Interdiffusion in the α Phase of an Fe-Sb System*

By Keizo Nishida**, Harumitsu Murohashi*** and Tsuyoshi Yamamoto****

Iron test pieces were diffusion-annealed at 973~1223 K for 32.4~1584 ks in an evacuated quartz ampoule containing powdered (100~200 mesh) 50 wt% Sb-Fe alloy, consisting of α and ϵ phases, as an Sb vapor source. After annealing, cross-sections of the test pieces were analysed with an EPMA in order to determine the penetration of Sb.

Each penetration curve was analysed by the Matano-Boltzman method to calculate the interdiffusion coefficients, $\tilde{D}$. The activation energies for interdiffusion ($\tilde{Q}$) were also obtained.

The surface concentration of Sb in the test piece ($\alpha_{\max}$) at lower temperatures coincided approximately with the solubility limit reported in the phase diagram of the Fe-Sb system, while a significant deviation in solubility limit was found at higher temperatures. Fine alumina markers placed on the test pieces prior to diffusion remained on the surface after annealing, so that it is considered that Sb atoms diffuse predominantly into the α phase of this system. Each penetration curve except for 1223 K was similar to an error function curve for a particular $\tilde{D}$ value. The value of $\tilde{D}$ showed a relatively small dependence upon the Sb concentration at each temperature. There was a gap in the Arrhenius plot of $\tilde{D}$ owing to magnetic transformation. The activation energies for interdiffusion ($\tilde{Q}$) obtained from the data at higher temperatures decreased with increasing Sb concentration from 249 kJ/mol for 1 at% Sb to 220 kJ/mol for 4 at% Sb. The activation energy for the impurity diffusion of Sb in iron ($Q_{\text{Sb}}^{\text{Fe}}$) was evaluated to be about 262 kJ/mol.

(Received January 6, 1979)

I. Introduction

Up to the present, there are many reports about interdiffusion in Fe-based alloys^{(1)~(9)}. The elements N, P, As, and Sb are involved in the Vb group of the periodic table. As those elements except Sb are involved in steel during its refining process and give a significant deterioration to steel, some of them have been chosen as the subjects of investigation in order to clarify their effects on its mechanical properties. However, except a report for the impurity diffusion of Sb in Fe⁽¹⁰⁾ only a small number of investigations have been performed on the Fe-Sb system. Sb is one of the so-called

metalloid elements and is attracting both technical and theoretical interests because of its characteristic behavior in iron and steel. Diffusion studies on this system can be considered to be of technical interest in view of Sb coating of steel to improve its corrosion resistance⁽¹¹⁾⁽¹²⁾. The phase diagram of the Fe-Sb system and other properties of the alloy have been investigated by Vogel *et al.*⁽¹³⁾ According to a recent investigation reported by Maier *et al.*⁽¹⁴⁾ this system has an α solid solution region containing a γ loop and the α phase has a maximum solubility limit of 30 wt% Sb. There are only two intermediate compounds in this system, i.e., ϵ (suggested as an Fe_3Sb_2 or an Fe_{1+x}Sb) and FeSb_2 . Except Yamaguchi *et al.*⁽¹⁵⁾ no detailed work on its properties has been performed. In a previous diffusion study of the α solid solution of the Fe-Zn system⁽³⁾, it has been observed that Zn atoms diffuse predominantly in this phase at its maximum Zn concentration. As the diameter of Sb atoms is larger than that of Zn atoms, it is important to know interdiffusion coefficients in the Fe-Sb alloy system to summarize the diffusion behavior of different atoms in iron.

* This paper was originally published in Japanese in J. Japan Inst. Metals, **41** (1977), 1101.

** Metals Research Institute, Faculty of Engineering, Hokkaido University, Sapporo 060, Japan.

*** Department of Metallurgy, Faculty of Engineering, Hokkaido University. Present: Graduate School of Education, Hokkaido University, Sapporo 060, Japan.

**** Department of Mechanical Engineering, Hokkaido Institute of Technology, Sapporo 061-24, Japan.

It has been well established that Sb has three vapor species at high temperatures, i.e., Sb, Sb₂, and Sb₄ and that the total pressure of them shows a relatively high value of $1.3 \times 10^{-1} \sim 1.3 \times 10^2$ Pa at 873~1273 K⁽¹⁶⁾. The vapor diffusion method used in previous studies^{(1)~(3)} can be used for this system. The main purpose of the present investigation is to obtain interdiffusion coefficients in the α phase of the Fe-Sb system by a vapor-diffusion method.

