Volume and Grain Boundary Diffusion of Chromium in Ni-Base Ni–Cr–Fe Alloys

Tien-Fu Chen¹, Gyanendra Prasad Tiwari¹, Yoshiaki Iijima¹ and Kiyoshi Yamauchi²

¹Department of Materials Science, Graduate School of Engineering, Tohoku University, Sendai 980-8579, Japan

²Kure Research Laboratory, Babcock Hitachi K.K., Kure 737-8508, Japan

Volume and grain boundary diffusion of chromium in Ni–16 mass%Cr–7 mass%Fe alloys containing 0.004, 0.015 and 0.07 mass% of carbon have been measured using radioactive tracer ⁵¹Cr over the temperature range of 858–1424 K by serial radio-frequency sputter-microsectioning technique. While the volume diffusion coefficients are largely unaffected by the presence of carbon, the increase in carbon content markedly reduces the mobility of chromium atoms along the grain boundaries. As a result, the difference between the activation energy for lattice and grain boundary diffusion decreases with increase in carbon content. In fact, for 0.07 at% carbon, the activation energies for volume and the grain boundary diffusion are nearly same. Among all three alloys, the difference between the volume diffusion coefficient, D_v , as well as δD_{gb} (δ = grain boundary width; D_{gb} = grain boundary diffusion coefficient) decreases gradually in a regular manner with the rise of temperature. Grain boundary energy is reduced by addition of carbon and enhanced by temperature. At higher temperatures, there is no difference between the grain boundary energies of the three alloys.

(Received August 21, 2002; Accepted November 8, 2002)

Keywords: volume diffusion, grain boundary diffusion, chromium diffusion, nickel–chromium–iron alloy, grain boundary energy, carbide, grain boundary precipitate, activation energy

1. Introduction

The incorporation of chromium in iron- and nickel-base alloys gives rise to two main advantages. It contributes significantly to the solid solution strengthening and at the same time, enhances the oxidation resistance. These alloys usually contain some amount of carbon as well to further enhance their load-bearing capacity. The advantages accruing from the combined presence of chromium and carbon are severely compromised if they react to form $M_{23}C_6$ -type of carbides. These carbides are mainly formed at the grain boundaries and lead to the depletion of the chromium from the matrix which decreases the strength as well as the heat resistance capacity. Grain boundary precipitation also causes the embrittlement of the alloy. The rate controlling processes for this phenomenon are the volume and grain boundary diffusion of chromium in the alloy matrix. Quite often, some strong carbide forming elements such as niobium, vanadium and titanium etc. are added to alleviate the situation. However, the phenomenon can be properly controlled only by the adoption of proper heat treatment procedure. The knowledge of the diffusion coefficient of chromium within the matrix as well as along the grain boundaries is great importance as an aid in the design of better alloys. It also serves a very useful purpose in the selection of proper heat treatment so as to avoid carbide precipitation.

In view of the above considerations, the present paper reports the volume and grain boundary diffusion coefficient of chromium using ⁵¹Cr tracer in three nickel-base alloys over a temperature range of 858–1424 K. The composition of the alloys studied is within the range of commercial inconel 600 alloy. The present results, together with the literature data on diffusion in Ni–Cr alloys, are analyzed to establish the influence of carbon on volume and grain boundary diffusion of chromium in this system.

2. Experimental Procedure

The compositions of alloys are given in Table 1. The materials were supplied in the form of rods by Babcock-Hitachi K.K. and solution treated at 1373 K for an hour and then quenched in ice-cold water. After the heat treatment, the grain size varied between 50–70 μm . The rods were then cut into the disc specimens of 8 mm in diameter and 3 mm in thickness. One of the flat faces of the specimens was ground on water-proof abrasive papers and then polished with fine alumina paste. To remove the surface layers which were deformed/strained while polishing, approximately 3 μm depth was sputtered off using argon with the help of a radio-frequency sputtering unit.

