Interdiffusion in the ζ -Solid Solution of a Ni–Al System*

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For the purpose of studying interdiffusion in the ζ -solid solution of a Ni–Al system, the experiments were performed using a method of vapor-solid couple at 1273~1573 K. As a vapor source, the fine chips of 12 mass % Al–Ni alloy ($\zeta + \varepsilon$ phases) were used. The surface concentration of Al in the diffusion annealed test pieces almost coincided with the solubility limit reported in the phase diagram of the Ni–Al system at each experimental temperature.

Fine alumina markers placed on the surface of test pieces prior to diffusion were found in its inside after annealing at each temperature. The composition at the marker position indicated a higher Al concentration with an increase in annealing temperature. The ratio of the intrinsic diffusion coefficients of these two constituents, D_{Al}/D_{Ni} , was 1.3~7.0 at the marker position.

The interdiffusion coefficients ($\bar{D}$) were dependent upon the annealing temperature and Al concentration, and were evaluated to be the orders of $10^{-15} \sim 10^{-13}$ m²/s in this experimental temperature range. Log $\bar{D}$ increased almost linearly with increasing Al concentration.

The activation energies for interdiffusion ($\bar{Q}$) obtained from the temperature dependence of $\bar{D}$ decreased from 282 to 258 kJ/mol with increasing Al concentration. The impurity diffusion coefficient of Al in Ni, D_{Al}^* , at each temperature was obtained from extrapolating of $\bar{D}$ to 0 at % Al and its activation energy, Q_{Al}^* , obtained from the Arrhenius plot of D_{Al}^* was evaluated to be 284 kJ/mol.

The relationship between the entropy term, $\bar{D}_0$, and $\bar{Q}$ can be represented by the following equation:

$$\ln (\bar{D}_0/\text{m}^2 \cdot \text{s}^{-1}) = 3.1 \times 10^{-5} (\bar{Q}/\text{J} \cdot \text{mol}^{-1}) - 16.0.$$

(Received June 2, 1980)

I. Introduction

It is well known that aluminizing treatments on the surface of Ni metal or Ni-base alloys improve resistance against oxidation at high temperature^{(1)~(3)}. Among the Ni–Al alloy phases, the δ (NiAl)-phase has the most oxidation resistance and offers the anomalous properties, so that many investigations such as diffusion in this alloy phase have been reported^{(4)~(7)}. However, only a few studies on the ζ (Ni)-phase have been reported, since the aluminide phase layers produced by diffusion on Ni metal ordinarily consist of γ (Ni₂Al₃), δ , and ε (Ni₃Al), whereas only a thin layer of the ζ -phase is produced.

According to the reports on the ζ -phase,

Hickl *et al.*⁽⁸⁾ studied the phase layer growth during aluminide coating of Ni metal and Swalin *et al.*⁽⁹⁾ and Janssen *et al.*⁽¹⁰⁾⁽¹¹⁾ examined the interdiffusion by applying a solid-solid couple. However, even in the latter reports, their detailed interdiffusion data were not shown over all concentration range of the ζ -phase. The purpose of this study is to investigate in detail the interdiffusion behavior in the ζ -phase and to obtain the impurity diffusion data, which are not reported up to this time, by applying a vapor-diffusion technique used in our previous studies^{(7)(12)~(14)(27)}.

II. Experimental

In this experiment, a so-called vapor-solid method was applied with the fine chips of a Ni–Al alloy as a vapor source. The test piece used for the present experiment was re-electrolytic Ni metal (99.98 mass %). The Ni block was rolled and encapsulated in a quartz tube at 5.3×10^{-4} Pa, and annealed at 1473 K for 21 d. An average grain size of the Ni sheet ($\phi 1.6$ mm) was obtained. The test piece was in a size of

* This paper was originally published in Japanese in J. Japan Inst. Metals, **44** (1980), 294.

