Interdiffusion in Co Solid Solutions of Co–Al–Cr–Ni System at 1423 K

Yoritoshi Minamino¹, Yuichiro Koizumi¹, Nobuhiro Tsuji¹, Toru Yamada^{1,*} and Tomoshi Takahashi²

¹Department of Adaptive Machine Systems, Graduate School of Engineering, Osaka University, Suita 565-0871, Japan

²Department of Materials Science and Engineering, Niihama National College of Technology, Niihama 792-8580, Japan

Binary, ternary and quaternary interdiffusion experiments have been investigated in cobalt solid solutions including Al, Cr, and Ni elements at 1423 K. The direct interdiffusion coefficients of Al, Cr and Ni are positive. Among them, the coefficients of Al are the largest, and those of Ni are the smallest. The indirect interdiffusion coefficients between Al and Cr are positive, but those between Al (or Cr) and Ni are negative. The addition of Al element to Co solid solution largely enhances diffusion but the addition of Cr and Ni elements slightly enhances diffusion. The effect of the addition of elements on interdiffusion are evaluated quantitatively from the factors related to the solidus temperature of Co solid solutions, the diffusivity of elements in pure Co and the interaction parameters between solute elements. The evaluated values of interdiffusion coefficients are in good agreement with the experimental ones.

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1. Introduction

According to the phase diagrams of Co alloys, there are a lot of solute elements which extend the Co solid solutions over a wide composition range.¹⁾ This Co solid solution with the wide composition ranges enables us newly to develop their good mechanical and physical properties or widely to improve them by controlling their compositions. For instance, the industrial heat-resistance Co alloys include a lot of solute elements: the Cr, Al and Si elements for improvement in resistance of oxidation and vanadium attack, and the Ni, Mo and W elements for improvement in high temperature strength. The interdiffusion coefficients play an important role to understand the phenomena in these multi-component Co alloys caused by the interdiffusion process at high temperatures such as oxidation, creep, transformation, aging and so on. Accordingly, a lot of reports have been published on diffusion in pure Co and binary Co alloys.²⁾ But, these data are often insufficient or unavailable against the complicated phenomena in multi-components alloys, because the diffusion coefficients are sensitive to the solute concentrations and the interactions exist between solute elements. In spite of this necessity, the interdiffusion studies in multi-components Co alloys have been performed only in Co–Cr–Ni and Co–Fe–Ni systems.^{3–6)} However, there is no report on interdiffusion in quaternary Co alloys. Thus, the accumulation of diffusion data on multi-component alloys is required, because the commercial Co alloys contain the various elements as mentioned above.

From the Fick's law, the interdiffusion flux of element i in a n -component alloy, $\tilde{J}_i$, is expressed by following equation:⁷⁾

$$\tilde{J}_i = - \sum_{j=1}^{n-1} \tilde{D}_{ij}^n \frac{\partial C_j}{\partial x} \quad (i = 1, 2, \dots, n-1) \quad (1)$$

where C_i is the concentration of solute element i , $\tilde{D}_{ii}^n$ and $\tilde{D}_{ij}^n$ are the interdiffusion coefficients (here, $\tilde{D}_{ii}^n$ is also called

“direct interdiffusion coefficient, and $\tilde{D}_{ij}^n$ “indirect one”). It is clear from eq. (1) that the $(n-1)^2$ interdiffusion coefficients are needed to describe interdiffusion in the n -component alloy. This increase in number of coefficients is due to the interactions between the solute elements, namely, the direct coefficients represent the influences of concentration gradient of element i on its own flux, while the indirect ones represent the influence of the concentration gradients of element j on the flux of element i . Therefore, many interdiffusion coefficients in n -components alloys and an understanding of diffusional and thermodynamic interaction among the solute elements make the diffusion experiments more complicated and require more endeavors for evaluation of interdiffusion coefficients in the higher order alloys.

The purposes of this report are systematically to investigate the interdiffusion at 1473 K in the Co solid solutions of binary Co alloys (Co–Al, Co–Cr and Co–Ni systems), ternary alloys (Co–Al–Cr, Co–Al–Ni and Co–Cr–Ni systems) and quaternary alloys (Co–Al–Cr–Ni system) because the elements of Al, Cr and Ni are usually added to the Co metals for the industrial use, and quantitatively to express the interdiffusion coefficients in ternary and quaternary alloys in taking consideration with interactions between solute elements.

2. Experimental Procedures

2.1 Preparation of diffusion couples

Ingots of pure cobalt, various kinds of binary, ternary and quaternary alloys were prepared with pure metals of 99.99 mass% Al, 99.9 mass% Co, 99.9 mass% Cr and 99.9 mass% Ni by an argon arc melting. Their compositions are given in Table 1. According to the phase diagrams, these alloys are in the area of Co solid solution at 1423 K and 1573 K. The ingots were cut into alloy bars of about $10 \times 10 \times 50 \text{ mm}^3$. These bars were sealed into quartz capsules with argon gas about 20 kPa and then annealed at 1573 K for 108 ks for homogenization. After the homogenization, these bars were quenched into ice water. The single

*Graduate Student, Osaka University. Present address: Torai Co. Ltd., Otsu 520-0842, Japan.

Table 1 Initial alloy compositions for binary, ternary and quaternary diffusion couples.