The isotope ⁵¹Cr (γ -ray, 0.320 MeV; half-life 27.8 d) was procured from ICN Radiochemicals, USA in the form of CrCl_3 in a 0.5 kmol m^{-3} HCl solution. It was electroplated onto the polished surface of the specimen. To avoid the oxidation of the specimen during the diffusion annealing, it was sealed in vacuum at one end of a U-shape quartz tube. The other end of the sealed tube contained sponge zirconium. For annealing, the both ends of the tube were introduced in an electric furnace preset at the desired temperatures ranging from 858 to 1424 K. The temperatures were controlled within ± 1 K and the time of anneal was varied from 1.6 ks to 2.8 Ms.

The serial radio-frequency sputter-microsectioning technique was employed to determine the concentration profile of the diffusing isotope in the matrix. This technique can be used to take out the fine sections so that the lattice and grain boundary regions of the diffusion penetrations can be easily

Table 1 Chemical composition of H, A and B alloys (in mass%).

Alloy	Ni	Cr	Fe	Mn	Si	P	S	Ti	Nb	C
H	75.85	15.18	7.76	0.35	0.33	0.007	0.004	0.19	—	0.07
A	72.85	16.49	7.40	0.25	0.22	0.007	0.003	—	2.52	0.015
B	74.32	16.24	6.78	0.19	0.06	0.008	0.0008	—	2.34	0.004

differentiated. The specimen was sputtered in argon glow discharge by applying radio-frequency power with a peak-to-peak voltage of 1.6 kV at 13.56 MHz. An aluminium foil was used to collect the sputtered-off material. The collector aluminium foil was moved step by step akin to a camera roll film without interrupting the radio-frequency supply. A constant fraction of more than 60% of the sputtered material could be collected on the foil. For each specimen, 20–40 sections were sputtered. The sectioning rate was measured from the net reduction in thickness and the total time of sputtering. The thickness of the section removed is determined with the help of an interferometric microscope by analyzing the interference step between the protected and sputtered parts of the surface. The total reduction in thickness was also measured by the weight loss method. The intensity of γ -ray emitted from each section was measured with the help of a well-type Tl-activated NaI detector attached to a 1024 channel pulse height analyzer.

3. Results

The boundary conditions used in these experiments are an instantaneous source and a semi-infinite medium. The appropriate solution of Fick's law is given by

$$C(x, t) = \frac{M}{(\pi D_v t)^{1/2}} \exp\left(-\frac{x^2}{4D_v t}\right) \quad (1)$$

where $C(x, t)$ is the concentration of the radioactive tracer at a distance x from the original surface, D_v the volume or lattice diffusion coefficient, t the time of diffusion anneal and M the total amount of deposited tracer at $x = 0$ and $t = 0$. This equation represents the material transport within the lattice through volume diffusion. To determine the rate of material transport within the lattice as well as the grain boundary simultaneously, we need an analytical procedure to separate the contributions of the lattice and the grain boundary to the overall depth profile of the diffusing species. The problem was analyzed independently by Fisher,¹⁾ Suzuoka^{2,3)} and Whipple.⁴⁾ A comparative study of all three treatments was carried out by LeClaire.⁵⁾ According to LeClaire,⁵⁾ Whipple's expression for concentration contour produced through conjoint action of lattice and grain boundary can be adopted for standard boundary conditions used in tracer experiments. Following LeClaire,⁵⁾ it is possible to write

$$\delta D_{gb} = \left(\frac{\partial \ln \bar{C}}{\partial x^{6/5}}\right)^{-5/3} \left(\frac{4D_v}{t}\right)^{1/2} \left(\frac{\partial \ln \bar{C}}{\partial (\eta \beta^{-1/2})^{6/5}}\right)^{5/3} \quad (2)$$

