Measurement of the Kirkendall Marker Shift by a New Technique

By T. Shimozaki*, N. Saita**, M. Onishi*
and Y. Wakamatsu*

In order to measure the Kirkendall marker shift in a precise manner a new technique has been proposed. By the technique one can measure the marker shift as a distance between the Kirkendall marker position after annealing and the edge of the inert foil embedded in a diffusion couple parallel to the diffusion direction as it acts as an indicator for the initial marker position. Since the Kirkendall markers and the edge of the inert foil can be seen in a sight of a microscope, the measurement is very easy and the accuracy of the data on the marker shifts is expected to be improved. The marker shifts in Cu-Sn alloys have been determined experimentally by this technique.

(Received January 6, 1989)

Keywords: *interdiffusion, Kirkendall effect, marker shift, thin foil, new technique, copper-tin alloy*

I. Introduction

Up to the present, in order to determine the intrinsic diffusivity, many investigators have measured the Kirkendall marker shifts by using the sandwich type diffusion couples⁽¹⁾ as well as the diffusion couples⁽²⁾ in which inert thin foils such as molybdenum are inserted into the edges of the welded interface vertical to the diffusion direction. In spite of a requirement of laborious work for measurement of the marker shifts, degree of experimental error in the marker shifts determined by these methods is extensively large. Therefore the degree of experimental errors in the intrinsic diffusivity is also larger than those in tracer diffusivity and interdiffusivity. Recently, in order to improve the accuracy of the marker shifts or intrinsic diffusivity, some new techniques such as the thin plate method⁽³⁾⁽⁴⁾ and the multiple markers method⁽⁵⁾ have been proposed. The purpose of this work is to show a new technique (the parallel inert foil method) by which the marker shifts may be determined

more precisely and simply in comparison with the previous thin plate method, the multiple markers method and so on. Applying this method, the marker shifts in Cu-Sn alloys were experimentally measured.

II. Principle of Measurement of the Kirkendall Marker Shift by the Parallel Inert Foil Method

Schematic diagrams of a diffusion couple used in this experiment are shown in Fig. 1(a) and (b) for the ones before and after annealing. In a half of the diffusion couple, inert foils about 5 μm in thickness are inserted parallel to the diffusion direction so that one of the edges of the inert foils may be just in contact with the surface of the other half of the diffusion couple. When one chooses an appropriate material for the inert foils to satisfy the conditions that the foils do not react with metals and alloys of the diffusion couple and are not elongated or shrunk before and after diffusion annealing, the position of the edge, designated by X_e , is fixed on the non diffused end of diffusion couple whenever the length of the foil is enough long in comparison with the diffusion length, and X_e can be considered as the initial position, X_0 , of the welded interface. So, one can determine the marker shift as a distance be-

* Department of Materials Science and Engineering, Kyushu Institute of Technology, Tobata, Kitakyushu 804, Japan.

** Present address: Atsugi Motor Parts Co., LTD., Atsugi 243, Japan.

Fig. 1 Schematic diagram of the diffusion couple for precise measurement of the Kirkendall marker shift.

tween X_e (before annealing the Kirkendall markers are also located at this position) and the position, X_k , of the Kirkendall markers after the annealing. Since the position X_e , i.e., X_0 and X_k can be detected in a sight of an optical microscope or a scanning electron microscope even if the degree of marker shifts is less than a few micron meters, it is expected that measurement of the marker shift will become considerably easy and precise.

For the materials, mica may be useful because the mica itself easily peels off and therefore the shear stress produced at the metal/foil and alloy/foil interfaces will be released even if mica reacted with metal and alloy specimens. In this experiment Mo foils were also used as another example.