No	Al (at%)	Cr (at%)	Ni (at%)	Co (at%)
P	—	—	—	100
A1	10	—	—	90
C1	—	15	—	85
C2	—	20	—	80
C3	—	25	—	75
C4	—	30	—	70
AC1	10	5	—	85
AC2	10	10	—	80
AC3	10	15	—	75
AC4	5	30	—	65
AC5	10	20	—	70
N1	—	—	15	85
N2	—	—	20	80
N3	—	—	25	75
N4	—	—	30	70
AN1	10	—	5	85
AN2	10	—	10	80
AN3	10	—	15	75
AN4	5	—	30	65
AN5	10	—	20	70
AN6	10	—	30	60
CN1	—	10	25	65
CN2	—	15	20	65
CN3	—	20	15	65
CN4	—	25	10	65
CN5	—	30	30	40
ACN1	2.5	12.5	14.25	70.75
ACN2	7.5	17.5	16.25	58.75
ACN3	2.5	16.25	17.35	63.75
ACN4	7.5	13.75	12.5	66.25
ACN5	3.75	17.5	12.5	66.25
ACN6	6.25	12.5	17.5	63.75

phase and homogeneity of bars were verified by a metallurgical optical microscope and an electron probe microanalyzer (EPMA). The blocks of about $8 \times 8 \times 2 \text{ mm}^3$ were cut from the homogenized bars, and their surfaces were polished metallographically with $0.3 \mu\text{m}$ alumina powder. Immediately, the diffusion couples were assembled with the alloy blocks according to the combinations of alloys in Table 2, and they were bonded by using a diffusion bonding apparatus; each couple was heated from the room temperature to 1123 K within 306 s under the vacuum of

$9.3 \times 10^{-2} \text{ Pa}$ and then pressed for 100 s with the loading of 3.4–13.4 kN as the first bonding. Subsequently, this couple was heated from 1123 to 1273 K for 54 s without loading, pressed again for 90 s with the loading of 3.4–13.4 kN and then held at 1273 K for 300 s without loading. After this bonding, the diffusion couple was cooled from 1273 K to room temperature for 380 s by using the argon gas. The diffusion distance during this bonding treatment is less than $1 \mu\text{m}$, and it can be ignored when compared with the diffusion distance due to a long diffusion annealing at higher temperature of 1423 K as mentioned later.

2.2 Diffusion profiles

The diffusion couples were sealed into quartz capsules with argon gas, whose pressure was 90 kPa at annealing temperature of 1423 K, and then all of them were annealed at 1423 K for 172.8 ks. After the diffusion annealing, the diffusion couples were cooled by quenching the capsules into ice water and then breaking the capsules in ice water. These diffusion couples were mounted in quick-mount resin, and then they were sectioned parallel to the direction of diffusion in order to expose the cross section in the middle part of diffusion couples where there are no affect of oxidation and evaporation from surface of the couples. The sections were polished with $0.3 \mu\text{m}$ alumina powder. The X-ray spectra of Al-K α , Cr-K α and Ni-K α radiations were then measured on the polished surface of diffusion couples parallel to the diffusion direction by EPMA. The X-ray intensities were converted to the concentrations for the diffusion profiles by the ZAF method and with help of standard alloys.⁸⁾

2.3 Interdiffusion coefficients

The binary interdiffusion coefficients were evaluated from the diffusion profiles in the binary diffusion couples by Matano method and Hall method.^{9,10)} Here, these binary interdiffusion coefficient, $\tilde{D}_{ii}^2$, is described as $\tilde{D}_{\text{Al}}^2$ for Co–Al alloy, $\tilde{D}_{\text{Cr}}^2$ for Co–Cr alloy and $\tilde{D}_{\text{Ni}}^2$ for Co–Ni alloy. On the other hand, four kinds of ternary interdiffusion coefficients, $\tilde{D}_{ii}^3$, $\tilde{D}_{ij}^3$, $\tilde{D}_{jj}^3$ and $\tilde{D}_{ji}^3$, were calculated from the diffusion profiles in ternary couples by the extended Matano method.¹¹⁾ This extended Matano method needs the diffusion profiles to have a common concentration, that is, the diffusion paths in two independent ternary diffusion couples annealed at same temperatures must intersect in isothermal ternary phase diagram. These ternary interdiffusion coefficients in Co– i – j system, $\tilde{D}_{ii}^3$ and $\tilde{D}_{ij}^3$, are written as follows: $\tilde{D}_{\text{AlAl}}^{3\text{AlCr}}$,

Table 2 Alloy combinations of the diffusion couples for binary, ternary and quaternary Co alloys.

Binary couples Co–X	Ternary couples Co–Al–Cr	Ternary couples Co–Al–Ni	Ternary couples Co–Cr–Ni	Quaternary couples Co–Al–Cr–Ni
P-A1	P-AC4	P-AN4	P-CN1	ACN1-ACN2
P-C4	P-AC5	P-AN5	P-CN2	ACN3-ACN4
P-N4	C1-AC1	P-AN6	P-CN3	ACN5-ACN6
	C2-AC2	N1-AN1	P-CN4	
	C3-AC3	N2-AN2	P-CN5	
		N3-AN3	C3-N3	
			C4-N4	

$\tilde{D}_{AlCr}^{3AlCr}$, $\tilde{D}_{CrCr}^{3AlCr}$ and $\tilde{D}_{CrAl}^{3AlCr}$ for Co–Al–Cr system, $\tilde{D}_{AlNi}^{3AlNi}$, $\tilde{D}_{CrNi}^{3AlNi}$ and $\tilde{D}_{NiAl}^{3AlNi}$ for Co–Al–Ni system, and $\tilde{D}_{CrNi}^{3CrNi}$, $\tilde{D}_{CrNi}^{3CrNi}$ and $\tilde{D}_{NiCr}^{3CrNi}$ for Co–Cr–Ni system. The detailed procedure for determining the interdiffusion coefficients in binary alloys by Hall method and Matano method, and those in ternary alloys by the extended Matano method also has been thoroughly given elsewhere.^{12,13)}

The nine kinds of quaternary interdiffusion coefficients, $\tilde{D}_{AlAl}^4$, $\tilde{D}_{AlCr}^4$, $\tilde{D}_{AlNi}^4$, $\tilde{D}_{CrAl}^4$, $\tilde{D}_{CrCr}^4$, $\tilde{D}_{CrNi}^4$, $\tilde{D}_{NiAl}^4$, $\tilde{D}_{NiCr}^4$ and $\tilde{D}_{NiNi}^4$, were evaluated from the diffusion profiles in quaternary diffusion couples by square root diffusivity method.¹⁴⁾ It is quite difficult to evaluate them by applying the extended Matano method, because the extended Matano method requires a common concentration of nine diffusion profiles as the intersection of three diffusion paths in isothermal three-dimensional quaternary phase diagram space and this requirement is quite difficult to be satisfied. In order to avoid this difficulty, Morral *et al.* have presented the square root diffusivity method, which did not strictly need one intersection of three diffusion paths.