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about $5\text{ mm} \times 5\text{ mm} \times 10\text{ mm}$. The surface of the test piece was finished with No. 1000 emery paper, washed, and degreased. Alumina powder ($\phi 0.3\text{ }\mu\text{m}$) was placed on its surface as the marker.

As an aluminum vapor source, the fine chips of 12 mass% Al–Ni alloy ($\zeta + \varepsilon$ phases) were used in order to hold a constant vapor pressure during diffusion anneal. This alloy was prepared from re-electrolytic Ni (99.98 mass%) and pure aluminum (99.99 mass%) in an argon-high frequency induction furnace.

A steel pipe container ($\phi 14\text{ mm}$, 0.2 mm thick) was prepared, as the previous study on Fe–Al system, in order to protect a reaction between the quartz capsule and the aluminum vapor during the diffusion anneal. This container was beforehand plated with nickel (about 1 mm thick) and aluminized sufficiently to minimize consuming aluminum vapor in the container during diffusion anneal. The test piece and the Ni–Al alloy chips as a vapor source (about 40 g) were charged in this container. This container was then encapsulated in a quartz tube ($\phi 16\text{ mm}$) at $5.3 \times 10^{-4}\text{ Pa}$ (Fig. 1).

The diffusion-anneal was performed in a horizontal electric furnace in the temperature range of $1273 \sim 1573\text{ K}$ within $\pm 1\text{ K}$ for $3.6 \sim 608.4\text{ ks}$. After the diffusion-anneal, the test piece was plated with nickel with the thickness of about 1 mm on its surface in order to keep the cross section flat in case of mechanical polishing. Then it was put into a polyester resin and sectioned vertically to the surface at its center. The cross section was polished and was analysed with an EPMA to obtain the Al concentration profile. Both of the calibration curves for the intensity of Ni–K α and Al–K α rays from the standard Ni–Al alloys showed

considerable deviations from the ideal linear relationships with Al concentration, so that in this experiment for the analytical accuracy, the Al–K α ray was chosen for the spot analyses.

On the calculation of interdiffusion coefficients, the molar volume of these alloys were obtained from the lattice spacing data of pure Ni and Al metals, and the ζ -phase⁽¹⁵⁾ in order to examine the volume change by interdiffusion. There is considerable difference in molar volume between pure Ni ($6.586 \times 10^{-6}\text{ m}^3/\text{mol}$) and pure Al ($9.995 \times 10^{-6}\text{ m}^3/\text{mol}$). In the ζ -solid solution, however, the change in molar volume showed a linear increase with Al concentration. Therefore, the partial molar volume of both constituents in this phase are constant. When the ordinate is represented by a mol/m^3 unit of Al in the penetration profile, no other correction is necessary for the present graphical calculation⁽¹⁶⁾. Consequently, the interdiffusion coefficients were calculated, using mol/m^3 as a concentration unit, by the Matano-Boltzmann method according to an analytical treatment of a vapor-solid diffusion couple by Balluffi *et al.*⁽¹⁷⁾

III. Experimental Results and Discussion

1. Observation of the diffusion-annealed test pieces

As an example, Photo. 1 shows a surface appearance of the test piece diffusion-annealed at 1323 K for 291.6 ks . The surface shows a

Fig. 1 Schematic representation of evacuated quartz capsule.

Photo. 1 Surface appearance of the test piece diffusion-annealed at 1323 K for 291.6 ks .

slight unevenness at the grain boundary as well as the inside. Photograph 2 shows a sectional view of the test piece diffusion-annealed at 1473 K for 32.4 ks. In this photograph unevenness can be similarly observed at the surface of the test piece. The alumina markers placed on the surface of the test piece can be seen in its inside.

2. Master curves and surface concentrations in the test pieces

As an example of the penetration curves analysed with an EPMA, C_{Al} (mol/m³)— $x/t^{1/2}$ curves for the specimens diffusion-annealed at 1523 K for 3.6, 8.1, and 14.4 ks are shown in Fig. 2, where the origin of the abscissa lies at the marker position. These curves are in good

Photo.2 Sectional appearance of the test piece diffusion-annealed at 1473 K for 32.4 ks, showing the marker inside the surface.