III. Experimental Procedure

The pure copper specimens were cut from a sheet of 99.96% purity and 1.5 mm thickness to the form of 5 mm × 10 mm × 1.5 mm. Both flat surfaces were ground on abrasive paper and polished on a buff with fine alumina powder. The six pure copper specimens were piled up and Mo or mica foils of 4 mm × 10 mm × 5 μm were inserted into the five interfaces. They were cramped by a stainless steel holder and annealed in an evacuated furnace at 1073 K. This treatment also yielded crystal grains about 1 mm in diameter. After the annealing the holder was removed and a surface of the welded specimen was ground on water proofed abrasive papers till inert foils were exposed and polished on a buff as mentioned

above. When mica was used as inert foils, the Cu specimens often peeled off at mica foils during these procedures. Further mica foils easily absorb water and the absorption was a cause for oxidation in the diffusion layer. Then the surface must be ground carefully. A reason for the utilization of Mo foils in place of mica foils is to avoid this disadvantage.

Cu-Sn alloy rods having 1.5, 3, 5 and 7 at% Sn were made by melting pure copper chips of 99.99% purity and pure tin granules of 99.99% purity at 1373 K in an evacuated quartz capsule about 11 mm in diameter. They were annealed at 1073 K for 1200 ks to yield homogenization. The rods were then rolled and cut to the form about 10 mm × 10 mm × 5 ~ 6 mm. The specimens were recrystallized in the evacuated quartz capsule as described above. The surface of each alloy specimen was polished metallographically on a buff.

Mo powder about 1 ~ 2 μm in diameter were inserted between the pure copper and the alloy specimens as the Kirkendall markers. The diffusion couples consisted of pure Cu and 1.5, 3, 5 and 7 at% Sn alloys, respectively, were designated as Cu-1.5Sn diffusion couple, as an example. They were annealed with the stainless steel cramp in an evacuated furnace at 1073 K for 7.2 ks. The diffusion couple removed from the cramp was sealed in an evacuated quartz capsule and the capsule was annealed at 1073 K for various periods of annealing time in an electric furnace controlled within ±1 K. After the annealing the couple was cut parallel to the diffusion direction and vertical to the foils. The section was then polished metallographically on a buff.

The marker shifts, $X_k - X_e$, were measured by an optical microscope equipped with a calibrated eye piece which has scaled crossed line.

In order to determine the intrinsic diffusivity by this method concentration-penetration profiles are indispensable. The concentration-penetration profiles were obtained by E.P.M.A. (JEOR JXA 733) under the following operating conditions: the accelerating voltage 25 kV; the take off angle of Sn L_{α} X-rays 0.222 rad; the specimen current about

5×10^{-6} A and the line scanning speed 1.667×10^{-6} m/s. The intensity of Sn L_{α} X-ray was translated to the concentration of Sn by the ZAF method. During the analysis the marker position X_k was marked on the E.P.M.A. chart.

The interdiffusivity was determined from the concentration-penetration profiles by using the Sauer and Freise equation⁽⁶⁾.

IV. Results and Discussions

1. Distance between X_k and X_e

Photomicrograph of a section of the Cu-7Sn diffusion couple annealed at 1073 K for 518.4 ks in which Mo foils were inserted parallel to the diffusion direction is shown in Fig. 2. The array of Mo powder in Fig. 2 was kept straight and left from the edge of the Mo foil, X_e , while some arrays of Mo markers near the Mo foils were curved because ordinary diffusion might be prevented near this region.

Fig. 2 Photomicrograph of the edge of Mo foil and the Kirkendall markers in the Cu-7Sn diffusion couple annealed at 1073 K for 518.4 ks.

Fig. 3 Relationship between the marker shift, $X_k - X_e$ and square root of annealing time, $\sqrt{t}$.

Even in this case the distances could be measured in a sight of microscope by interpolating the markers array with the aid of the eye piece. The distances thus measured at the five edges of the Mo foils coincide with one another within $\pm 1 \mu m$.