The square root diffusivities are defined by the following relationship:¹⁴⁾

$$[\tilde{D}] = [r][r] \quad (2)$$

Elements of $[r]$ matrix for quaternary system, r_{ij} , are calculated from the diffusion profiles by eq. (4), which is derived on the assumption that the diffusivities are constant:

$$[S] = -\sqrt{t/\pi}[r][\Delta C] \quad (3)$$

$$S_i = \int_0^\infty (C_i - C_i^+) dx = -\sqrt{t/\pi} \sum_k^3 r_{ik} \Delta C_k^0 \quad (4)$$

where i refers to one of three solutes in quaternary alloy, ΔC_i^0 is the concentration difference from initial concentrations on the right side of the couple to that of the left side, $\Delta C_i^0 = C_i^+ - C_i^-$, and S_i is the amount of solute i which has passed $x = 0$ (Matano interface) in time t . On the assumption that the diffusivity is constant, the initial concentration differences in the diffusion couples are needed to be small on the order of 5 at% or less. Therefore, $\Delta C_i^0 = C_i^+ - C_i^-$ in this research is designed to be 5 at%. The experimental procedures to determine the nine interdiffusion coefficients are to measure the diffusion profiles of each element in three kinds of independent diffusion couples with the same average composition of initial concentrations in both side of the couples, and to calculate $[\tilde{D}]$ by eq. (2) with the elements of $[r]$ solved from nine values of S_i and nine values of ΔC_j^0 of the diffusion profiles by using eq. (3).

3. Experimental Results

3.1 Diffusion profiles

Figures 1(a), (b), and (c) show, as examples, the diffusion profiles of quaternary diffusion couples of ACN1-ACN2, ACN3-ACN4 and ACN5-ACN6 annealed at 1423 K for 172.8 ks, respectively. On these profiles, $x = 0$ refers to the Matano plane. All profiles exhibit the typical symmetrical S-shaped profiles and they have the average concentrations of initial concentrations in both sides of the couples (5 at%Al, 15 at%Cr and 15 at%Ni) quite near the Matano plane because

Fig. 1 The diffusion profiles in Co–Cr–Ni–Al systems; the (a) ACN1/ACN2, (b) ACN3/ACN4 and (c) ACN5/ACN6 diffusion couples annealed at 1423 K for 172.8 ks.

of the diffusion couples with small difference in terminal compositions of diffusion couples. The diffusion distance of aluminum is the longest and that of nickel is the shortest among them. These indicate that the diffusivities are almost constant in the small concentration range between terminal compositions and that the aluminum element diffuses fast and nickel element does slow. The diffusion profile of nickel in the ACN1/ACN2 diffusion couple exposes “up-hill diffusion” as shown in Fig. 1(a); there are maximum on the high Ni concentration side and minimum on the low Ni concentration side in the diffusion couple. The up-hill diffusion is also on the Cr diffusion profile as shown in Fig. 1(c). According to eq. (1), the up-hill diffusion of an element occurs in a higher order than three components alloy, because the diffusion flux of the element in multi-components alloy is brought out by the concentration gradient of other element as well as its own concentration gradient. The magnitude of this diffusion flux due to the gradients of other elements depends on interactions between solute elements.

The typical S typed profiles similar to the quaternary profiles were observed in the binary and ternary diffusion couples. Especially, the up-hill diffusion also appeared in the ternary diffusion profiles. Guy and Philibert reported the up-hill diffusion of Ni element due to the Cr concentration

Fig. 2 Diffusion paths in (a) Co–Al–Cr system, (b) Co–Al–Ni system and (c) Co–Cr–Ni system.

Fig. 3 Projections of diffusion paths in CNA1/CNA2, CNA3/CNA4 and CNA5/CNA6 couples onto the (a) Al concentration–Cr concentration plane, (b) Al concentration–Ni concentration plane, and (c) Ni concentration–Cr concentration plane.

gradient in Co–Cr–Ni system at 1573 K.⁵⁾ Their experiment results is consistent with the observation of up-hill diffusion in Co–Cr–Ni alloys at 1423 K of this research.

3.2 Diffusion paths

The ternary diffusion paths drawn by re-plotting the concentration profiles are shown for all ternary couples on Co–Al–Cr, Co–Al–Ni and Co–Cr–Ni ternary triangles in Figs. 2(a), (b), and (c), respectively. The diffusion paths show the typical S-shaped curves. The initial direction of the diffusion path tends to run along the line of constant composition of more slowly diffusing component. Therefore, the initial directions of the diffusion paths indicate that Al element diffuses faster than the Cr element and Ni in Co–Al–Cr and Co–Al–Ni systems respectively, and that the Cr element is the faster diffusing element than the Ni one in Co–Cr–Ni system. This is consistent with the results of diffusion profiles as mentioned above. It is also apparent from Fig. 2 that the magnitude of the curvature of Co–Al–Ni system is the largest among three systems. This also indicates the fastest diffusing Al element and the slowest diffusing Ni element, since the curvature mainly depends on the difference in the diffusivities of components. The diffusion paths intersect one another at many composition points, at which

the interdiffusion coefficients are evaluated from the diffusion profiles by the extended Matano method. The quaternary diffusion paths are also shown as the projection onto the Al–Cr plane, the Al–Ni plane and the Cr–Ni plane in Figs. 3(a)–(c), respectively. These projections also show the curvature with the initial directions nearly along the line of constant composition of more slowly diffusing component; the constant compositions of Cr in Co–Al–Cr system, Ni in Co–Al–Ni system and Ni in Co–Cr–Ni system. Furthermore, the curvature of the diffusion path on Co–Al–Ni plane is also largest. The three kinds of diffusion paths intersect each other quite near the composition of Co–5 at%Al–15 at%Cr–15 at%Ni. This small deviation from the average concentrations of terminal compositions to the composition of intersections enables us to evaluate the quaternary interdiffusion coefficients without a significant effect by square root diffusivity method on the results.