Fig. 2 Penetration curves obtained from the Ni-Al (vapor) diffusion couples diffusion-annealed at 1523 K for 3.6, 8.1 and 14.4 ks.

agreement with each other and similarly good agreements are shown at other diffusion-temperatures. The final $C_{Al}-x/t^{1/2}$ curves (the master curves) obtained from the arithmetical mean of every penetration curve at various temperatures are shown in Fig. 3.

The surface concentrations analysed with an EPMA in the diffusion-annealed test pieces are plotted at various temperatures on the Ni-Al phase diagram reported by Hansen *et al.*⁽¹⁸⁾ in Fig. 4. The ζ -phase solubility limits obtained from 55 at% Ni(δ)-Ni and 75 at% Ni(ϵ)-Ni

Fig. 3 Penetration curves: Change in the concentration of Al (mol/m³) with (distance/time)^{1/2} at various temperatures.

Fig. 4 Surface concentrations of diffusion-annealed test pieces at various temperatures.

couples by Janssen⁽¹¹⁾ have been found to be somewhat higher Al concentration at every temperature than those of the phase diagram. In this experiment, however, the results coincide at every temperature sufficiently with the solubility limits except for a slight deviation towards a higher Ni concentration at 1273 K.

3. Interdiffusion coefficients ($\bar{D}$) and intrinsic diffusion coefficients (D_{Al} , D_{Ni})

The interdiffusion coefficients calculated by the Matano-Boltzmann method using the master curve obtained at each temperature are shown in Fig. 5 as a function of the concentration of Al. These interdiffusion coefficients are dependent upon the annealing temperature and Al concentration. In this figure the data obtained from a solid-solid couple method by Swalin *et al.*⁽⁹⁾ and Janssen⁽¹¹⁾ are also plotted for comparison. The experiment by Swalin *et al.* was undertaken in a narrow concentration range of Al as 0~0.7 or 2.0~3.7 at % Al and the interdiffusion coefficients indicated no dependence on the concentration of Al. Although no data at the same temperatures are

available, the present results are found to be in approximate agreement with them. Janssen's data were obtained from the study using ϵ -Ni and δ -Ni diffusion couples at the same diffusion-annealing temperature range as the present work, and the interdiffusion coefficients were also calculated using the Matano-Boltzmann analysis. The interdiffusion coefficients, however, only at 14 at % Al were reported and the volume effect was neglected. As seen in Fig. 5, a certain difference can be recognized between these $\bar{D}$ values obtained from ϵ -Ni couple and δ -Ni couple. The reason for these differences, however, remained unclarified.

It can be considered that ϵ -Ni couples are less affected by disregarding the volume effect than δ -Ni couples for the calculation of $\bar{D}$. In comparison with the $\bar{D}$ values for ϵ -Ni couples, these values are 1.3~1.6 times higher than those in the present experiment. The difference of them seems first to come from the difference in the experimental method. But in considering the volume effect on $\bar{D}$ values, the molar volumes of ζ and ϵ -phase are smaller than those for the ideal solid solution, and these values increase with increasing concentration of Al (at %). Therefore, if the volume effect is disregarded, the dx/dc value at the concentration profiles should become greater and this effect must increase with increasing concentration of Al. Accordingly, it can be considered that above every difference in $\bar{D}$ value is brought about.