Here $\bar{C}$ is the average concentration of the tracer in the section taken at a depth x perpendicular to the surface of the specimen:

$$\bar{C} = \frac{1}{L} \int_{-L/2}^{L/2} C(x, y, t) dy \quad (3)$$

where y is a coordinate perpendicular to the x axis and L is the length of the crystal in the y -direction.⁶⁾ The quantities η and β in eq. (2) are defined as

$$\eta = \frac{x}{(4D_v t)^{1/2}} \quad (4)$$

and

$$\beta = \left(\frac{\delta D_{gb}}{2D_v^{3/2} t^{1/2}}\right) \quad (5)$$

It was first pointed out by Levine and MacCallum⁷⁾ that for $\beta > 10$, the last term within the bracket in eq. (2) asymptotically approaches the value 0.78. This condition is realized when the flow of diffusing species into the lattice from the grain boundaries becomes comparable to that reaching directly via the lattice and $\ln \bar{C}$ becomes linear in $x^{6/5}$. These are the ideal conditions for the evaluation of the parameter δD_{gb} with the help of eq. (2). From physical considerations, the requirement is that the deeper sections of the matrix should receive a significant amount of the diffusant via the grain boundary. Mathematically, this condition can be expressed as

$$(4D_v t)^{1/2} < 0.2d, \quad (6)$$

where d is the grain diameter. According to Harrison's classification of preferential diffusion along short-circuiting paths, this corresponds to B-type kinetics.⁸⁾ In other words, we need fine grained specimens and sectioning to the depth when $\ln \bar{C}$ is no longer linear in x^2 . The grain sizes used in the present experiments are appropriate for our purpose as shown later by the linearity of $\ln \bar{C}$ in $x^{6/5}$. After proper substitutions, the eq. (2) is transformed to

$$\delta D_{gb} = 0.661 \left(-\frac{\partial \ln \bar{C}}{\partial x^{6/5}}\right)^{-5/3} \left(4\frac{D_v}{t}\right)^{1/2}. \quad (7)$$

Figures 1 and 2 show the plots of $\ln C$ vs. x^2 for the three alloys studied here. The initial linear portion of the curve is used for estimation of D_v with the help of eq. (1). Figures 3 and 4 show the plots of $\ln \bar{C}$ vs. $x^{6/5}$. Here also, the linear portion of the plot is used to calculate the value of δD_{gb} . The Arrhenius plots of D_v and δD_{gb} are shown in Figs. 5 and 6.

Fig. 1 Penetration profiles for volume diffusion of ^{51}Cr in H, A and B alloys at 1073 K.

Fig. 2 Penetration profiles for volume diffusion of ^{51}Cr in H, A and B alloys at 894 K.

Fig. 3 Penetration profiles for grain boundary diffusion of ^{51}Cr in H, A and B alloys at 1073 K.

Fig. 4 Penetration profiles for grain boundary diffusion of ^{51}Cr in H, A and B alloys at 894 K.

Fig. 5 Arrhenius plots for volume diffusion of ^{51}Cr in H, A and B alloys.

Fig. 6 Arrhenius plots of grain boundary diffusion parameters for ^{51}Cr in H, A and B alloys.

The lattice diffusion coefficients and the values of δD_{gb} are recorded in Tables 2 and 3.

According to Guiraldenq and Poyet,⁹⁾ the volume and grain boundary diffusion parameters are related to the grain boundary energy E as follows:

$$E = k/2a^2 [\ln(s\delta D_{\text{gb}}^0/D_v^0) + \ln(1/a)]T + (Q_v - Q_{\text{gb}})/2Na^2, \quad (8)$$

where k is Boltzmann's constant and s is the segregation coefficient indicating the solute enrichment of the grain boundary with respect to the matrix. D_{gb}^0 and D_v^0 , respectively, are the frequency factors for the grain boundary and lattice diffusion. Similarly, Q_{gb} and Q_v are the corresponding

Table 2 Volume diffusion coefficients of ^{51}Cr in H, A and B alloys.