3.3 Interdiffusion coefficients

The experimentally evaluated values of binary, ternary and quaternary interdiffusion coefficients are presented on Co-rich parts of the Co–Al–Cr, Co–Al–Ni and Co–Cr–Ni composition triangles in Figs. 4, 5, and 6, to show their concentration dependence. For simplicity, the interdiffusion

Fig. 4 Experimental interdiffusion coefficients ($10^{-15} \text{ m}^2/\text{s}$) in Co-Al, Co-Cr, Co-Cr-Al and Co-Cr-Ni-Al systems at 1423 K, and calculated contour lines of interdiffusion coefficients.

Fig. 5 Experimental interdiffusion coefficients ($10^{-15} \text{ m}^2/\text{s}$) in Co-Al, Co-Ni, Co-Ni-Al and Co-Cr-Ni-Al systems at 1423 K, and calculated contour lines of interdiffusion coefficients.

Fig. 6 Experimental interdiffusion coefficients ($10^{-15} \text{ m}^2/\text{s}$) in Co-Cr, Co-Ni, Co-Cr-Ni and Co-Al-Cr-Ni systems at 1423 K, and calculated contour lines of interdiffusion coefficients.

coefficients at concentration C (at%i) are described as $\tilde{D}_i^2$ (at%i), $\tilde{D}_{ij}^3$ (at%i) and $\tilde{D}_{ij}^4$ (at%i). The diffusion coefficients of Al, Cr and Ni elements in pure Co, $\tilde{D}_{Al}^2(0)$, $\tilde{D}_{Cr}^2(0)$ and $\tilde{D}_{Ni}^2(0)$, plotted at the Co corners of composition triangles are $9.3 \times 10^{-15} \text{ m}^2/\text{s}$, $2.2 \times 10^{-15} \text{ m}^2/\text{s}$ and $1.3 \times 10^{-15} \text{ m}^2/\text{s}$ respectively. The $\tilde{D}_{Al}^2(0)$ is the largest and $\tilde{D}_{Ni}^2(0)$ is the smallest. The binary interdiffusion coefficients are plotted on the binary Co–Al, Co–Cr and Co–Ni sides of triangles. It can be seen that the binary coefficients increase with solute concentrations from $\tilde{D}_{Al}^2(0) = 9.3 \times 10^{-15} \text{ m}^2/\text{s}$ to $\tilde{D}_{Al}^2(10) = 3.6 \times 10^{-14} \text{ m}^2/\text{s}$, from $\tilde{D}_{Cr}^2(0) = 2.2 \times 10^{-15} \text{ m}^2/\text{s}$ to $\tilde{D}_{Cr}^2(25) = 3.2 \times 10^{-15} \text{ m}^2/\text{s}$, and from $\tilde{D}_{Ni}^2(0) = 1.3 \times 10^{-15} \text{ m}^2/\text{s}$ to $\tilde{D}_{Ni}^2(25) = 1.8 \times 10^{-15} \text{ m}^2/\text{s}$. It appears from these increases that the Al element enhances the interdiffusion largely when compared with Cr and Ni elements.

As shown in Figs. 4, 5, and 6, all of direct coefficients in ternary alloys, $\tilde{D}_{AlAl}^{3CrAl}$, $\tilde{D}_{CrCr}^{3CrAl}$, $\tilde{D}_{NiAl}^{3NiAl}$, $\tilde{D}_{NiNi}^{3NiAl}$, $\tilde{D}_{CrCr}^{3CrNi}$ and $\tilde{D}_{NiNi}^{3CrNi}$, are positive. The $\tilde{D}_{AlAl}^{3CrAl}$, $\tilde{D}_{CrCr}^{3CrAl}$, $\tilde{D}_{NiAl}^{3NiAl}$ and $\tilde{D}_{NiNi}^{3NiAl}$ increase largely with the Al concentration, but slightly with the Cr or Ni concentrations. On the other hand, the $\tilde{D}_{CrCr}^{3CrNi}$ and $\tilde{D}_{NiNi}^{3CrNi}$ reveal a slight increase with Cr and Ni concentrations, their concentration dependence being similar to each other. From the research of Guy *et al.*,⁶⁾ the concentration gradient of element j becomes essentially zero and then the diffusion flux of element i in ternary alloy must be essentially the same as that in binary alloy, when the concentration of solute element j approaches to zero. Therefore, the direct coefficients become equal to the binary interdiffusion coefficients as follows;

$$\lim_{C_j \rightarrow 0} \tilde{D}_{ii}^{3ij} = \tilde{D}_i^2 \quad (5)$$

Thus the ternary direct coefficients are closely linked to the binary coefficients, and their concentration dependence is similar to that of binary interdiffusion in the dilute region of solute element j .

