i is shown for a typical isolated-cell in Fig. 2(c). According to the treatment reported by Gust *et al.*,¹⁵⁾ l indicates the mean migration distance of the moving cell boundary. This treatment was adopted also in the present study. The evaluation is shown in Fig. 5. Figure 5(a)–5(d) indicates the results of alloys A1–A4, respectively. In Table 1, the raw result of the chemical analysis for the concentration of each component in the alloy is shown in mass%. Neglecting minor components, the concentration in mass% was converted into the mol fraction. The result is indicated in Table 2. In this table, x_i^0 stands for the mol fraction of component i in each alloy. Hereafter, the mol fraction is used to describe the chemical composition. In Fig. 5, the ordinate and the

Table 2 Mol fraction x_i^0 of component i for alloys A1–A4.

Alloy	X	x_{Ni}^0	x_{Cr}^0	x_X^0
A1	—	0.5830	0.4170	—
A2	Fe	0.5744	0.4165	0.0091
A3	W	0.5688	0.4212	0.0100
A4	Mo	0.5728	0.4175	0.0098

abscissa show the migration distance l and the annealing time t , respectively, and various open symbols with error bars indicate the results at different annealing temperatures. Hereafter, the error bar stands for the standard error of the mean value. As can be seen, most of the open symbols are located well on a straight line at each annealing temperature. Thus, the migration distance l of the moving cell boundary is proportional to the annealing time t as follows.

$$l = vt \quad (2)$$

Fig. 6 The migration rate v of the moving cell boundary versus the annealing temperature T for alloys A1, A2, A3 and A4 shown as open circles, triangles, squares and rhombuses, respectively, with error bars. The corresponding results of alloys A5, A6 and A7¹⁵⁾ are also indicated as thin dotted, dashed and dashed-and-dotted lines, respectively.

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 Fig. 5 by the least-squares method as shown with the straight lines. The values of v estimated for alloys A1, A2, A3 and A4 are plotted as open circles, triangles, squares and rhombuses, respectively, with error bars against the annealing temperature T in Fig. 6. In this figure, the corresponding results of the binary Ni-0.42Cr, Ni-0.45Cr and Ni-0.48Cr alloys reported by Gust *et al.*¹⁵⁾ are indicated as thin dotted, dashed and dashed-and-dotted lines, respectively. The Ni-0.42Cr, Ni-0.45Cr and Ni-0.48Cr alloys are hereafter called alloys A5, A6 and A7, respectively. For alloys A2–A4, the migration rate v monotonically increases with increasing annealing temperature T . On the other hand, for alloy A1, v reaches the maximum value at $T = 973$ K and becomes slightly smaller at $T = 1023$ K than at $T = 973$ K. At most of the annealing temperatures, v is close to each other between alloys A1 and A2 but smaller for alloys A3 and A4 than for alloys A1 and A2. Thus, the addition of $X = W$ or $X = Mo$ with $x_X^0 = 0.01$ into the Ni-0.42Cr alloy decelerates the growth of the cell. The deceleration is more remarkable for $X = Mo$ than for $X = W$. At $T = 873$ K, v is almost one order of magnitude smaller for alloy A4 than for alloy A1. Although v is close to each other between alloys A1 and A5 at $T = 1023$ K, it is slightly smaller for alloy A5 than for alloy A1 at $T = 873$ – 973 K. Among alloys A5–A7, v gradually increases with increasing Cr concentration. Hence, the higher Cr concentration is detrimental to the deceleration of the cell growth. According to the result by Gust *et al.*,¹⁵⁾ the incubation period for nucleation of cell was clearly observed at some annealing temperatures for each alloy. On the other hand, the open symbols are slightly scattered in Fig. 5. Hence, it cannot be conclusively determined whether the incubation period appears in Fig. 5.

Fig. 7 The interlamellar spacing s of the cell versus the annealing temperature T for alloys A1, A2, A3 and A4 shown as open circles, triangles, squares and rhombuses, respectively, with error bars. The corresponding results of alloys A5, A6 and A7¹⁵⁾ are also indicated as thin dotted, dashed and dashed-and-dotted lines, respectively.

From SEM photographs like Fig. 3, the interlamellar spacing s_i between the neighboring α 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.