In Fig. 3 the relationships between the average distance, $X_k - X_e$, and the square root of annealing time, $\sqrt{t}$, for Cu-1.5Sn, Cu-3Sn, Cu-5Sn and Cu-7Sn diffusion couples are shown. The closed circles in Fig. 3 mean that these data are obtained by use of the diffusion couples having mica foils. They coincide with data obtained by the diffusion couples having Mo foils (represented by open circles). The relationship between the marker shifts and $\sqrt{t}$ is represented by a good linear line for all kinds of diffusion couple although the values of the distance at $t=0$ have a negative value of about $-1 \mu m$ excepting the one for Cu-7Sn diffusion couples. In order to investigate this reason, the sections of the diffusion couples after annealing for 7.2 ks were observed. In Fig. 4 a photomicrograph of the section of the Cu-1.5Sn diffusion couple and its illustration are shown. It is found that the Mo foil projects out about $1 \mu m$ from the arrays of Mo markers and thrust into the alloy specimen. The reason may be that the copper and the alloy specimens were deformed plastically when the diffusion couples were tightly cramped to yield ordinary diffusion. In the Cu-Sn system the degree of projection is not very large, but in the Ag-Sn

Fig. 4 Photomicrograph of the edge of Mo foil and the Kirkendall markers in the Cu-1.5Sn diffusion couple annealed at 1073 K for 7.2 ks.

system, the marker shifts were more than $5 \mu\text{m}$ and varied in the degree. Then this phenomenon may be important for the diffusion couples consisting of soft metals and alloys.

In this experiment, any reactions between inert foils of Mo and mica and specimens of pure Cu and Cu-Sn alloy could not be detected by E.P.M.A. Further, the data on the marker shifts obtained by the diffusion couples having mica foils coincide with those obtained by the diffusion couples having Mo foils as described previously. These results indicate that the expansion or shrinking of the inert foils may be negligibly small in this system even if the foils reacted with copper and alloy specimens. Therefore, in the following, the distance, $X_k - X_e$, is regarded as the Kirkendall marker shift, $X_k - X_0$.

2. Ratio of the intrinsic diffusivities

In Fig. 5, typical concentration (Y/V : mol/m^3)-penetration ($\lambda = (X - X_0)/\sqrt{t}$: 10^{-6}

Fig. 5 Concentration (Y/V)-penetration (λ) profiles for Cu-5Sn diffusion couple.

$\text{m}/\text{s}^{1/2}$) profiles and $1/V - \lambda$ curves for the Cu-5Sn diffusion couple are shown. Here Y is the relative mole fraction defined by $(N_{\text{Sn}} - N_{\text{Sn}}^-)/(N_{\text{Sn}}^+ - N_{\text{Sn}}^-)$, N_{Sn}^- and N_{Sn}^+ are the mole fraction N_{Sn} of tin at $X = -\infty$ and $+\infty$ and V is the molar volume. The interdiffusivities were determined for all type of diffusion couples. The diffusivities were in good agreement to one another within the limits of experimental error and the concentration dependence was represented by the following equation

$$\tilde{D}(N_{\text{Sn}}) = 4.9 \times 10^{-14} \exp(27.6N_{\text{Sn}})(\text{m}^2/\text{s}).$$

This concentration dependence of $\tilde{D}(N_{\text{Sn}})$ is in good agreement with those obtained by Hoshino *et al.*⁽⁷⁾

The initial position of the welded interface, X_0 , was determined by the so called extended Matano's equation⁽⁸⁾,

$$C_{\text{Cu}}^+ \int_{-\infty}^{\infty} (X - X_0) dC_{\text{Sn}} - C_{\text{Sn}}^+ \times \int_{-\infty}^{\infty} (X - X_0) dC_{\text{Cu}} = 0. \quad (1)$$

Here C_{Cu} and C_{Sn} are the mole concentrations of Cu and Sn. C_{Cu} and C_{Sn} with super script + mean that these are the concentrations at $X = +\infty$. The position X_0 , thus determined from the concentration-penetration profile is designated by X_{0e} as in the following.