The indirect coefficients of $\tilde{D}_{AlCr}^{3CrAl}$ and $\tilde{D}_{CrAl}^{3CrAl}$ are positive, while the $\tilde{D}_{NiAl}^{3NiAl}$, $\tilde{D}_{AlNi}^{3NiAl}$, $\tilde{D}_{CrNi}^{3CrNi}$ and $\tilde{D}_{NiCr}^{3CrNi}$ are negative. The $\tilde{D}_{AlCr}^{3CrAl}$ and $\tilde{D}_{AlNi}^{3NiAl}$ decrease to zero on the Co–Cr and Co–Ni sides with decreasing Al concentration, being almost independent of the Cr and Ni concentration. Likewise, the $\tilde{D}_{CrNi}^{3CrNi}$ and $\tilde{D}_{NiCr}^{3CrNi}$ respectively approach to zero with decreasing Cr and Ni concentrations, being independent of the Ni and Cr concentrations. On the other hand, the $\tilde{D}_{CrAl}^{3CrAl}$ and $\tilde{D}_{NiAl}^{3NiAl}$ show a complicated concentration dependence but they respectively decrease to zero with decreasing Cr and Ni concentrations. Their trend to decrease to zero is in good accordance with the relation between $\tilde{D}_{ij}^{3ij}$ and concentration i presented by Guy *et al.*,⁶⁾

$$\lim_{C_i \rightarrow 0} \tilde{D}_{ij}^{3ij} = 0 \quad (6)$$

In the Co–Cr–Ni system at 1573 K, Guy *et al.* reported that the $\tilde{D}_{CrCr}^{3CrNi}$, $\tilde{D}_{NiNi}^{3CrNi}$, $\tilde{D}_{CrNi}^{3CrNi}$ and $\tilde{D}_{NiCr}^{3CrNi}$ were 6×10^{-14} , 2×10^{-14} , -1×10^{-15} and $-1 \times 10^{-16} \text{ m}^2/\text{s}$ at Co–9 at%Cr–21.4 at%Ni respectively.⁶⁾ On the other hand, the average values of $\tilde{D}_{CrCr}^{3CrNi} = 4.8 \times 10^{-15}$, $\tilde{D}_{NiNi}^{3CrNi} = 2.0 \times 10^{-15}$, $\tilde{D}_{CrNi}^{3CrNi} = -1.8 \times 10^{-16}$ and $\tilde{D}_{NiCr}^{3CrNi} = -4.3 \times 10^{-16} \text{ m}^2/\text{s}$ are evaluated from the present results near the concentration of Co–9 at%Cr–21.4 at%Ni at 1423 K. Though these values

cannot be directly compared to each other, the signs of coefficients by Guy *et al.* are consistent with those of this research, and the value of $\tilde{D}_{CrCr}^{3CrNi} / \tilde{D}_{NiNi}^{3CrNi} = 3$ by Guy *et al.* is close to 2.4 of the present research.

Figures 4, 5, and 6 also show nine quaternary interdiffusion coefficients at Co–5 at%Al–15 at%Cr–15 at%Ni evaluated by the square root diffusivity method as projections onto the Co–Al–Cr, Co–Al–Ni and Co–Cr–Ni planes. The direct coefficients, $\tilde{D}_{AlAl}^4$, $\tilde{D}_{CrCr}^4$ and $\tilde{D}_{NiNi}^4$, and some of indirect coefficients, $\tilde{D}_{AlCr}^4$ and $\tilde{D}_{CrAl}^4$, are positive, while the other indirect coefficients, $\tilde{D}_{AlNi}^4$, $\tilde{D}_{NiAl}^4$, $\tilde{D}_{CrNi}^4$ and $\tilde{D}_{NiCr}^4$, are negative. These signs of quaternary coefficients are in accordance with those of ternary coefficients. The absolute values of quaternary coefficients projected on Co–Al–Cr and Co–Al–Ni planes are almost equal to or slightly larger than those of ternary coefficients around the concentrations of Co–5 at%Al–15 at%Cr and Co–5 at%Al–15 at%Ni respectively. On the other hand, the quaternary absolute values on Co–Cr–Ni plane are comparatively large when compared with those of ternary coefficients around the Co–15 at%Cr–15 at%Ni. These facts indicate that the Al solute element largely enhances interdiffusion in the quaternary alloy.

4. Discussion

It often becomes necessary to make reasonable approximations for diffusion coefficients in higher order alloys, since the experimental data on interdiffusion in multi-component alloys are quite limited because of their complicated and elaborated experiments. Therefore, it is helpful to establish quantitative procedures for estimation of interdiffusion in n-component alloys. In this research, it is found that the binary and ternary interdiffusion coefficients are sensitive to the concentrations of solute elements, and that the quaternary coefficients are also enhanced from the ternary coefficients by additions of the elements to ternary alloys. These results of this research are consistent with the experimental observation by Birchenall¹⁵⁾ that alloying elements which lower the melting point of an alloy enhance the diffusivity as their amounts dissolving to the alloy is increased.¹⁵⁾ The quantitative approximations can be made for estimation of interdiffusion coefficients in high order alloys under the concept of the generalization by Birchenall,¹⁵⁾ as follows.

An empirical relationship that the activation energy for diffusion, Q , is a function of melting temperature, T_m , and the reasonable value of frequency factor is approximately constant of $D_0 = 5 \times 10^{-5} \text{ m}^2/\text{s}$, has been given by Cahoon and Sherby as follows.¹⁶⁾ For all elements with face centered cubic structure,

$$Q = 19RT_m \quad (7)$$

where R is the gas constant. This relation is supported by Beke who theoretically has shown that the bonding strength of metal atoms and the Q are proportional to the T_m .¹⁷⁾ In the vacancy mechanism, the Q for diffusion is the sum of the vacancy formation energy and migration energy. The vacancy formation energy is evaluated to be about half of the total bonding energy between atoms, since an atom is removed from the inner part of crystal by breaking the

bonding with surrounding atoms and then attached to the surface of crystal by producing new atomic bonding with some surface atoms.¹⁸⁾ The migration energy is also related to the bonding energy, because some of the atomic bonds are broken when atom jumps to the nearest neighbor vacancy site. On the other hand, the melting temperature gives an indication of the bonding energy; a crystal has the higher melting point if the atomic bonding is larger because the crystal with stronger atomic bondings sustain its solid structure by overcoming more severe atomic vibration at higher temperatures.¹⁹⁾ It is reasonable to assume that eq. (7) is qualitatively held for diffusion in alloys, because the correlation in alloys can be explained by similar way to what described above.

