Lattice and Grain Boundary Diffusion of Copper in γ -Iron*

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The lattice diffusion and the grain boundary diffusion of copper in γ -iron were measured in the temperature range from 1105 to 1210°C by the residual activity method with radio-active tracer ^{64}Cu . The experimental penetration profiles were analysed by the instantaneous source model of grain boundary diffusion proposed by Suzuoka. The temperature dependence of the lattice diffusion coefficient D_ℓ and the grain boundary diffusion coefficient D_{gb} are expressed by the following equations:

$$D_\ell = 4.16 \times 10^{-4} \exp(-305.0 \text{ kJ} \cdot \text{mol}^{-1}/RT) \text{ m}^2 \text{ s}^{-1}$$

$$D_{gb} \cdot \delta = 4.27 \times 10^{-13} \exp(-167.8 \text{ kJ} \cdot \text{mol}^{-1}/RT) \text{ m}^3 \text{ s}^{-1}.$$

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I. Introduction

Fe-Cu binary sintered compacts containing 3–25 wt% Cu are widely used as the mechanical parts, and many papers⁽¹⁾ have been published on the sintering mechanism of Fe-Cu binary mixed powder compacts and sintering methods for the improvement of the mechanical properties. According to these papers, it has been confirmed that the Fe-Cu binary mixed powder compacts expand abruptly at about 1083°C due to Cu melting, and this expansion (swelling) is an obstacle to the sintering of the compacts.

In order to clarify the cause of the above-mentioned anomalous expansion, it is desired to determine the diffusion coefficient of Cu into γ -Fe at above 1083°C. At present, there are a few reports^{(2)~(7)} about the Cu diffusion into γ -Fe at below 1083°C, or into α -Fe. Above the temperature range there is only one report by Rothman⁽⁸⁾ whose measurement, however, was in the temperature range above 1283°C where the effect of boundary diffusion is almost negligible. No reports have been published in the temperature range from 1083°C of Cu melting to 1250°C where the boundary diffusion is effective.

In this experiment, the lattice diffusion and the grain boundary diffusion of copper in γ -

iron were measured in the temperature range from 1105 to 1210°C using radioactive tracer ^{64}Cu , and the data were analysed by the theory of grain boundary diffusion based on the instantaneous source model proposed by Suzuoka^{(9)~(11)}.

II. Experimental Procedure

Iron specimens used in this experiment were cylindrical, 10 mm in length and 11 mm in diameter. Electrolytic iron with the chemical composition listed in Table 1 was used.

The specimens were first annealed under a vacuum of 1.3332×10^{-3} Pa at 1250°C for 24 h, to have the grain size of about 0.8 mm. The parallel sides of specimens were then carefully cleaned through light pickling. The radioactive tracer ^{64}Cu was subsequently chemically plated onto the flat faces of the specimens from a solution of chloride containing both radioactive and inert copper ions. The final thickness of thin layers containing ^{64}Cu was about 0.5 μm , and more than 5×10^5 counts per minute were recorded for all of the specimens. The specimens thus plated with ^{64}Cu were sealed in quartz amples under a

Table 1 Chemical composition of specimen (wt%).

C	Mn	Si	P	S	Cu
0.0035	0.0050	0.0041	0.0011	0.0062	0.0015
Ni	Cr	Al	O	N	Fe
0.0013	0.0017	0.0120	0.0036	0.0020	rest

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Fig. 1 Energy spectrum of γ -ray from ^{64}Cu .

vacuum of 1.3332×10^{-3} Pa, and diffusion-annealed in the temperature range from 1105 to 1210°C in furnaces controlled within $\pm 1^\circ\text{C}$. After the diffusion anneal, the sample diameters were decreased about 1 mm on a precision lath, and the diffusion coefficients were determined by the residual-activity technique, where activity measurements were made on the disc specimen after the removal of successive layers of 5–10 μm from the surface, in a well-type scintillation counter. Figure 1 shows the energy spectrum of γ -ray from ^{64}Cu . The activity was measured by counting the 0.51 and 1.34 MeV γ radiations of ^{64}Cu , and the correction for the decay of ^{64}Cu was done by using the half-time value of ^{64}Cu (12.8 h) during subsequent counting.