II. Experimental

1. Test pieces

The test pieces used for the present experiment contained impurities shown in Table 1. The size of a test piece was 10 mm $\times$ 7 mm, cut from a plate rolled to 2 mm-thick, with its surface polished slightly. The test piece was encapsulated in a quartz tube at 5.3×10^{-4} Pa, and annealed at 1173 K for 4 d. The grain size was controlled to about 0.5~1 mm. The 100~200 mesh powder of 50 wt% Sb-Fe alloy ($\alpha + \epsilon$ phases) as the Sb vapor source was prepared from pure Sb (99.9999 wt%) and electrolytic iron powder (99.8 wt%).

2. Preparation of diffusion couple and diffusion-anneal

The surface of the test piece was finished with No. 1000 emery paper, washed, and degreased. Alumina powder (ϕ 0.3 μ m) was placed on its

Table 1 Impurities in the iron test piece (in wt ppm).

Element	O	C	Si	Mn	P	S	Al
Concentration	35	10	50	10	20	10	40

Fig. 1 Experimental apparatus.

surface as the marker. The test piece was supported in the center of a quartz tube (ϕ 12 mm) by an Fe-Cr alloy wire and the Sb vapor source was charged. Air in the quartz tube was replaced by argon gas several times. The quartz tube was then sealed at 5.3×10^{-4} Pa. The capsule was 80~100 mm long. The test piece was diffusion-annealed in a horizontal electric furnace as shown in Fig. 1 at a temperature within the range of 973~1223 K (± 1 K) for 32.4~1584 ks and the capsule was quenched in cold brine after diffusion-annealing.

3. Analysis by use of an electron probe microanalyser (EPMA) and solution methods of results obtained

After the diffusion-anneal the surface of a test piece was first examined by optical microscopy and analysed by X-ray diffraction. The concentration profile of Sb in the cross-section was analysed with an EPMA after the surface of the test piece was plated with nickel about 1 mm thick. The intensity of the Fe-K α ray from the standard Fe-Sb alloys showed a considerable deviation from an ideal linear relationship with Sb concentration (wt%), whereas that of the Sb-K α ray showed a slight deviation, 4% at most, from the ideal value near 50 wt% Sb. Hence, no correction was performed on the Sb concentration profile obtained by the Sb-K α ray in the cross-section. According to the lattice spacing data of Fe, Sb, ϵ , and FeSb₂⁽¹⁷⁾⁽¹⁸⁾ in this system, the molar volume of ϵ is about 19.7% smaller than that of the ideal value, and for FeSb₂ it is about 15.6% smaller. However, if the ordinate is represented by the volume-fraction of Sb (C_{Sb}) in the Sb penetration curve, no other correction is necessary for the present graphical calculation, because the deviation from the ideal molar volume is less than 4% in the present experimental range of Sb concentration (up to 5 at% Sb).

III. Experimental Results and Discussion

1. Observation of the diffusion-annealed test pieces

Photograph 1 shows a sectional view of the

Photo. 1 Diffusion-annealed cross-section of a test piece showing markers (as polished).

test piece diffusion-annealed at 1073 K for 90 ks. The alumina markers placed on the surface of the test piece prior to diffusion can still be seen on the surface after annealing. The same results were also observed at other temperatures. From these facts, it can be assumed that in case of the formation of the α phase in iron by vapor-diffusion, Sb atoms diffuse predominantly at the marker position. This phenomenon is equal to the result for the Fe-Zn system⁽³⁾.

2. Master curves and surface concentrations in the test pieces

Figure 2 shows the $C_{Sb} - x/\sqrt{t}$ curves, where C_{Sb} is the volume fraction of Sb, x the penetration distance in m and t the diffusion-annealing time in s. They are the Sb penetration curves obtained by EPMA analysis of the specimens diffusion-annealed at 1073 K for 32.4, 57.6, and 90 ks. The curves obtained from these specimens are in good agreement with each other. The difference was within $\pm 0.3\%$.

Figure 3 summarizes the master curves for each diffusion-annealing temperature. The master curve for 1223 K contains the γ phase as shown in the phase diagram but the analysis of the γ phase could not be made, because its concentration range was within the analytical error. The appearance of the master curves seen in the figure is similar to that of an error function at each diffusion-annealing temperature, except at 1223 K, for the α phase of the Fe-Sb system. As an example, the master

Fig. 2 Penetration curves obtained from Fe-Sb (vapor) diffusion couples annealed at 1123 K.

Fig. 3 Penetration curves: Change in the volume fraction of Sb with (distance/time)^{1/2} at various temperatures.

Fig. 4 The penetration curve at 1173 K obtained from Fe-Sb diffusion couples with that obtained from the equation, $c/c_0 = 1 - \text{erf}(x/2\sqrt{Dt})$, where $D = 4.85 \times 10^{-14} \text{ m}^2/\text{s}$.

curve for 1173 K and the error function curve obtained from $c/c_0 = 1 - \text{erf}(x/2\sqrt{Dt})$ are shown in Fig. 4, here $\bar{D} = 4.85 \times 10^{-14} \text{ m}^2/\text{s}$. The

presence of the difference between those two curves indicates that the interdiffusion coefficient in the α phase of the Fe-Sb system depends on the Sb concentration.