When eq. (7) is applied to diffusion in alloys, eq. (7) is rewritten as follows;

$$Q(C) = 19RT_m(C) \quad (8)$$

where $Q(C)$ is the activation energy for diffusion in alloys with concentration C , and $T_m(C)$ is the melting temperature of alloy, in other word, the solidus temperature in alloys with concentration C . For simplicity, the solidus temperatures in Co-rich solid solution of higher order Co alloys are represented in linear relation with the solute concentrations, as follows;

$$T_m(C) = T_m(0) + \sum_i^{n-1} A_i C_i \quad (9)$$

where the melting point of pure Co, $T_m(0)$, is 1768 K, and A_i is the solidus temperature change due to addition of 1 at% solute element in binary alloys. The direct interdiffusion coefficients are represented as the Arrhenius-type equation, by inserting eqs. (8) and (9) to eq. (10) and assuming that the pre-exponential factor, D_0 , is constant against the concentration;

$$\begin{aligned} \tilde{D}_{ii}^n(C) &= D_0 \exp\left(\frac{-Q(C)}{RT}\right) \\ &= D_0 \exp\left(-\frac{19T_m(0)}{T}\right) \exp\left(\frac{-19 \sum_i A_i C_i}{T}\right) \quad (10) \\ &= \tilde{D}_i^2(0) \exp\left(\frac{-19 \sum_i A_i C_i}{T}\right) \end{aligned}$$

where $\tilde{D}_i^2(0)$ is the binary diffusion coefficient at the solute concentration of zero, namely, the impurity diffusion coefficient in pure Co plotted at the Co-corners in Figs. 4, 5, and 6. Figure 7 shows the concentration dependence of interdiffusion coefficients in Co–Al, Co–Cr and Co–Ni alloys and their calculated lines by eq. (10) with $\tilde{D}_{Al}^2(0) = 9.3 \times 10^{-15} \text{ m}^2/\text{s}$ and $A_{Al} = -11.2 \text{ K/at\%Al}$ for Co–Al alloy, $\tilde{D}_{Cr}^2(0) = 2.2 \times 10^{-15} \text{ m}^2/\text{s}$ and $A_{Cr} = -1.1 \text{ K/at\%Cr}$ for Co–Cr alloy, and $\tilde{D}_{Ni}^2(0) = 1.3 \times 10^{-15} \text{ m}^2/\text{s}$ and $A_{Ni} = -1.1 \text{ K/at\%Ni}$ for Co–Ni alloy. From the Co-rich parts of binary phase diagrams,¹⁾ the values of A_i 's were also evaluated to be about $-5.8 \text{ K/at\%Al}$ for Co–Al system, about $-1.2 \text{ K/at\%Cr}$ for Co–Cr system and about $-0.5 \text{ K/at\%Ni}$. Though there are some difference between the A_i 's used in calculation for the concentration dependence of diffusion coefficients and the A_i 's from the solidus lines, they are equivalent to each other

Fig. 7 Concentration dependence of binary interdiffusion coefficients and calculated lines by eqs. (9) and (10).

in order of magnitude.

From the procedures by Kirkaldy *et al.* for ternary alloys,²⁰⁾ we have derived the following relations between the quaternary direct and indirect coefficients in Co– i – j – k alloys ($i, j, k = \text{Al, Cr, Ni}$ and $i \neq j \neq k$);

$$\frac{\tilde{D}_{ij}^4}{\tilde{D}_{ii}^4} = \frac{N_i(N_i + N_{Co})\varepsilon_{ij} + N_i(1 + N_j\varepsilon_{jj}) + N_iN_k\varepsilon_{jk}}{(N_i + N_{Co})(1 + N_i\varepsilon_{ii}) + N_iN_j\varepsilon_{ij} + N_iN_k\varepsilon_{ik}} \quad (11)$$

where N_i is the molar fraction of solute element i , and ε_{ii} and ε_{ij} are Wagner's interaction parameter defined by $\ln \gamma_i = \ln \gamma_i^0 + \sum_{k=1}^{n-1} N_k \varepsilon_{ik} + \dots$, where γ_i is the activity coefficient. In the case of interdiffusion in ternary alloy (Co– i – j system), eq. (11) becomes as follows;

$$\frac{\tilde{D}_{ij}^3}{\tilde{D}_{ii}^3} = \frac{N_i(1 - N_j)\varepsilon_{ij} + N_i(1 + N_j\varepsilon_{jj})}{(1 - N_j)(1 + N_i\varepsilon_{ii}) + N_iN_j\varepsilon_{ji}} \quad (12)$$

When $N_i \cong 0$ and $N_j \cong 0$, eq. (12) has the same equation as the relation in ternary alloys derived by Kirkaldy *et al.*²⁰⁾

Figures 4, 5, and 6 show the contour lines of interdiffusion coefficients in ternary Co–Al–Cr, Co–Al–Ni and Co–Cr–Ni alloys calculated by eqs. (10) and (12) with the values of $\tilde{D}_{Al}^2(0)$, $\tilde{D}_{Cr}^2(0)$, $\tilde{D}_{Ni}^2(0)$ and the interaction parameters given in Table 3. According to the calculated contour lines (Figs. 4 and 5), the similar concentration dependence are calculated for the $\tilde{D}_{AlAl}^{3CrAl}$, $\tilde{D}_{CrCr}^{3CrAl}$, $\tilde{D}_{AlAl}^{3NiAl}$, $\tilde{D}_{NiNi}^{3NiAl}$, $\tilde{D}_{AlCr}^{3CrAl}$ and $\tilde{D}_{AlNi}^{3NiAl}$. The $\tilde{D}_{AlAl}^{3CrAl}$, $\tilde{D}_{CrCr}^{3CrAl}$, $\tilde{D}_{AlAl}^{3NiAl}$ and $\tilde{D}_{NiNi}^{3NiAl}$ increase with Al concentration, being almost independent of the Cr and Ni concentrations, and the $\tilde{D}_{AlCr}^{3CrAl}$ and $\tilde{D}_{AlNi}^{3NiAl}$ approach to zero when the Al concentration goes to zero. They also satisfy the relations of eqs. (5) and (6). On the other hand, the contour lines of $\tilde{D}_{CrAl}^{3CrAl}$ and $\tilde{D}_{NiAl}^{3NiAl}$ are similar to each other, but they reveal their complicated concentration dependence. The $\tilde{D}_{CrAl}^{3CrAl}$ and $\tilde{D}_{NiAl}^{3NiAl}$ largely depend on the Al concentration in the lower Al concentration region, but their dependence on Al concentration becomes smaller with increasing Al concentrations. In addition, the $\tilde{D}_{CrAl}^{3CrAl}$ or $\tilde{D}_{NiAl}^{3NiAl}$ are calculated to approach to zero as the concentration of Cr or Ni goes to zero