T/K	t/s	$D_v/\text{m}^2\text{s}^{-1}$		
		H	A	B
1424	2.74×10^2	2.0×10^{-14}	3.1×10^{-14}	4.3×10^{-14}
1346	1.62×10^3	1.1×10^{-15}	1.5×10^{-15}	4.2×10^{-15}
1303	2.28×10^3	2.8×10^{-16}		
1298	3.60×10^3		8.0×10^{-16}	1.9×10^{-15}
1240	7.20×10^3			6.1×10^{-16}
1235	7.20×10^3		3.4×10^{-16}	
1223	3.60×10^3	5.1×10^{-17}		
1173	3.60×10^3	1.2×10^{-17}	4.2×10^{-17}	9.0×10^{-17}
1138	5.76×10^4			3.2×10^{-17}
1113	6.04×10^4	2.7×10^{-18}		
1113	1.04×10^4			1.3×10^{-17}
1080	5.40×10^4		3.5×10^{-18}	
1073	7.02×10^4	5.1×10^{-19}	2.5×10^{-18}	5.5×10^{-18}
997	1.54×10^6		1.9×10^{-19}	6.1×10^{-19}
973	2.62×10^5		1.4×10^{-19}	
973	5.91×10^5		7.0×10^{-20}	
973	9.50×10^5		5.5×10^{-20}	2.2×10^{-19}
973	1.36×10^6	1.3×10^{-20}		
921	2.07×10^6		9.4×10^{-21}	
894	1.64×10^6	1.8×10^{-22}		
894	2.84×10^6		3.4×10^{-21}	1.2×10^{-20}
858	2.31×10^6		5.2×10^{-22}	

Table 3 Grain boundary diffusion parameters for ^{51}Cr in H, A and B alloys.

T/K	t/s	$\delta D_{\text{gb}}/\text{m}^3\text{s}^{-1}$		
		H	A	B
1346	1.62×10^3		4.4×10^{-20}	6.1×10^{-20}
1303	2.28×10^3	3.9×10^{-21}		
1235	7.20×10^3		2.5×10^{-21}	
1173	3.60×10^3		9.8×10^{-22}	5.4×10^{-21}
1113	1.03×10^4	1.1×10^{-23}		1.4×10^{-21}
1073	7.02×10^4	4.9×10^{-24}	5.7×10^{-24}	4.8×10^{-22}
973	2.62×10^5		3.9×10^{-24}	5.5×10^{-23}
973	5.90×10^5		2.1×10^{-24}	
973	9.50×10^4	5.7×10^{-26}	1.6×10^{-24}	
894	2.84×10^4	1.7×10^{-27}	1.4×10^{-25}	6.6×10^{-24}

activation energies. a is the average distance between the equilibrium positions of the atoms in the host matrix and N Avogadro's number. According to Moulin *et al.*,¹⁰⁾ segregation coefficient of carbon in the grain boundaries with respect to lattice is practically unity in the concentration level of our interest here. Hence, in calculating the grain boundary energy, the value of the parameter s is taken as unity. Grain boundary energies estimated from eq. (8) are plotted in Figs. 7 and 8.

4. Discussion

4.1 Volume diffusion:

The measurements on volume diffusion coefficient of ^{51}Cr in the three alloys listed in the Table 2 can be represented as follows:

Fig. 7 Temperature dependence of grain boundary energy for H, A and B alloys.

Fig. 8 Plot of grain boundary energy vs. carbon concentration in H, A and B alloys.

Alloy H ($C = 0.070$ mass%)

$$D_v = (1.8_{-0.8}^{+1.4}) \times 10^{-2} \exp\left(\frac{340 \pm 5.4 \text{ kJmol}^{-1}}{RT}\right) \text{m}^2\text{s}^{-1} \quad (9)$$

Alloy A ($C = 0.015$ mass%)

$$D_v = (1.0_{-0.5}^{+1.6}) \times 10^{-3} \exp\left(\frac{300 \pm 4.8 \text{ kJmol}^{-1}}{RT}\right) \text{m}^2\text{s}^{-1} \quad (10)$$