III. Experimental Results

When the infinitesimally thin layer of isotope deposited onto semi-infinite specimen was diffusion-annealed, the integral activity (I_n) is given by

$$I_n = \int_{-x_n}^{\infty} \exp \{-\mu(x-x_n)\} \cdot dx, \quad (1)$$

where I_n is the integral activity in units of cpm, μ is the linear absorption coefficient from the radiation by iron, and x_n is the distance from the initial surface to the surface being counted.

Therefore the activity concentration at point x_n from the initial surface is given by

$$\mu I_n - dI_n/dx_n = K \cdot C(x). \quad (2)$$

In this experiment, μI_n is negligibly small for the value of $(-dI_n/dx_n)$, where it is obvious from eq. (2) that the activity concentration is proportional to the term $(-dI_n/dx_n)$, and the penetration curve necessary for analysing by the instantaneous source model of grain boundary diffusion proposed by Suzuoka is given by plotting the logarithm of activity concentration against the 6/5 power of the depth.

Figure 2(a) shows the typical penetration curve of ^{64}Cu into γ -Fe for the specimen

Fig. 2 Typical penetration curve of Cu into γ -Fe. Broken line represents volume diffusion term C_1 and the dotted line represents boundary diffusion term C_2 .

diffusion-annealed at 1105°C for 1.446×10^5 s, analysed by the above-mentioned procedure. The linear part of this penetration curve represents the pure contribution of grain boundary diffusion, and its slope- γ follows the following relation:

$$0.973 \log (\Delta-1) = 6.567 - 1.644 \log \gamma - \log \sqrt{D_\ell \cdot t}, \quad (3)$$

where Δ is $D_{g.b.}/D_\ell$. According to the eq. (3), it is obvious that $D_{g.b.}$ is easily obtained where D_ℓ is known. However, the reliable value of D_ℓ for the Cu into γ -Fe has not yet been reported. Therefore, in this experiment, we used the self-consistent method which allowed us to make the simultaneous determination of D_ℓ and $D_{g.b.}$, in which the observed values are analysed by the relation

$$C_{\text{obs}} = K(C_1 + 1/n C_2), \quad (4)$$

where K is constant, $n = b/\sqrt{D_\ell \cdot t}$, and $2b$ is the mean linear grain size.

At first, assuming the value of D_ℓ , we separate the term C_2 of grain boundary dif-

fusion from the observed value according to eq. (3), and plot the term of lattice diffusion against y^2 as shown in Fig. 2(b), from the slope of which the value of D_ℓ can be obtained. This procedure is repeated until the assumed value of D_ℓ coincides with the calculated value of D_ℓ .

Figures 3 and 4 show the penetration curves and the lattice diffusion part C_ℓ separated by the above-mentioned procedure for all of the specimens, where $C_\ell - y^2$ curves are satisfactorily linear. The values of D_ℓ , $D_{g.b.}$ and other parameters obtained through the analysis by a self-consistent method, are listed in Table 2, where $\beta = \delta(\Delta - 1)/\sqrt{D_\ell \cdot t}$, and δ is the thickness of grain boundary, the value of which is 5×10^{-8} cm according to Fisher⁽¹²⁾.

The temperature dependences of D_ℓ and $D_{g.b.}$ obtained in this experiment, are presented by black dots in Figs. 5 and 6, both of which are found to be in Arrhenius' relation, and the least squares calculation gives the relation (5) for the lattice diffusion coefficient, and the

Fig. 3 Penetration curves of Cu in Fe and lattice diffusion separated from grain boundary diffusion.

Fig. 4 Penetration curves of Cu in Fe and lattice diffusion separated from grain boundary diffusion.

Table 2 Grain boundary diffusion coefficients and other parameters of Cu in γ -Fe.