Table 3 Wagner's interaction parameters of Co alloys, diffusion coefficients of elements in pure Co and changes of solidus temperatures due to addition of solute elements used in calculation by eqs. (9)–(12).

$\varepsilon_{\text{AlAl}}$	16.3
$\varepsilon_{\text{CrCr}}$	3.47
$\varepsilon_{\text{NiNi}}$	0.19
$\varepsilon_{\text{AlCr}}$	3.2
$\varepsilon_{\text{AlNi}}$	−5.8
$\varepsilon_{\text{CrAl}}$	3.2
$\varepsilon_{\text{CrNi}}$	−2.1
$\varepsilon_{\text{NiAl}}$	−9.5
$\varepsilon_{\text{NiCr}}$	−3
$D_{\text{Al}}^2(0)$	$9.3 \times 10^{-15} \text{ m}^2/\text{s}$
$D_{\text{Cr}}^2(0)$	$2.2 \times 10^{-15} \text{ m}^2/\text{s}$
$D_{\text{Ni}}^2(0)$	$1.3 \times 10^{-15} \text{ m}^2/\text{s}$
A_{Al}	−11.2 K/at%Al
A_{Cr}	−1.1 K/at%Cr
A_{Ni}	−1.1 K/at%Ni

respectively. In the Co–Cr–Ni alloys (Fig. 6), it is calculated that the $\tilde{D}_{\text{CrCr}}^{3\text{CrNi}}$ and $\tilde{D}_{\text{NiNi}}^{3\text{CrNi}}$ increase slightly with both Cr and Ni concentrations, while the $\tilde{D}_{\text{CrNi}}^{3\text{CrNi}}$ and $\tilde{D}_{\text{NiCr}}^{3\text{CrNi}}$ approach to zero with decreasing the Cr and Ni concentrations respectively. Thus, the calculated contour lines fittingly represent the experimental concentration dependence of interdiffusion coefficients in the Co ternary alloys of this research.

The interaction parameters with which the contour lines were calculated (Table 3), give us information about the interaction among solute atoms in ternary Co alloys. The interaction parameters in Co–Al–Ni alloys are $\varepsilon_{\text{AlNi}} = -5.8$ and $\varepsilon_{\text{NiAl}} = -9.5$, and those in Co–Cr–Ni alloys are $\varepsilon_{\text{CrNi}} = -2.1$ and $\varepsilon_{\text{NiCr}} = -3.0$. These negative values indicate that the Al and Ni atoms more strongly attract to each other than

the Cr and Ni atoms. The relatively strong attraction between Al and Ni atoms is in agreement with the formations of many intermetallic compounds such as NiAl and Ni₃Al compounds between fcc-Al and fcc-Ni metals, while the small interaction between Cr and Ni atoms is also consistent with the simple feature of Cr–Ni phase diagram which has the two phase equilibrium of bcc-Cr and fcc-Ni phases. On the other hand, the positive values of $\varepsilon_{\text{AlCr}} = 3.2$ and $\varepsilon_{\text{CrAl}} = 3.2$ indicate that there is repulsive force between Al and Cr atoms in Co–Al–Cr alloys. However, these positive values are not directly related to the aspect of Al–Cr phase diagram; the Cr element solves in fcc-Al phase quite little, while the Al element can be soluble in bcc-Cr phase over 14 at%Al, and there are a lot of intermetallic compounds in Al–Cr system. Tanaka *et al.* have presented the estimation method for interaction parameters ε_{ij} in the dilute solid solutions.^{21,22)} By this method, the $\varepsilon_{\text{AlCr}} = \varepsilon_{\text{CrAl}} = 3.7$, $\varepsilon_{\text{AlNi}} = \varepsilon_{\text{NiAl}} = -0.85$ and $\varepsilon_{\text{CrNi}} = \varepsilon_{\text{NiCr}} = -0.51$ are calculated. The interaction parameters of this research are consistent with the calculated ones, especially on the signs of the parameters. But the absolute values of calculated ε_{ij} and experimental ones of this research have some discrepancies except the $\varepsilon_{\text{AlCr}}$ and $\varepsilon_{\text{CrAl}}$. This discrepancy is mainly due to the difference in concentrations at which the ε_{ij} is evaluated: Co–5Al–15Cr–15Ni for this study and the dilute solid solution range for calculation by method of Tanaka *et al.*^{21,22)}

Figure 8 shows the comparison between the experimental and calculated quaternary interdiffusion coefficients in Co alloys with various concentrations: pure Co, Co–5Al, Co–15Cr, Co–15Ni, Co–5Al–15Cr, Co–5Al–15Ni, Co–15Cr–15Ni and Co–5Al–15Cr–15Ni (at%). The ternary coefficients drawn in Fig. 8 are the average values of the coefficients around three ternary concentrations, $\tilde{D}_{ii}^3$ and $\tilde{D}_{ij}^3$: Co–5Al–15Cr, Co–5Al–15Ni and Co–15Cr–15Ni. The nine kinds of