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

Like eq. (1), $N = 40$. It is reported by Saltykov¹⁶⁾ that s_m is related with s as follows for pearlite with a constant interlamellar spacing s .

$$s = \frac{s_m}{2} \quad (4)$$

According to his metallographical treatment,¹⁶⁾ the mean true interlamellar spacing s was evaluated from eq. (4) using the value of s_m experimentally determined on the cross-section. The results for alloys A1, A2, A3 and A4 are plotted as open circles, triangles, squares and rhombuses, respectively, with error bars against the annealing temperature T in Fig. 7. In this figure, the corresponding results of alloys A5, A6 and A7¹⁵⁾ are indicated as thin dotted, dashed and dashed-and-dotted lines, respectively. For all the alloys, s monotonically increases with increasing annealing temperature T at $T = 873$ – 1023 K. Although s is the largest for alloy A2 but the smallest for alloy A3, it is not so dissimilar among alloys A1–A4. On the other hand, s is slightly greater for alloy A5 than for alloy A1. For alloys A5–A7, s gradually decreases with increasing Cr concentration. Even in this case, however, the difference between alloys A5 and A7 is much smaller for s in Fig. 7 than for v in Fig. 6.

3.3 Kinetic analysis

Various kinetic models for discontinuous precipitation in binary alloy systems have been proposed by many

Fig. 8 Schematic drawing of the moving cell boundary for the cell consisting of the γ and α lamellae.

investigators.^{11,17–27}) In order for the model to express accurately the kinetics, many parameters are necessary. The more the parameters are adopted, the better the accuracy of model becomes. However, some of the parameters may not be reliably estimated in a highly sophisticated model. A kinetic model for the discontinuous precipitation controlled by boundary diffusion was proposed by Aaronson and Liu.¹¹) Although a relatively small number of parameters are used, the kinetics in the binary Pb–Sn system is satisfactorily reproduced by the Aaronson and Liu (AL) model.¹¹) The moving cell boundary for the cell consisting of the γ and α lamellae is schematically shown in Fig. 8. According to the AL model, the migration rate v of the moving cell boundary for the discontinuous precipitation in the binary Ni–Cr system is related with the interlamellar spacing s by the following equation.

$$v = \frac{4\delta D_i^b (x_p - x_m)}{s^2 (x_p - x_0)} \quad (5)$$

Here, D_i^b is the boundary diffusion coefficient of solute i along the moving cell boundary, δ is the thickness of the moving cell boundary, x_0 is the mol fraction of solute i in the untransformed γ_0 matrix, x_p is that in the α lamella, and x_m is that in the untransformed γ_0 matrix just ahead the α lamella. Here, $i = \text{Cr}$ for the binary Ni–Cr system. In Fig. 8, the thickness of the moving cell boundary is exaggerated to emphasize the boundary diffusion rate-controlling process. Equation (5) is expressed in a different manner as follows.

$$D_i^b = \frac{s^2 v (x_p - x_0)}{4\delta (x_p - x_m)} \quad (6)$$

As previously mentioned, the AL model was proposed for discontinuous precipitation in binary alloy systems.¹¹) As shown in Table 2, however, x_X^0 is merely 0.01 for alloys A2–A4. Therefore, we may expect that the AL model is conveniently used to analyze quantitatively the discontinuous precipitation in the ternary Ni–Cr– X system as long as the cell growth is controlled by the boundary diffusion of Cr

along the moving cell boundary. The chemical composition of the γ/α two-phase tie-line passing through the composition x_i^0 in Table 2 was calculated by the Calphad technique reported in a previous study.²⁸) The results at $T = 873$ – 1023 K for alloys A1–A4 are shown in Table 3. In this table, x_i^γ and x_i^α indicate the mol fractions of component i in the γ and α phases, respectively, for the γ/α two-phase tie-line. If the local equilibrium is realized at the moving cell boundary between the γ_0 matrix and the α lamella, $x_m = x_i^\gamma$ and $x_p = x_i^\alpha$ in Fig. 8. Using the mean values of v and s in Figs. 6 and 7 and the relationships $x_m = x_{\text{Cr}}^\gamma$, $x_p = x_{\text{Cr}}^\alpha$ and $x_0 = x_{\text{Cr}}^0$, the boundary diffusion coefficient D_{Cr}^b of Cr was calculated from eq. (6). In this calculation, the value $\delta = 0.5$ nm was adopted. The results for alloys A1, A2, A3 and A4 are plotted as open circles, triangles, squares and rhombuses, respectively, against the annealing temperature T in Fig. 9. In this figure, the ordinate shows the logarithm of D_{Cr}^b , and the abscissa indicates the reciprocal of T . As can be seen, the plotted points lie well on a straight line for each alloy. Thus, for $i = \text{Cr}$, the dependence of D_i^b on T is expressed as follows.