Specimen No.	1	2	3	4	5
T ($^{\circ}\text{C}$)	1210	1188	1159	1131	1105
$1/T \times 10^4$ (K^{-1})	6.7431	6.8446	6.9832	7.1225	7.2569
$t \times 10^{-5}$ (s)	0.4475	0.8364	1.177	1.633	1.446
$D_{\ell} \times 10^{15}$ (m^2/s)	7.64	4.97	2.94	2.01	1.09
$(D_{\ell} \cdot t)^{1/2} \times 10^5$ (m)	1.85	2.04	1.86	1.81	1.26
$\gamma \times 10^{-2}$	4.20	3.38	3.05	2.99	3.08
$\Delta \times 10^5$	1.34	1.74	2.28	2.42	3.36
$D_b \cdot \delta \times 10^{19}$ (m^3/s)	5.10	4.33	3.35	2.43	1.83
β	3.61	4.28	6.13	6.69	13.38
n	25.2	25.8	58.6	18.3	24.8
Effective grain size (mm)	0.93	1.05	2.18	0.66	0.62

Fig. 5 Temperature dependence of D_L of ^{64}Cu in Fe.

relation (6) for the grain boundary diffusion coefficient, respectively.

$$D_{\ell} = 4.16 \times 10^{-4} \times \exp(-305.0 \text{ kJ} \cdot \text{mol}^{-1}/RT) \text{ m}^2 \text{ s}^{-1}, \quad (5)$$

$$D_{g-b} \cdot \delta = 4.27 \times 10^{-13} \times \exp(-167.8 \text{ kJ} \cdot \text{mol}^{-1}/RT) \text{ m}^3 \text{ s}^{-1}, \quad (6)$$

Fig. 6 Temperature dependence of $D_b \cdot \delta$ of ^{64}Cu in Fe.

IV. Discussion

The solid lines in Fig. 5 show the data of Speich *et al.*⁽⁴⁾ concerning with the lattice diffusion coefficient obtained by a microprobe analysis using the iron specimen plated with inert copper, and their data is reliable.

Anand and Agarwala⁽³⁾, using the residual activity technique, measured the lattice diffusion coefficient of ^{64}Cu into iron in the temperature range from 800 to 1050 $^{\circ}\text{C}$. However, they did not find any discontinuity at the $\alpha \rightarrow \gamma$ transformation temperature in the Arrhenius plot of D_{ℓ} , and their values of D_{ℓ} were some-

Table 3 Published data on diffusion of Cu in Fe.

$D_0 \times 10^4$ (m^2/s)	Q (kJ/mol)	Temperature range ($^\circ\text{C}$)	Worker
3.0	255.2	800–1200	Linder and Karnik
0.57	238.5	800–1050	Anand and Agarwala
1.8	295.0	910–1020	Speich <i>et al.</i>
2.86	306.7	1285–1368	Rothman <i>et al.</i>
92	301.3	910–1050	Lazarev and Golikov
4.16	305.0	1105–1210	Present work

Table 4 Published data on grain boundary diffusion of Cu in Fe.

$\delta \cdot D_0$ ($\text{m}^3 \cdot \text{s}$)	Q (kJ/mol)	Temperature range ($^\circ\text{C}$)	Worker
4.0×10^{-12}	181.6	677– 722	Bergh
13.0×10^{-12}	159.0	707– 870	Lazarev and Golikov
3.2×10^{-12}	177.8	910–1050	Lazarev and Golikov
4.27×10^{-13}	167.8	1105–1210	Present work

what higher than those of Speich *et al.*, in the γ region.

In determining the lattice diffusion of Cu into iron, Rothman *et al.*⁽⁸⁾ at first examined the temperature range where the grain boundary diffusion was predominant, and found that the grain boundary diffusion was predominant at temperatures lower than 815 $^\circ\text{C}$ in the α region, and at temperatures lower than 1250 $^\circ\text{C}$ in the γ region. Therefore the data of Rothman *et al.*, shown in Fig. 5, are concerned with the lattice diffusion coefficients obtained in the temperature range where the contribution of grain boundary diffusion is negligible, and their data are in good agreement with Speich *et al.* However, they only suggested that the grain boundary diffusion was dominant in the γ region lower than 1250 $^\circ\text{C}$, and did not determine the value of D_ℓ separated from grain boundary diffusion.