The surface concentration ($\alpha_{\max}$) in the diffusion-annealed test pieces are plotted at various temperatures on the Fe-Sb phase diagram (Fig. 5). The result coincides at lower temperatures approximately with the solubility limit reported by Maier *et al.*⁽¹⁴⁾ However, a significant deviation from the solubility limit is found at higher temperatures. In order to ascertain the difference between the above results, an alloy having two equilibrated phases ($\alpha + \varepsilon$) was prepared and the Sb concentration in these phases was determined by EPMA and X-ray analyses. The results are shown in Fig. 5 by crosses. It was found that the Sb concentration in the ε phase of the alloy coincided approximately with the phase diagram, but that the concentration in the α phase coincided with the solubility limit obtained in this study. From these results it seems that the Sb solubility limit in the α phase at 1173 K is significantly low compared with the value reported by Maier *et al.* It will, therefore, be necessary to work in detail on the solubility limit, because the data in the present experiment were only obtained at 1173 K.

Fig. 5 Surface concentration of diffusion-annealed test piece at various temperatures.

3. Interdiffusion coefficients ($\tilde{D}$)

The interdiffusion coefficients were calculated by the Matano-Boltzmann method. These values were compared with the results calculated by means of the methods of Hall⁽¹⁹⁾ and Bruni *et al.*⁽²⁰⁾

Figure 6 shows interdiffusion coefficients for 1173 K calculated by three methods. It can be seen from the figure that the interdiffusion

Fig. 6 Interdiffusion coefficients ($\tilde{D}$) obtained by three different methods at 1173 K.

Fig. 7 Variation in interdiffusion coefficients ($\tilde{D}$) with Sb concentration at various temperatures.

coefficients calculated by the Matano-Boltzmann and Bruni *et al.* methods almost agree with each other, but the results by the Hall method are somewhat different from the others. It seems from these results that the method of Bruni *et al.* is useful to examine the accuracy of the penetration behavior similar to an error function curve. In Fig. 7 the interdiffusion coefficients calculated by the Matano-Boltzmann method are shown as a function of the concentration of Sb for each temperature. The variation in $\tilde{D}$ with Sb concentration for each temperature is relatively small but it has a tendency to be accentuated at low temperatures. In spite of the existence of the γ phase, as seen in the penetration curve at 1223 K in Fig. 3, $\log \tilde{D}$ varies linearly with Sb concentration.

4. Temperature dependence of $\tilde{D}$

Figure 8 shows the Arrhenius plot of $\tilde{D}$ for various Sb concentration. In this figure, a gap is observed between the lower temperature side (973 and 1023 K) and the higher side (1073~1223 K). It is considered that this gap is due to the existence of the magnetic transformation in the α solid solution in Fe-Sb alloys near 1038 K. The data obtained at higher tem-

Fig. 8 Temperature dependence of $\tilde{D}$ in α phase of Fe-Sb alloys.

peratures were used to determine the activation energy for interdiffusion, $\tilde{Q}$. The calculated values of $\tilde{Q}$ are shown in Fig. 9. The activation energies for interdiffusion obtained from the data at higher temperatures varied from 220 kJ/mol for 4 at% Sb to 249 kJ/mol for 1 at% Sb. The value for the so-called impurity diffusion of Sb in α iron (Q_{Sb}^*) was evaluated to be about 264 kJ/mol, which was calculated from the Arrhenius plot of D^* obtained by extrapolating $\tilde{D}$ to 0 at% Sb. This value shows reasonable agreement with the value of Q_{Sb}^* reported to be 270 kJ/mol by Bruggeman *et al.* The value for the impurity diffusion of Zn in α iron (Q_{Zn}^*) for an Fe-Zn system is 262 kJ/mol and is nearly equal to Q_{Sb}^* in this study.

Comparing $\tilde{Q}_{\text{Sb}}$ with $\tilde{Q}_{\text{Zn}}$, $\tilde{Q}_{\text{Sb}} < \tilde{Q}_{\text{Zn}}$ in the same concentration of solute (Sb or Zn). Atomic radius of Sb atoms, however, is greater than that of Zn atoms ($d_{\text{Sb}}/d_{\text{Zn}} = 1.09$). Accordingly, the present result for $\tilde{Q}$ will have to be explained by other concepts from the difference in atomic radius.

5. The relationship between $\ln \tilde{D}_0$ and $\tilde{Q}$

Figure 10 shows the relationship between $\tilde{Q}$ and $\ln \tilde{D}_0$ obtained from the data at higher temperatures shown in Fig. 8. The relationship between these two terms is generally recognized to be linear and can be represented by the following equation:

$$\ln \tilde{D}_0 = a \cdot \tilde{Q} + b.$$

Fig. 9 Change in the activation energy with Sb concentration shown with other data.