$$D_i^b = D_{i0}^b \exp\left(-\frac{Q}{RT}\right) \quad (7)$$

Here, D_{i0}^b is the pre-exponential factor, Q is the activation enthalpy, and R is the gas constant. From the plotted points in Fig. 9, $D_{\text{Cr}0}^b$ and Q for D_{Cr}^b were estimated by the least-squares method as shown with solid lines. The estimated values are indicated in Fig. 9. As can be seen, D_{Cr}^b is lightly greater for alloy A2 than for alloy A1 but smaller for alloys A3 and A4 than for alloys A1 and A2. At lower annealing temperatures, D_{Cr}^b becomes slightly smaller for alloy A4 than for alloy A3. Therefore, it is concluded that the boundary diffusion of Cr along the moving cell boundary is decelerated by W and Mo but marginally accelerated by Fe. The deceleration effect is more remarkable for Mo than for W. In Fig. 9, the corresponding results of alloys A5, A6 and A7¹⁵) are shown as thin dotted, dashed and dashed-and-dotted lines, respectively. For alloys A5–A7, D_{Cr}^b monotonically increases with increasing Cr concentration. Consequently, the increase in the Cr concentration causes acceleration of the cell growth in the binary Ni–Cr system. On the other hand, $Q = 185$ and 219 ¹⁵) kJ/mol for alloys A1 and A5, respectively. Hence, at first glance, Q is slightly greater for alloy A5 than for alloy A1. Between alloys A1 and A5, there exist certain differences of v and s in Figs. 6 and 7, respectively. Although these differences may yield dissimilarity in D_{Cr}^b through eq. (6), the resultant values of D_{Cr}^b are rather close to each other between alloys A1 and A5 in Fig. 9. Furthermore, v and s possess experimental uncertainty as shown with the error bars in Figs. 6 and 7, respectively. Such uncertainty influences accuracy for the estimation of D_{Cr}^b . Since Q corresponds to the slope of D_{Cr}^b in Fig. 9, the estimation accuracy is much lower for Q than for D_{Cr}^b . As a consequence, in the present article, attention is focused on the absolute value of D_{Cr}^b but not on the slope of D_{Cr}^b .

For the calculation in Fig. 9, it is assumed that the local equilibrium is realized at the moving cell boundary between the γ_0 matrix and the α lamella. According to the calculation, Mo and W decelerate the boundary diffusion of Cr along the moving cell boundary. This implies that the boundary

Table 3 Chemical compositions x_i^γ and x_i^α for the γ/α two-phase tie-line passing through the composition x_i^0 in Table 2. The values of r calculated from eq. (8) are also shown at the last column.

Alloy	X	T/K	γ			α			r
			x_{Ni}^γ	x_{Cr}^γ	x_X^γ	x_{Ni}^α	x_{Cr}^α	x_X^α	
A1	—	873	0.6828	0.3172	—	0.0029	0.9971	—	0.8532
		923	0.6672	0.3329	—	0.0046	0.9954	—	0.8730
		973	0.6510	0.3490	—	0.0069	0.9931	—	0.8944
		1023	0.6344	0.3656	—	0.0102	0.9898	—	0.9176
A2	Fe	873	0.6764	0.3131	0.0105	0.0029	0.9960	0.0011	0.8482
		923	0.6608	0.3290	0.0103	0.0045	0.9941	0.0014	0.8680
		973	0.6447	0.3453	0.0100	0.0069	0.9914	0.0017	0.8894
		1023	0.6281	0.3621	0.0098	0.0102	0.9878	0.0020	0.9125
A3	W	873	0.6862	0.3026	0.0113	0.0028	0.9931	0.0041	0.8232
		923	0.6706	0.3185	0.0109	0.0045	0.9902	0.0053	0.8408
		973	0.6545	0.3349	0.0106	0.0068	0.9866	0.0066	0.8584
		1023	0.6381	0.3516	0.0103	0.0100	0.9819	0.0081	0.8728
A4	Mo	873	0.6763	0.3126	0.0111	0.0029	0.9947	0.0024	0.8424
		923	0.6610	0.3281	0.0108	0.0046	0.9926	0.0028	0.8614
		973	0.6453	0.3442	0.0106	0.0070	0.9898	0.0033	0.8818
		1023	0.6291	0.3606	0.0103	0.0103	0.9860	0.0037	0.9039