Lazarev and Golikov⁽⁶⁾ measured the value of D_ℓ separated from D_{g-b} in the γ region from 910 to 1050 $^\circ\text{C}$ lower than the Cu melting point of 1083 $^\circ\text{C}$ and their values of D_ℓ are higher than those of Speich *et al.* and Rothman *et al.*

In this experiment, we determined the values of lattice diffusion coefficient and grain boundary diffusion coefficient simultaneously, in the temperature range between 1105 and 1210 $^\circ\text{C}$. The data is necessary for the sintering of Fe–Cu

binary mixed powder compacts. The temperature dependence of D_ℓ is represented by a straight line as shown in Fig. 5, indicating also that our data is in good accord with those reported by Speich *et al.* and Rothman *et al.* As shown in Table 3, there are no marked differences in activation energy: 295.0 $\text{kJ} \cdot \text{mol}^{-1}$ by Speich *et al.*, 306.7 $\text{kJ} \cdot \text{mol}^{-1}$ by Rothman *et al.*, and 305.0 $\text{kJ} \cdot \text{mol}^{-1}$ in this experiment.

No reports have yet been reported on the grain boundary diffusion coefficient in the temperature range higher than 1083 $^\circ\text{C}$. There is only one report by Lazarev *et al.* in the temperature range between 910 and 1050 $^\circ\text{C}$. The temperature dependence of grain boundary diffusion coefficient obtained in this experiment is represented by a solid line as shown in Fig. 6, and the activation energy calculated from the slope of it is 167.8 $\text{kJ} \cdot \text{mol}^{-1}$ as shown in Table 4. It has been confirmed by James and Leak⁽¹³⁾ that the ratio of the activation energy necessary for the grain boundary diffusion against that for the lattice diffusion coefficient is 0.53. Therefore the value (Q_{g-b}/Q_ℓ) of 0.55 obtained in this experiment is reasonable.

V. Conclusion

The temperature dependences of the volume diffusion coefficient and the grain boundary

diffusion coefficient are given by

$$D_{\ell} = 4.16 \times 10^{-4} \\ \times \exp(-305.0 \text{ kJ} \cdot \text{mol}^{-1}/RT) \text{ m}^2 \text{ s}^{-1},$$

$$D_{g-b} \cdot \delta = 4.27 \times 10^{-13} \\ \times \exp(-167.8 \text{ kJ} \cdot \text{mol}^{-1}/RT) \text{ m}^3 \text{ s}^{-1}.$$

REFERENCES

- (1) For example, H. Mitani, K. Majima and Y. Hanatate: *J. Japan Inst. Metals*, **25** (1961), 639.
- (2) R. Linder and F. Karnik: *Acta Met.*, **3** (1955), 297.
- (3) M. S. Anand and R. P. Agarwala: *J. Appl. Phys.*, **37** (1966), 4248.
- (4) G. R. Speich, J. A. Gula and R. M. Fisher: *The Electron Microprobe*, John Wiley & Sons, Inc., New York, (1966), 525.
- (5) V. A. Lazarev and V. M. Golikov: *Fiz. Metal. Metalloved*, **29** (1970), 154.
- (6) V. A. Lazarev and V. M. Golikov: *Fiz. Metal. Metalloved*, **31** (1971), 885.
- (7) Sigge Bergh: *Jernkont. Ann.*, **155** (1971), 143.
- (8) S. J. Rothman, N. L. Peterson, C. M. Walter and L. T. Nowicki: *J. Appl. Phys.*, **39** (1968), 5041.
- (9) T. Suzuoka: *Trans. JIM*, **2** (1961), 25.
- (10) T. Suzuoka: *Trans. JIM*, **2** (1961), 176.
- (11) T. Suzuoka: *J. Phys. Soc. Japan*, **19** (1964), 839.
- (12) J. C. Fisher: *J. Appl. Phys.*, **22** (1951), 74.
- (13) D. W. James and G. M. Leak: *Phil. Mag.*, **12** (1965), 491.