As shown Photo. 2, the alumina markers placed on the surface of the test piece prior to diffusion are found in its inside after annealing and the composition at the marker position is almost constant at the same temperature. Then, the intrinsic diffusion coefficients (D_{Al} , D_{Ni}) at that composition were calculated from the ratio (D_{Al}/D_{Ni})⁽¹⁷⁾⁽¹⁹⁾ of the intrinsic diffusion coefficients obtained as the ratio of the area calculated schematically from the penetration curve on both sides of the marker position and Darken's equation ($\bar{D} = D_{Al}\bar{V}_{Ni}C_{Ni} + D_{Ni}\bar{V}_{Al}C_{Al}$, where $\bar{V}_{Ni}$, $\bar{V}_{Al}$ and C_{Ni} , C_{Al} are partial molar volume and molar concentration of both constituents, respectively)⁽¹⁶⁾⁽²⁰⁾. These values are plotted in Fig. 5 in the composition at the marker position which varies from 12.4 at % Al

Fig. 5 Variation in interdiffusion coefficients ($\bar{D}$) with Al concentration shown with other data and also intrinsic diffusion coefficients (D_{Al} and D_{Ni}) obtained from marker movements.

at 1273 K to 18.9 at% Al at 1573 K. Since there are no data for the true drift velocity of the marker (v_m), v_m was temporarily calculated using a position of the Matano-interface instead of an original surface of the test piece. Thus, the intrinsic diffusion coefficients were also calculated from the equation suggested by Balluffi⁽¹⁶⁾. Each ratio calculated by these two methods is plotted as a function of temperature in Fig. 6, comparing with those of D_{Al}/D_{Fe} for an Fe–Al system⁽¹²⁾. This ratio calculated schematically seems to increase from about 1.3 to 7.0, and shows a similar tendency to the results for the Fe–Al system. On the other hand, the values of the ratio calculated from the drift velocity of the marker are about 1.3 to 3.3, and about one half of those values calculated schematically except the result at 1273 K. It is considered that the principal reason for the difference in these results is due to the difference in the partial molar volumes of the two constituents. It was reported by Janssen⁽¹¹⁾ that the ratio, D_{Al}/D_{Ni} , obtained by a marker method at 9.6–13.4 at% Al was greater than unity, but detailed data were not described on account of an inaccurate experiment. However,

the above result ($D_{Al}/D_{Ni} > 1$) is in agreement with this experiment.

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

As an example, Fig. 7 shows the temperature dependence of $\tilde{D}$ for several concentrations. In this figure, the broken line shows the temperature dependence of the so-called impurity diffusion coefficients of Al in Ni, D_{Al}^* , which were obtained by extrapolating $\tilde{D}$ to 0 at% Al. From this figure, all of these plots obviously indicate good linearities and for other Al concentrations the same relation will be held as well. The position of the marker, as shown previously, shifted towards higher concentrations of Al with increasing temperature. The Arrhenius plots of D_{Al} and D_{Ni} indicate also good linear relations, as shown in Fig. 8, and thus Q_{Al} and Q_{Ni} are calculated in a sense of the average value within a range of these Al concentrations at the marker position. All these values of activation energies for diffusion are plotted in Fig. 9, together with the results of solid-solid couple diffusion by Janssen⁽¹¹⁾ and Swalin *et al.*⁽⁹⁾ and the previously reported results of the vapor-solid couple diffusion for the Fe–Al system. The activation energies for interdiffusion ($\bar{Q}$) decreased from 282 kJ/mol

Fig. 6 Change in ratio of intrinsic diffusion coefficients (D_{Al}/D_{Ni}) obtained from marker movements with diffusion temperature, comparing with those of D_{Al}/D_{Fe} for the Fe–Al system.

Fig. 7 Temperature dependence of $\tilde{D}$ in the ζ -phase of the Ni–Al alloys.

Fig. 8 Temperature dependence of intrinsic diffusivities (D_{Al} and D_{Ni}) in the ζ -phase of the Ni-Al alloys.