Fig. 9 The boundary diffusion coefficient D_{Cr}^b of Cr versus the reciprocal of the annealing temperature T for alloys A1, A2, A3 and A4 shown as open circles, triangles, squares and rhombuses, respectively. Bold solid lines indicate the calculations from eq. (7). The corresponding results of alloys A5, A6 and A7¹⁵⁾ are also represented as thin dotted, dashed and dashed-and-dotted lines, respectively.

diffusion is more sluggish for Mo and W than for Cr. If the boundary diffusion coefficient D_X^b of component X is much smaller than D_{Cr}^b , the local equilibrium at the moving cell boundary may be violated. In such a case, the assumption cannot be valid for alloys A2–A4. To test the validity of the assumption, D_X^b was estimated from eq. (6) using the mean values of v and s in Figs. 6 and 7 as well as the relationships $x_m = x_X^\gamma$, $x_p = x_X^\alpha$ and $x_0 = x_X^0$. The results for $X = \text{Fe}$, W and Mo are plotted as open triangles, squares and rhombuses, respectively, against the annealing temperature T in Fig. 10. In this figure, like Fig. 9, the ordinate shows the logarithm of

Fig. 10 The boundary diffusion coefficient D_X^b of component X versus the reciprocal of the annealing temperature T for $X = \text{Fe}$, W and Mo shown as open triangles, squares and rhombuses, respectively. Bold solid lines indicate the calculations from eq. (7).

D_X^b , and the abscissa indicates the reciprocal of T . As can be seen, the plotted points are located well on a straight line for each component X . Thus, the dependence of D_X^b on T is also expressed by eq. (7). From the plotted points in Fig. 10, D_{X0}^b and Q were estimated by the least-squares method as shown with the straight lines. At $T = 873$ – 1023 K, D_{Mo}^b and D_W^b are smaller than D_{Fe}^b . Although D_{Mo}^b is close to D_W^b at $T = 973$ – 1023 K, it becomes slightly smaller than D_W^b at $T = 873$ – 923 K. Thus, Mo and W are actually sluggish diffusion components. As shown in Figs. 9 and 10, however, D_{Fe}^b , D_W^b and D_{Mo}^b are close to D_{Cr}^b for alloys A2, A3 and A4, respectively, at each annealing temperature. Since the same values of v and s in Figs. 6 and 7 are used for both

calculations of D_{Cr}^b and D_X^b ($X = Fe, W, Mo$), the difference between D_{Cr}^b and D_X^b is attributed to the values of x_m , x_p and x_0 in eq. (6). From eq. (6), the parameter r is defined as

$$r = \frac{x_p - x_0}{x_p - x_m}. \quad (8)$$

Using the relationships $x_m = x_{Cr}^y$, $x_p = x_{Cr}^a$ and $x_0 = x_{Cr}^0$ for D_{Cr}^b and those $x_m = x_X^y$, $x_p = x_X^a$ and $x_0 = x_X^0$ for D_X^b , r was calculated from eq. (8). The result is listed at the last column in Table 3. At each annealing temperature, r is not so dissimilar to one another among alloys A1–A4, and thus D_{Cr}^b and D_X^b are predominantly determined by v and s . As a result, D_{Fe}^b , D_W^b and D_{Mo}^b become close to D_{Cr}^b for alloys A2, A3 and A4, respectively. Therefore, as long as the AL model¹¹⁾ is valid for the estimation of D_{Cr}^b and D_X^b , we may consider that the boundary diffusion concurrently occurs between Cr and component X in alloys A2–A4.

3.4 Thermodynamic influence on diffusion

Thermodynamic influence of a third component on the diffusion of a second component in a ternary solution phase is discussed by Kirkaldy and Young.²⁹⁾ According to their discussion,²⁹⁾ the diffusion coefficient of the second component increases for the attractive thermodynamic interaction between the second and third components but decreases for the repulsive thermodynamic interaction. The moving cell boundary is considered to be a separate thermodynamic phase with a certain thickness.³⁰⁾ If the thermodynamic properties of the second and third components in the moving cell boundary are known, the thermodynamic influence may be quantitatively estimated. Unfortunately, however, no reliable information is available for such thermodynamic properties. Since the atomic arrangement is more disordered in the moving cell boundary than in the fcc- γ and bcc- α phases, the thermodynamic property of each component in the moving cell boundary may be similar to that in the liquid (L) phase. The most predominant thermodynamic interaction between Cr and component X ($X = Fe, W, Mo$) in the L phase is expressed by the following equation.³¹⁾