As the authors⁽⁹⁾ have previously shown, when a marker position, X_k , on the E.P.M.A. charts is known, one can determine the ratio of the intrinsic diffusivities $D_{\text{Sn}}^N/D_{\text{Cu}}^N$ with respect to the mole fixed frame of reference without knowing the position at the Matano's interface by the following equation

$$\frac{D_{\text{Sn}}^{\text{N}}}{D_{\text{Cu}}^{\text{N}}} = \frac{N_{\text{Sn}}^- S_{k1} - N_{\text{Sn}}^+ S_{k2}}{N_{\text{Cu}}^+ S_{k2} - N_{\text{Cu}}^- S_{k1}}, \quad (2)$$

here S_{k1} and S_{k2} are the areas defined by

$$S_{k1} = \int_{X_k}^{\infty} [(1-Y)/V] dX \quad (3)$$

and

$$S_{k2} = \int_{-\infty}^{X_k} Y/V dX. \quad (4)$$

In order to make the data on the marker shifts to be useful, a new marker position, X'_k , was estimated on the concentration-penetration profile so that the distance $X'_k - X_{0c}$ may coincide with the distance $X_k - X_e$. The marker position thus determined is shown in Fig. 5 as a distance, $\lambda'_k \{ = (X'_k - X_{0c})/\sqrt{t} \}$. Though the position X'_k will differ from the position X_k because absolute position X_{0c} is ambiguous, when relative distance, i.e., $X'_k - X_{0c}$, is reliable the ratios at X'_k is also expected to be reliable. From this point of view, the ratios $D_{\text{Sn}}^{\text{N}}/D_{\text{Cu}}^{\text{N}}$ at the position X'_k instead of X_k have been determined with the aid of eq. (2).

The ratios $D_{\text{Sn}}^{\text{N}}/D_{\text{Cu}}^{\text{N}}$ thus calculated are listed in Table 1 together with the values of the concentration, N_{Sn} , at X'_k and the values $X_k - X_e$ for Cu-7Sn, Cu-5Sn, Cu-3Sn and Cu-1.5Sn diffusion couples. The average values of the ratios thus determined increase with increasing of N_{Sn} and were found to be about 1.2, 1.8, 3.1 and 3.8 at 0.74, 1.63, 2.86 and 4.27 at% Sn, respectively. The concentration dependence of the ratio is shown in Fig. 6. With the aid of this relationship, the value of the ratio $D_{\text{Sn}}^{\text{N}}(0)/D_{\text{Cu}}^{\text{N}}(0)$ at zero at% Sn, which is very important in calculating the so-called vacancy flow factor $G^{(10)}$, was determined to be 1.1. The ratio $D_{\text{Sn}}^{\text{N}}/D_{\text{Cu}}^{\text{N}}$ is equal to $(D_{\text{Sn}}^{\text{V}}/D_{\text{Cu}}^{\text{V}})/(V_{\text{Sn}}/V_{\text{Cu}})$, where $D_{\text{Sn}}^{\text{V}}/D_{\text{Cu}}^{\text{V}}$ is the ratio of the intrinsic diffusivities with respect to the volume fixed frame of reference and $V_{\text{Sn}}/V_{\text{Cu}}$ is the ratio of the partial molar volumes of Sn and Cu and is 1.82⁽¹¹⁾, respectively. Using 1.95 for the value of $D_{\text{Sn}}^{\text{V}}(0)/D_{\text{Cu}}^{\text{V}}(0)$ at 1089 K which was determined by Hoshino *et al.*⁽⁷⁾ and 1.82 for the value of $V_{\text{Sn}}/V_{\text{Cu}}$, one gets 1.07 for the value of $D_{\text{Sn}}^{\text{N}}(0)/D_{\text{Cu}}^{\text{N}}(0)$. This value is in good agreement with the value, 1.1, obtained in this

Table 1 The values of N_k , ΔX , ΔX_{max} , $X_N - X_0$ and $D_{\text{Sn}}^{\text{N}}/D_{\text{Cu}}^{\text{N}}$.