Alloy B ($C = 0.004$ mass%)

$$D_v = (5.1_{-1.8}^{+2.8}) \times 10^{-4} \exp\left(\frac{286 \pm 4.1 \text{ kJmol}^{-1}}{RT}\right) \text{m}^2\text{s}^{-1} \quad (11)$$

In Fig. 9, available data on diffusion of chromium in Ni-Cr (15–30 mass%) alloys are plotted along with the present data. The volume diffusion coefficient measured in our experiments compares very favorably with the literature data on identical alloy composition. Pruthi *et al.*¹¹⁾ have studied the volume diffusion of chromium in inconel 600 between the temperature range of 1073–1523 K using Gruzin's residual activity method and obtained the values of $1.6 \times 10^{-4} \text{ m}^2\text{s}^{-1}$ and 278 kJmol^{-1} for frequency factor and activation energy, respectively. Their D_v values lie in between those for alloys A and B in Fig. 9. Million and Kucera¹²⁾ have studied tracer diffusion of chromium along with iron and nickel in Cr-Fe-Ni system. For Ni-21.5 mass%Cr alloy, their value of $Q_v = 297.8 \text{ kJmol}^{-1}$ and $D_v^0 = 8.63 \times 10^{-4} \text{ m}^2\text{s}^{-1}$ can be considered to be in good agreement with our Q_v and D_v^0 for

Fig. 9 Arrhenius plots for volume diffusion coefficients of ^{51}Cr in Ni-Cr (15–30 mass%) alloys.

low carbon alloy A having a nominal composition of 16 mass%Cr and 7 mass%Fe (Table 1). Present measurements also compare favorably with those of Monma *et al.*¹³⁾ on the diffusion of chromium in Ni-18 mass%Cr alloy. As seen in Fig. 9, the literature data are limited in a higher temperature region above 1073 K, whereas the present data cover a wide temperature range because of the use of the sputter-microsectioning technique.

An inspection of Fig. 5 shows that volume diffusion coefficients among different alloys differ by less than an order of magnitude over the entire temperature range of measurements. Same is true of data in the literature plotted in Fig. 9. More significantly, the difference among different alloys tends to narrow down with the rise in temperature. This is too a common feature of Figs. 5 and 9. This fact suggests that the extrapolated volume diffusion rates will be the same in all alloys at the melting point. It has been shown by Brown and Ashby¹⁴⁾ that the self-diffusion rates for groups of fcc, bcc (alkalies as well as transition), hcp metals and alkali halides are same at the melting point. This is a reflection of close relationship between diffusion and melting parameters which is based on several well established empirical relationships.^{15,16)} We can conclude, therefore, that the diffusion behavior in inconel and Ni-Cr alloys follows the general pattern observed in pure metals.

Figure 10 presents a linear graph between $\ln D_v^0$ and Q_v for the data in Figs. 5 and 9. Such a linear relationship between these two parameters was first suggested by Dienes¹⁷⁾ and Zener¹⁸⁾ on empirical consideration. It was later pointed out by Swalin¹⁹⁾ and Pelleg²⁰⁾ that the identical behavior between $\ln D_v^0$ and Q_v is also predicted by the electrostatic theories of solute diffusion in metals. Past experience has shown that this behavior is generally always seen in solute diffusion²⁰⁾ and interdiffusion in metallic materials²¹⁾ and considered as a characteristic of volume diffusion. A nearly identical diffu-

Fig. 10 Plot of logarithm of preexponential factor, D_v^0 vs. activation energy, Q_v for volume diffusion of ^{51}Cr in Ni-Cr (15–30 mass%) alloys.