Fig. 10 Relationship between the frequency term ($\tilde{D}_0$) and the activation energy ($\tilde{Q}$) for the Fe-Sb and Fe-Zn systems.

In this experiment a linear relationship was also obtained. These coefficients are $a = 9.3 \times 10^{-5}$ and $-b = 25.9$, here the unit of $\tilde{Q}$ is J/mol. These values for the interdiffusion in *bcc* type Fe-based alloys have been reported as $a = (7.6 \sim 15.8) \times 10^{-5}$ and $-b = 24.9 \sim 31.5$ (1)(3)(4)(7).

IV. Summary

The experimental results on the interdiffusion in the α solid solution of the Fe-Sb system using an Sb vapor source can be summarized as follows:

(1) Fine alumina markers placed on the surface of test pieces prior to diffusion still remained on the surface after annealing. This fact indicates that Sb atoms diffuse predominantly into the α solid solution at the marker position.

(2) The diffusion penetration curves of this system obtained from EPMA analysis were similar to an error function curve except for 1223 K. The surface concentration in the test

pieces ($\alpha_{\max}$) after diffusion-annealing at lower temperatures nearly coincided with the solubility limit reported by Maier *et al.* At higher temperatures it deviated significantly from the solubility limit towards low Sb concentration.

(3) Variation in the interdiffusion coefficient ($\tilde{D}$) with Sb concentration at each temperature was relatively small except at lower temperatures.

(4) In the Arrhenius plot of $\tilde{D}$ a gap was observed except for 4 at% Sb. It is considered that this gap is due to the existence of the magnetic transformation near 1038 K. The Arrhenius plot of $\tilde{D}$ at higher temperatures varied linearly. Activation energies for interdiffusion ($\tilde{Q}$) decreased significantly with increasing Sb concentration.

(5) The relationship between the frequency term, $\tilde{D}_0$, and $\tilde{Q}$ can be represented by the following equation:

$$\ln(\tilde{D}_0/\text{m}^2 \cdot \text{s}^{-1}) = 9.3 \times 10^{-5}(\tilde{Q}/\text{J} \cdot \text{mol}^{-1}) - 25.9.$$

REFERENCES

- (1) K. Nishida, T. Yamamoto and T. Nagata: J. Japan Inst. Metals, **34** (1970), 591.
- (2) K. Nishida and T. Narita: J. Japan Inst. Metals, **35** (1971), 269.
- (3) H. Suzuki, Y. Masuda and K. Nishida: J. Japan Inst. Metals, **36** (1972), 509.
- (4) K. Hirano and A. Hishinuma: J. Japan Inst. Metals, **32** (1968), 516.
- (5) V. I. Andryushechkin and I. N. Kidin: Fiz. Metal. Metalloved., **23** (1967), 164.
- (6) M. Lasocka and W. Raczynsky: Bull. Acad. Pol. Sci., Ser. Sci. Chim., **15** (1967), 31.
- (7) G. F. Carter: J. Less-Common Metals, **37** (1974), 189.
- (8) D. W. James and G. M. Leak: Phil. Mag., **14** (1966), 701.
- (9) H. Mitani, M. Onishi and S. Shikano: J. Japan Inst. Metals, **30** (1966), 56.
- (10) G. A. Bruggeman and J. A. Roberts, Jr.: Met. Trans., **6** (1975), 755.
- (11) T. Kase: Kinzoku no Kenkyu, **11** (1934), 251.
- (12) B. Jones and J. D. D. Morgan: J. Iron Steel Inst., **1** (1934), 115.
- (13) R. Vogel and W. Dannöhl: Arch Eisenhüttenw., **8** (1934), 39.
- (14) J. Maier and E. Wachtel: Z. Metallk., **63** (1972), 411.
- (15) K. Yamaguchi, H. Yamamoto, Y. Yamaguchi and H. Watanabe: J. Phys. Soc. Japan, **33** (1972), 1292.

- (16) R. Hultgren, R. L. Orr, P. D. Anderson and K. K. Kelley: *Selected Values of Thermodynamic Properties of Metals and Alloys*, John Wiley & Sons, Inc., New York, (1963), p. 247.
 - (17) W. B. Pearson: *A Handbook of Lattice Spacings and Structures of Metals and Alloys*, Pergamon Press, London, (1958), p. 653.
 - (18) E. Maey: *Z. Physik. Chem.*, **38** (1901), 292.
 - (19) L. D. Hall: *J. Chem. Phys.*, **21** (1953), 87.
 - (20) F. J. Bruni and J. W. Christian: *Acta Met.*, **21** (1973), 385.
-