$${}^E G_m = x_{Cr} x_X L_{CrX} \quad (9)$$

Here, ${}^E G_m$ is the excess molar Gibbs energy, and L_{ij} is the interaction parameter between components i and j . Since x_i is dimensionless, L_{ij} as well as ${}^E G_m$ possesses a dimension of J/mol. The composition dependence of L_{ij} is described according to a Redlich-Kister polynomial as follows.³²⁾

$$L_{ij} = {}^0 L_{ij} + {}^1 L_{ij}(x_i - x_j) + {}^2 L_{ij}(x_i - x_j)^2$$

$$i = Cr; j = Fe, Mo, W \quad (10)$$

The parameter ${}^k L_{ij}$ ($k = 0, 1, 2$) is usually a function of the temperature T . The values of ${}^k L_{ij}$ in the binary Cr–Fe,³³⁾ Cr–Mo³⁴⁾ and Cr–W³⁵⁾ systems are summarized in Table 4. Using the values in Table 4, the dependence of ${}^E G_m$ on T at $x_X = 0.01$ ($x_{Cr} = 0.99$) was calculated from eqs. (9) and (10). The results for $X = Fe, W$ and Mo are shown as dotted, dashed and solid curves, respectively, in Fig. 11. At $T = 873$ – 1023 K, ${}^E G_m$ is negative for $X = Fe$ but positive for $X = W$ and Mo . Furthermore, ${}^E G_m$ is greater for $X = Mo$ than for $X = W$. This means that the thermodynamic interaction between Cr and X is attractive for $X = Fe$ but

Table 4 Values of ${}^k L_{ij}$ for the liquid phase in the binary Cr–Fe,³³⁾ Cr–Mo³⁴⁾ and Cr–W³⁵⁾ systems measured in J/mol.

Cr–Fe system ³³⁾	
${}^0 L_{CrFe}$	$= -14550 + 6.657T$
${}^1 L_{CrFe}$	$= 0$
${}^2 L_{CrFe}$	$= 0$
Cr–Mo system ³⁴⁾	
${}^0 L_{CrMo}$	$= 15810 - 6.714T$
${}^1 L_{CrMo}$	$= -6220$
${}^2 L_{CrMo}$	$= 0$
Cr–W system ³⁵⁾	
${}^0 L_{CrW}$	$= -16800 + 10T$
${}^1 L_{CrW}$	$= 9000$
${}^2 L_{CrW}$	$= 0$

Fig. 11 The excess molar Gibbs energy ${}^E G_m$ at $x_X = 0.01$ versus the temperature T for $X = Fe, W$ and Mo shown as dotted, dashed and solid curves, respectively.

repulsive for $X = W$ and Mo . The repulsive interaction is more remarkable for $X = Mo$ than for $X = W$. According to the result in Fig. 10, D_W^b is smaller than D_{Fe}^b , and D_{Mo}^b is typically smaller than D_W^b . Consequently, as shown in Fig. 9, D_{Cr}^b is increased by Fe but decreased by W and Mo. This influence is more notable for $X = Mo$ than for $X = W$.

4. Conclusions

The kinetics of the discontinuous precipitation in the Ni–Cr and Ni–Cr– X systems was experimentally observed using the Ni–38Cr, Ni–38Cr–0.9Fe, Ni–38Cr–3.2W and Ni–38Cr–1.7Mo alloys with the single-phase microstructure of the fcc- γ phase. These alloys were isothermally annealed at temperatures of 873–1023 K for various periods up to 2300 h. During isothermal annealing, the discontinuous precipitation of the Cr-rich bcc- α phase takes place in the Ni-rich γ matrix. Owing to the discontinuous precipitation, the cell consisting

of the γ and α lamellae is formed along the grain boundary of the γ matrix and then grows into the γ matrix under steady-state conditions. The growth rate and the interlamellar spacing of the cell mostly monotonically increase with increasing annealing temperature at 873–1023 K. The cell growth is retarded by W and Mo but not by Fe. The retardation is more remarkable for Mo than for W. A kinetic model for the binary discontinuous precipitation controlled by boundary diffusion was proposed by Aaronson and Liu.¹¹⁾ Their model was used to analyze quantitatively the observation. The analysis shows that the boundary diffusion of Cr along the moving cell boundary is decelerated by W and Mo but slightly accelerated by Fe. The thermodynamic interaction between Cr and the alloying component in the moving cell boundary yields such influence of the alloying component on the boundary diffusion. Therefore, the retardation of the cell growth is attributed to the deceleration of the Cr boundary diffusion.

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