Fig. 11 Plot of activation energy for volume diffusion Q_v vs. carbon content in Ni-Cr (15–30 mass%) alloys.

sion coefficient at the melting point and the linear nature of plot between $\ln D_v^0$ and Q_v is indication for the operation of vacancy mechanism. The lattice diffusion data exhibit only a small dependence on the carbon content. This is reflected in a slight positive slope in the Fig. 11 which shows a plot between the activation energy and the carbon content. These observation are similar to those of Moulin *et al.*¹⁰⁾ who studied the effect of carbon content on volume diffusion of nickel and chromium in Ni-20 mass%Cr alloy. The volume diffusion rates for both the elements were not found to be affected by the presence of carbon. Similar effects have been reported for self-diffusion in Fe-B alloys²²⁾ and solute diffusion of phosphorus in Fe-P alloys.²³⁾

4.2 Grain boundary diffusion

The grain boundary diffusion data, listed in Table 3, are represented below:

Alloy H ($C = 0.070$ mass%)

$$\delta D_{gb} = (8.2_{-5.5}^{+6.5}) \times 10^{-8} \exp\left(\frac{335 \pm 9.6 \text{ kJmol}^{-1}}{RT}\right) \text{m}^3 \text{s}^{-1} \quad (12)$$

Alloy A ($C = 0.015$ mass%)

$$\delta D_{gb} = (1.9_{-1.2}^{+3.2}) \times 10^{-9} \exp\left(\frac{227 \pm 8.8 \text{ kJmol}^{-1}}{RT}\right) \text{m}^3 \text{s}^{-1} \quad (13)$$

Alloy B ($C = 0.004$ mass%)

$$\delta D_{gb} = (4.8_{-2.1}^{+3.8}) \times 10^{-12} \exp\left(\frac{203 \pm 5.2 \text{ kJmol}^{-1}}{RT}\right) \text{m}^3 \text{s}^{-1} \quad (14)$$

In contrast to the behavior of volume diffusion, grain boundary diffusion coefficients show a clear dependence on carbon content. This is obvious from Fig. 6. With the increase in carbon content, results point to a definite trend regarding the retardation of the mobility of chromium atoms along the grain boundaries. A similar effect was noticed by Moulin *et al.*¹⁰⁾ on the grain boundary diffusion in Ni-20 mass%Cr alloy. This phenomenon is most likely the consequence of close chemical affinity between carbon and the carbide forming elements, namely the chromium, niobium and titanium. As a result, the diffusing chromium atom sees an atmosphere of carbon atoms around itself. To diffuse, it must first pull itself out of this atmosphere. Only then it can diffuse further along. This phenomenon will have an adverse effect on the diffusion rate of chromium. Segregation of solute elements in the grain boundary is another factor which can slow down the diffusion rates of chromium. Grain boundary energy is lowered by the segregation of atoms. Further, according to Borisov,²²⁾ the reduction in grain boundary energy raises the activation energy for grain boundary diffusion. Equation (8), which is based on Borisov's model, shows that the activation energy for grain boundary diffusion is enhanced due to the lowering of the grain boundary energy if the lattice diffusion coefficient is held constant. In the present context, in addition to sulfur and phosphorus, carbide forming elements chromium, titanium and niobium may segregate in the grain boundary.

In Fig. 12, a plot of $\ln \delta D_{gb}^0$ against Q_{gb} is shown and it includes the literature data in alloys of similar compositions.^{10,11)} The linearity of this plot shows the consistency of the data from different investigators. This is similar to the behavior of lattice diffusion data. In the previous section, we have discussed the fact that the volume diffusion rates in inconel and Ni-Cr alloys approach to a fixed constant value on extrapolation to the melting point. Figure 6 shows that the grain boundary diffusion data for all three alloys shows the same trend. What it suggests is that the monovacancy migration is the operative diffusion mode along the grain boundaries as well.