Fig. 9 Change in the activation energy for interdiffusion with Al concentration shown with other data.

for 2 at% Al to 258 kJ/mol for 16 at% Al. Janssen's result shows 272 kJ/mol only for 14 at% Al, which is the same value for different diffusion couples and 9 kJ/mol higher than that obtained in this experiment (263 kJ/mol). On the other hand, the Fe-Al system as a whole shows smaller values than those in the Ni-Al

system primarily because of the difference in the structure of alloy crystals. The activation energy for impurity diffusion of Al in Ni, Q_{Al}^* , was evaluated to be 284 kJ/mol. At the present, there have been no reports about impurity diffusion of Al in this system using a tracer technique. Therefore, as compared with the data from Swalin *et al.* for interdiffusion in low concentration of Al, the value, 268 kJ/mol, is 16 kJ/mol smaller than that of the present work. There have been also no reports about impurity diffusion of Al in α -Fe and α -Co at the present except our previous experimental results from Q_{Al}^* in α -Fe, 280 kJ/mol⁽¹²⁾, estimated by extrapolating $\tilde{Q}$ to 0 at% Al and Q_{Al}^* in α -Co, 313.8 kJ/mol⁽²¹⁾, estimated in the same manner as this experiment. In comparing with those values, it is considered that the value obtained by Swalin *et al.* is somewhat small. Because, Q_{Al}^* in ζ -Ni and α -Co must be larger than Q_{Al}^* in α -Fe in considering the difference in alloy structures, that is, α -Fe is BCC, while α -Co and ζ -Ni are FCC, respectively. The values of Q_{Al} and Q_{Ni} , as shown in Fig. 9, were evaluated to be $Q_{Al}=299$ kJ/mol and $Q_{Ni}=197$ kJ/mol, which were calculated from the Arrhenius plots of D_{Al} and D_{Ni} obtained using the diffused area ratio and Darken's equation. As mentioned above, the concentration of Al at the marker position varies over a wide range, so that it is difficult to discuss the values of Q_{Al} and Q_{Ni} .

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

The relationship between $\ln \tilde{D}_0$ and $\tilde{Q}$ is generally recognized to be linear and can be represented by the following equation:

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

In this experiment a linear relationship is also obtained as shown in Fig. 10 and could be represented as follows:

$$\begin{aligned} \ln (\tilde{D}_0 / \text{m}^2 \cdot \text{s}^{-1}) \\ = 3.1 \times 10^{-5} (\tilde{Q} / \text{J} \cdot \text{mol}^{-1}) - 16.0. \end{aligned}$$

These coefficients, a and $-b$, for the interdiffusion in FCC alloys have been reported to be $a = (2.2 \sim 15.8) \times 10^{-5}$ and $-b = 13.4 \sim 31.2$ ^{(22)~(28)}. Among these values, for Ni-based alloys they are $a = (2.2 \sim 6.5) \times 10^{-5}$ and $-b = 13.4 \sim 27.6$ ^{(23)~(27)~(28)}. Both a and $-b$ obtained in

Fig. 10 Relationship between the frequency term ($\tilde{D}_0$) and the activation energy ($\tilde{Q}$) for the ζ -phase of the Ni–Al alloys.

this experiment are nearly equal to those for Ni-based alloys.

IV. Summary

The experimental results on the interdiffusion in the ζ -solid solution of a Ni–Al system using an Al vapor source can be summarized as follows:

(1) When the fine chips of the Ni–Al alloy ($\zeta + \epsilon$ phases) were used as a vapor source, the diffusion zone extended over the entire ζ -phase of the Ni–Al alloy and the surface concentration of Al in the diffusion annealed test piece almost coincided with the solubility limits reported in the phase diagram of the Ni–Al system at each temperature.

(2) Fine alumina markers placed on the surface of the test piece prior to diffusion were found in its inside after annealing at each temperature and the composition at the marker position varied from 12.4 at% Al at 1273 K to 18.9 at% Al at 1573 K.

(3) Log $\tilde{D}$ increased almost linearly with increasing Al concentration at every temperature. The ratio of the intrinsic diffusion coefficients, D_{Al}/D_{Ni} , obtained from the diffused area ratio was 1.3–7.0 at the marker position, but from v_m , it was 1.3–3.3.

(4) The Arrhenius plots of $\tilde{D}$ in each composition indicated good linear relations. Activation energies for interdiffusion, $\tilde{Q}$, calculated from these results decreased from 282 to 258 kJ/mol with increasing Al concentration.