	Time/s ^{1/2} (H)	N_k	ΔX	ΔX_{max}	$X_N - X_0$	$D_{\text{Sn}}^{\text{N}}/D_{\text{Cu}}^{\text{N}}$
Cu-1.5% Sn	420 (49)	0.72	1.2	1.7	0.9	1.3
	660 (121)	0.71	1.7	2.8	1.3	1.2
	1026(292.5)	0.81	2.2	4.0	1.9	1.1
	1140 (361)	0.79	3.0	4.4	2.1	1.7
	1284 (458)	0.74	3.1	5.1	2.4	1.3
	1506 (630)	0.72	3.2	6.3	2.9	1.03
	1860 (961)	0.72	4.2	7.6	3.5	1.1
	average	0.74	—	—	—	1.2 ^{+0.5} _{-0.2}
Cu-3% Sn	480 (64)	1.66	2.9	4.0	1.9	1.9
	660 (121)	1.68	4.4	5.5	2.5	1.8
	780 (196)	1.61	5.7	7.7	3.6	2.0
	1020 (289)	1.60	7.0	9.8	4.5	1.9
	1200 (400)	1.59	8.2	11.5	5.3	1.8
	1380 (529)	1.62	7.5	12.3	5.6	1.4
	average	1.63	—	—	—	1.8 ^{+0.2} _{-0.4}
Cu-5% Sn	240 (16)	2.86	3.5	4.2	1.9	3.0
	240 (16)	2.77	3.5	4.3	2.0	3.0
	240 (16)	2.82	3.5	4.2	1.9	3.3
	240 (16)	2.76	3.3	4.0	1.8	3.2
	480 (64)	2.92	7.0	8.1	3.7	3.8
	480 (64)	2.90	7.0	8.3	3.8	2.7
	777.7(168)	2.88	11.0	13.8	6.3	2.7
	929.5(240)	2.91	13.5	16.8	7.6	2.8
	929.5(240)	2.91	13.5	17.0	7.7	2.6
	1099.8(336)	2.88	16.5	17.6	8.0	6.5 [†]
	average	2.86	—	—	—	3.0 ^{+0.8} _{-0.4}
Cu-7% Sn	240 (16)	4.15	5.8	7.0	3.2	2.8
	360 (36)	4.27	8.9	9.9	4.5	5.3
	540 (81)	4.31	12.0	14.6	6.6	3.1
	720 (144)	4.29	16.1	20.3	9.2	2.8
	1020 (289)	4.32	22.8	26.7	12.0	4.2
	1140 (361)	4.27	27.3	30.8	13.9	4.6
	average	4.27	—	—	—	3.8 ^{+1.5} _{-1.0}

[†] This value is not used to calculate the average.

experiment.

In the Cu-Sn system an anormal Kirkendall effect has been reported previously⁽¹²⁾⁽¹³⁾ and it has been denied later by Hoshino *et al.*⁽⁷⁾

By analyzing the concentration-penetration profiles, one can determine the maximum limits, X_{max} , to which the markers can move as the position where the following relationship is satisfied (see appendix):

$$N_{\text{Sn}}^-/N_{\text{Sn}}^+ \ll S_2/S_1 \ll N_{\text{Cu}}^-/N_{\text{Cu}}^+. \quad (5)$$

Here S_1 and S_2 are the areas defined similarly as

Fig. 6 Concentration dependence of the ratio $D_{\text{Sn}}^{\text{N}}/D_{\text{Cu}}^{\text{N}}$.

Fig. 7 Relationships between $X_k - X_e$, ΔX_{max} ($=X_{\text{max}} - X_{0c}$) and $X_N - X_{0c}$ and $\sqrt{t}$.