There seems to be general agreement among different

Fig. 12 Plot of $\ln \delta D_{gb}^0$ vs. Q_{gb} for grain boundary diffusion of ^{51}Cr in Ni-Cr (15–30 mass%) alloys.

investigators that the diffusion along grain boundaries is mediated by the vacancies.^{24–27)} After analysing available data, Balluffi concluded that the data are not inconsistent with vacancy mechanism.²⁵⁾ Balluffi²⁵⁾ also showed that when the parameter δD_{gb} is plotted against the reduced inverse temperature, T_m/T , where T_m is the melting point, the data for various metals fall on a single line within one and a half order of magnitude. However, the most critical evidence in support of vacancy mechanism comes from the measurement of activation volume²⁶⁾ and isotope effect²⁷⁾ in grain boundary diffusion. The activation volume for grain boundary diffusion in silver is 1.1 ± 0.2 atomic volumes compared to 0.93 ± 0.01 atomic volumes for lattice diffusion. This change is in right direction considering the fact that the grain boundaries consist of assembly of various types of dislocation arrays. Isotope effect for grain boundary self-diffusion in silver was measured by Robinson and Peterson.²⁷⁾ The average value was about 0.46. This is again consistent only with the vacancy diffusion. It must be noted here that there is an important difference between the nature of vacancy diffusion between lattice and grain boundary. The vacancy migration within the lattice is random whereas within the grain boundary, it is strongly correlated. This is because except for the high angle boundary, the grain boundary structure does not favor the lateral diffusion onto the neighboring grains via vacancies or otherwise. On the contrary, the diffusion along the grain boundary length is strongly facilitated through vacancy migration. This fact is responsible for the high intrinsic atomic mobility along the grain boundaries.

An inspection of the data on D_v and δD_{gb} recorded in sections 4.1 and 4.2 points to an interesting aspect of the volume and grain boundary diffusion behavior which has not received attention in the literature so far. This is related to the difference in the grain boundary diffusion characteristics between pure metals and concentrated alloys. It is well known that the activation energy for diffusion along the grain boundaries in pure metals is nearly half of the value for volume diffusion; though the actual value varies with the

orientation of the grain boundary with the matrix.²⁸⁾ Against this, for the alloy A studied here, the values for Q_{gb} and Q_v are quite close to each other. For other two compositions also, the magnitudes of Q_{gb} are significantly greater than $0.5Q_v$. We believe that this difference in the grain boundary diffusion behavior between pure metals and concentrated alloys has its origin in the presence of precipitates and the alloying elements within the grain boundaries. It appears, therefore, that for a proper assessment of grain boundary diffusion data, the information regarding the presence of alloying elements within the grain boundaries is necessary.

4.3 Grain boundary energy

The relation between the grain boundary energy and the relative rates of volume and grain boundary diffusion was first derived by Borisov *et al.*²²⁾ In the form of eq. (8), it was adopted by Guiraldenq *et al.*⁹⁾ The important assumptions of doubtful validity made in the derivation by Borisov *et al.*²²⁾ are (a) the configurations of the activated complex in lattice and grain boundary diffusion are same, (b) the presence of grain boundary does not affect the lattice diffusion in the surrounding area, (c) the geometrical arrangements of atoms within the grain and the boundary itself are same and (d) the boundary consists of a single layer of atoms only. Pelleg²⁹⁾ stated that in view of these considerations, the equation derived by Borisov *et al.* must be considered of empirical nature only. However, Pelleg²⁹⁾ then proceeded to apply this equation to available relevant data and reached the surprising conclusion that this equation yields grain boundary energies of the right order in magnitude. It also correctly predicts the temperature effect.

Figure 7 shows the grain boundary energies as a function of the absolute temperature. Grain boundary energy increases with the temperature and decreases with the increase of carbon content. However, the difference between three alloys tends to narrow down and finally disappears on extrapolation at 1515 K. The same data is replotted as a function of carbon concentration for various temperatures in Fig. 8. By 1273 K, the effect of carbon content on the lowering of grain boundary energy wears off completely. The conclusion, therefore, is that carbon content and temperature influence grain boundary energy in opposite manner. Presence of carbon lowers and temperature raises the grain boundary energy. Temperature also tends to mask off the differences between the different alloys.