(5) The Arrhenius plots of impurity diffusion coefficients of Al in Ni, D_{Al}^* , obtained by extrapolating $\tilde{D}$ to 0 at % Al indicated also a good linear relation. The activation energy for impurity diffusion of Al in Ni, Q_{Al}^* , was evaluated to be 284 kJ/mol.

(6) The relationship between $\ln \tilde{D}_0$ and $\tilde{Q}$ can be represented by the following equation:

$$\ln (\tilde{D}_0 / \text{m}^2 \cdot \text{s}^{-1}) = 3.1 \times 10^{-5} (\tilde{Q} / \text{J} \cdot \text{mol}^{-1}) - 16.0.$$

REFERENCES

- (1) G. W. Goward, D. H. Boone and C. S. Giggins: Trans. ASM, **60** (1967), 228.
- (2) G. W. Goward: J. Metals, **22** (1970), 31.
- (3) T. K. Redden: Trans. Met. Soc. AIME, **242** (1968), 1695.
- (4) A. J. Bradley and A. Taylor: Proc. Roy. Soc., **159** (1937), 56.
- (5) G. F. Hancock and B. R. McDonnell: Phys. Status Solidi, (a)**4** (1971), 143.
- (6) K. Kenmotsu, Y. Iijima and K. Hirano: Report for the Research Grant given by Japan Ministry of Education, (1976).
- (7) H. Senzaki, T. Narita and K. Nishida: Abstract for the Autumn Meeting of Japan Inst. Metals, (1977), 164.
- (8) A. J. Hickl and R. W. Heckel: Met. Trans., **6** (1975), 431.
- (9) R. A. Swalin and A. Martin: Trans. Met. Soc. AIME, **206** (1956), 567.
- (10) M. M. P. Janssen and G. D. Rieck: Trans. Met. Soc. AIME, **239** (1967), 1372.
- (11) M. M. P. Janssen: Met. Trans., **4** (1973), 1623.
- (12) K. Nishida, T. Yamamoto and T. Nagata: J. Japan Inst. Metals, **34** (1970), 591.
- (13) H. Suzuki, Y. Masuda and K. Nishida: J. Japan Inst. Metals, **36** (1972), 509.
- (14) K. Nishida, H. Murohashi and T. Yamamoto: Trans. JIM, **20** (1979), 269.
- (15) W. B. Pearson: *A Handbook of Lattice Spacings and Structures of Metals and Alloys*, Pergamon Press, London, (1958), p. 377.
- (16) R. W. Balluffi: Acta Met., **8** (1969), 871.
- (17) R. W. Balluffi and L. L. Seigle: J. Appl. Phys., **25** (1954), 607.
- (18) M. Hansen and K. Anderko: *Constitution of Binary Alloys*, McGraw-Hill, New York, (1957), p. 118.
- (19) R. W. Balluffi and B. H. Alexander: J. Metals, **4** (1952), 1315.

- (20) L. S. Darken: Trans. AIME, **175** (1948), 184.
 - (21) S. Okazaki, T. Narita and K. Nishida: Abstract for the Autumn Meeting of Japan Inst. Metals, (1977), 164.
 - (22) S. Tsuji and H. Yamanaka: J. Japan Inst. Metals, **34** (1970), 486.
 - (23) Y. Iijima and K. Hirano: J. Japan Inst. Metals, **35** (1971), 511.
 - (24) K. Nohara and K. Hirano: J. Japan Inst. Metals, **37** (1973), 51.
 - (25) Y. Funamizu and K. Watanabe: Trans. JIM, **17** (1976), 59.
 - (26) Y. Iijima, K. Hirano and K. Sato: J. Japan Inst. Metals, **41** (1977), 142.
 - (27) T. Yamamoto, T. Takashima and K. Nishida: J. Japan Inst. Metals, **43** (1979), 1196.
 - (28) M. Yokota, R. Harada and H. Mitani: J. Japan Inst. Metals, **43** (1979), 793.
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