S_{k1} and S_{k2} in eqs. (3) and (4) at X_{max} instead of X_k . The values of the maximum marker shifts, $X_{\text{max}} - X_{0c}$, determined from the concentration-penetration profile are also shown in Table 1 together with the values of distance between X_{0c} and the Matano interface X_N with respect to the mole fixed frame of reference where S_2/S_1 becomes unity. For an example, the relationships between these values and $\sqrt{t}$ are shown in Fig. 7 for the Cu-7Sn diffusion couple. They satisfy the parabolic law well and the marker shifts $X_k - X_e$ are less than $X_{\text{max}} - X_{0c}$. This result supports the Hoshino's results.

V. Summary

In order to determine the intrinsic diffusivities in a precise manner, the inert foil method have been proposed. As long as the edge of inert foils can be considered to be identical to X_0 , this method is very useful for precise measurement of the marker shifts. In order to examine the usefulness of this method the marker shifts in Cu-Sn alloys were measured using mica as well as Mo foils. The results are summarized as follows.

Since mica foils as well as Mo foils did not react with pure Cu and Cu-Sn alloy specimens at this experimental temperature, the methods is considered to be useful. The relations between the marker shift and square root of annealing time satisfied a good linear relationship and the experimental errors around the average were less than $\pm 1 \mu\text{m}$. The ratios $D_{\text{Sn}}^{\text{N}}/D_{\text{Cu}}^{\text{N}}$ were found to be about 1.2, 1.8, 3.1 and 3.8 at 0.74, 1.63, 2.86 and 4.27 at% Sn, respectively.

Acknowledgment

The present work was partly supported by the Grant-in-Aid for General Scientific Research (63550480) from the Ministry of Education, Science and Culture, Japan.

REFERENCES

- (1) A. Smigelskas and E. Kirkendall: Trans. AIME, **171** (1947), 130.
- (2) Th. Heumann and P. Lohmann: Z. Elektrochemie., **59** (1955), 849.
- (3) Th. Heumann: Z. Naturforsch., **32a** (1977), 54.
- (4) Th. Heumann and R. Damkohler: Z. Metallk., **69** (1978), 364.
- (5) Y. Iijima, K. Hirano and M. Kikuchi: Trans. JIM, **23** (1982), 19.
- (6) F. Sauer and V. Freise: Z. Electrochem., **66** (1962), 353.
- (7) K. Hoshino, Y. Iijima and K. Hirano: Trans. JIM, **21** (1980), 674.
- (8) P. Son and T. Sano: J. Japan Inst. Metals, **41** (1977), 1113.
- (9) T. Shimozaki, K. Ito and M. Onishi: Trans. JIM, **27** (1986) 160.
- (10) Th. Heumann: J. Phys. F, **9** (1979), 1997.
- (11) W. B. Pearson: *A Handbook of Lattice Spacings and Structures of Metals and alloys*, Pergamon Press, New York, (1958), p. 597, 611.

(12) L. C. C. da Silva and R. F. Mehl: Trans. AIME, **191** (1951), 155.

(13) H. Oikawa and A. Hosoi: Scripta Met., **9** (1975), 823.

Rearranging eq. (a1), one gets

$$S_{k2}/S_{k1} = \frac{N_{Sn}^-/DR + N_{Cu}^-}{N_{Sn}^+/DR + N_{Cu}^+} \quad (a2)$$

Appendix

On the assumption that the Kirkendall markers are located at an arbitrary position, the division of the right hand side of eq. (2) by S_{k1} yields

$$\frac{D_{Sn}^N}{D_{Cu}^N} = \frac{N_{Sn}^- - N_{Sn}^+ S_{k2}/S_{k1}}{N_{Cu}^+ S_{k2}/S_{k1} - N_{Cu}^-} \quad (a1)$$

where $DR = D_{Sn}^N/D_{Cu}^N$. Under the condition that $D_{Sn}^N \gg D_{Cu}^N$ or $D_{Sn}^N \ll D_{Cu}^N$, DR becomes zero or ∞ . Then S_{k2}/S_{k1} is represented by eq. (6). The position X_{max} is determinable by plotting the relationship between the ratio S_2/S_1 and the distance X around the marker position.