5. Conclusion

Lattice and grain boundary diffusion has been investigated in a series of three nickel-base Ni–Cr–Fe alloys of varying carbon content. The effect of carbon on lattice diffusivity is minimal but it significantly reduces the diffusion rate of chromium along the grain boundaries. In concentrated alloys,

the mobility of atoms along grain boundaries appears to be hindered by the presence of precipitates and the alloying elements. With the help of grain boundary diffusion and volume diffusion data, grain boundary energy has also been calculated. The grain boundary energy decreases with the carbon content and increases with the temperature. At the highest temperature of the measurements, the grain boundary energy is practically independent of carbon content.

Acknowledgements

The authors are indebted to Kure Research Laboratory, Babcock Hitachi K.K. for support of the present work. The authors thank Mr. R. Nakamura for assistance in preparing the manuscript. The authors also thank referee for his useful comments.

REFERENCES

- 1) J. C. Fisher: J. Appl. Phys. **22** (1951) 74–77.
- 2) T. Suzuoka: Trans. JIM **2** (1961) 25–32.
- 3) T. Suzuoka: J. Phys. Soc. Japan **19** (1964) 839–850.
- 4) R. T. P. Whipple: Philos. Mag. **45** (1961) 1225–1236.
- 5) A. D. LeClaire: Brit. J. Appl. Phys. **14** (1963) 351–356.
- 6) I. Kaur and W. Gust: *Fundamentals of Grain and Interface Boundary Diffusion*, (Ziegler Press, Stuttgart, 1989) p. 36.
- 7) H. S. Levine and C. J. MacCallum: J. Appl. Phys. **31** (1960) 595–599.
- 8) L. G. Harrison: Trans. Faraday Soc. **57** (1961) 1191–1191.
- 9) P. Guiraldenq and P. Poyet: Mem. Sci. Rev. Met. **70** (1973) 715–723.
- 10) P. Moulin, A. M. Huntz and P. Lacombe: Acta Metall. **27** (1979) 1431–1443.
- 11) D. D. Pruthi, M. S. Anand and R. P. Agarwala: J. Nucl. Mater. **164** (1977) 206–210.
- 12) B. Million and J. Kucera: Acta Metall. **17** (1969) 339–344.
- 13) K. Monma, H. Suto and H. Oikawa: J. Japan. Inst. Metals **28** (1964) 188–192.
- 14) L. M. Brown and M. F. Ashby: Acta Metall. **28** (1980) 1085–1101.
- 15) P. G. Shewmon: *Diffusion in Solids*, Second edition, Chapter 2, (TMS, Warrendale, PA, 1989).
- 16) S. Mrowec: *Defect and Diffusion in Solids An Introduction*, Chapter 2, (Elsievers, 1980).
- 17) G. J. Dienes: J. Appl. Phys. **21** (1950) 1189–1192.
- 18) C. Zener: J. Appl. Phys. **22** (1951) 372–375.
- 19) R. A. Swalin: J. Appl. Phys. **27** (1956) 554–555.
- 20) J. Pelleg: Acta Metall. **14** (1966) 229–231.
- 21) K. Hirano, Y. Iijima, K. Araki and H. Homma: Trans. Iron Steel Inst. Japan **17** (1977) 194–203.
- 22) V. T. Borisov, V. M. Golikov and G. V. Scherbedinskiy: Phys. Met. Metall. **17** (1964) 80–84.
- 23) T. Matsuyama, H. Hosokawa and H. Suto: Trans. JIM **24** (1983) 589–594.
- 24) R. F. Canon and J. P. Stark: J. Appl. Phys. **40** (1969) 3466–3473.
- 25) R. W. Balluffi: Phys. Status Solidi **42** (1970) 11–34.
- 26) G. Martin, D. A. Blackburn and Y. Adda: Phys. Status Solidi **23** (1967) 223–228.
- 27) J. T. Robinson and N. L. Peterson: Surf. Sci. **31** (1972) 586–616.
- 28) P. G. Shewmon: *Diffusion in Solids*, Second Edition, Chapter 6, (TMS, Warrendale, PA, 1989).
- 29) J. Pelleg: Philos. Mag. **14** (1966) 595–601.