Fig. 8 Experimental and calculated values of interdiffusion coefficients in binary, ternary and quaternary Co alloys.

quaternary interdiffusion coefficients were also calculated by eqs. (10) and (11) with $\tilde{D}_{\text{Al}}^2(0)$, $\tilde{D}_{\text{Cr}}^2(0)$, $\tilde{D}_{\text{Ni}}^2(0)$ and the parameters used in the case of ternary coefficients. The direct coefficients in each alloy are higher in the order of Al, Cr and Ni. The calculated values are in good agreement with the experimental ones. Especially, it is noticed that the quaternary interdiffusion coefficients were calculated appropriately from the impurity diffusion coefficients in pure Co, the concentration dependence of binary coefficients and interaction parameters. The comparison between the diffusivities clarifies the effect of solute elements on diffusion in Co alloys. The ratios of coefficients are as follows; in the case of solute addition of 5 at%Al, $\tilde{D}_{\text{Al}}^2(5)/\tilde{D}_{\text{Al}}^2(0) = 2.3$, $\tilde{D}_{\text{CrCr}}^3/\tilde{D}_{\text{Cr}}^2(15) = 2.4$, $\tilde{D}_{\text{NiNi}}^{3\text{NiAl}}/\tilde{D}_{\text{Ni}}^2(15) = 3.4$, $\tilde{D}_{\text{CrCr}}^4/\tilde{D}_{\text{CrCr}}^3 = 2.9$, $\tilde{D}_{\text{NiNi}}^4/\tilde{D}_{\text{NiNi}}^3 = 2.7$, $\tilde{D}_{\text{CrNi}}^4/\tilde{D}_{\text{CrNi}}^3 = 3.7$ and $\tilde{D}_{\text{NiCr}}^4/\tilde{D}_{\text{NiCr}}^3 = 3$; in the case of addition of 15 at%Cr, $\tilde{D}_{\text{Cr}}^2(15)/\tilde{D}_{\text{Cr}}^2(0) = 1.2$, $\tilde{D}_{\text{AlAl}}^3/\tilde{D}_{\text{Al}}^2(5) = 0.7$, $\tilde{D}_{\text{NiNi}}^{3\text{CrNi}}/\tilde{D}_{\text{Ni}}^2(15) = 1.2$, $\tilde{D}_{\text{AlAl}}^4/\tilde{D}_{\text{AlAl}}^3 = 1.2$, $\tilde{D}_{\text{NiNi}}^4/\tilde{D}_{\text{NiNi}}^3 = 0.8$, $\tilde{D}_{\text{AlNi}}^4/\tilde{D}_{\text{AlNi}}^3 = 1.2$ and $\tilde{D}_{\text{NiAl}}^4/\tilde{D}_{\text{NiAl}}^3 = 1$; in the case of solute addition of 15 at%Ni, $\tilde{D}_{\text{Ni}}^2(15)/\tilde{D}_{\text{Ni}}^2(0) = 1.2$, $\tilde{D}_{\text{AlAl}}^{3\text{NiAl}}/\tilde{D}_{\text{Al}}^2(5) = 1.2$, $\tilde{D}_{\text{CrCr}}^3/\tilde{D}_{\text{Cr}}^2(15) = 1.7$, $\tilde{D}_{\text{AlAl}}^4/\tilde{D}_{\text{AlAl}}^3 = 1.9$, $\tilde{D}_{\text{CrCr}}^4/\tilde{D}_{\text{CrCr}}^3 = 2$, $\tilde{D}_{\text{AlCr}}^4/\tilde{D}_{\text{AlCr}}^3 = 1.5$ and $\tilde{D}_{\text{CrAl}}^4/\tilde{D}_{\text{CrAl}}^3 = 1.9$. Thus, the addition of Al to alloys has a greater enhancement in diffusivities than the Cr and Ni additions. These enhancements suggest that the large enhancement due to the Al element reduces the creep properties although the addition of Al element increases the oxidation resistance, while the Cr and Ni elements whose enhancement is small do not reduce the mechanical properties such as creep even by a lot of their addition to Co alloys. Thus, it is also noticed that the enhancements of interdiffusion due to the solute additions even in quaternary alloys is fittingly evaluated by the calculation.

5. Conclusions

Binary, ternary and quaternary interdiffusion have been investigated in cobalt solid solutions of Co–Al, Co–Cr, Co–Ni, Co–Al–Cr, Co–Al–Ni, Co–Cr–Ni and Co–Al–Cr–Ni alloys at 1423 K.

1) The diffusion profiles in binary, ternary and quaternary diffusion exhibit the typical symmetrical S-shaped. The up-hill diffusion appears in the ternary and quaternary diffusion profiles.

2) The ternary diffusion paths on Co–Al–Cr, Co–Al–Ni and Co–Cr–Ni ternary triangles show the typical S-shaped curves with the initial directions nearly along the line of constant composition of more slowly diffusing component. The quaternary diffusion paths as the projection onto the Al–Cr plane, the Al–Ni plane and the Cr–Ni plane also show the

curvatures, and they intersect each other quite near the composition of Co–5 at%Al–15 at%Cr–15 at%Ni.

3) The binary, ternary and quaternary interdiffusion coefficients evaluated from the diffusion profiles reveal that diffusivities of solute elements are larger in the order of Al, Cr and Ni, and that the solute element of Al enhances the interdiffusion largely when compared with Cr and Ni elements. The direct coefficients and some of indirect coefficients are positive, but the indirect coefficients conjugate to Ni element are negative.

4) The effect of the addition of elements on interdiffusion are evaluated quantitatively from the parameters related to the solidus temperature of Co solid solutions, the diffusivity of elements in pure Co and the interaction parameters between solute elements. The evaluated values are in good agreement with the experimental ones.

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