Kirkendall Effect and Movement of α/β Interface due to Interdiffusion in Cu-Zn System

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The Kirkendall effect and movement of the α/β interface in Cu-45 at%Zn β brass diffusion couples were investigated by use of a multiple marker method. After anneal a bend of the multiple marker array was observed at the α/β interface. This phenomenon was analyzed with the aid of the frame of the reference for diffusion.

The bend of the multiple marker array arises from lattice plane formation due to vacancy creation at the interface moving by reaction diffusion. Interfacial reaction consists of atom shift between α lattice and β lattices contacting each other and arrival of atoms by interchange with the vacancies created at the interface.

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I. Introduction

Since Seith⁽¹⁾ presented an equation to represent the movement of the two-phase boundary in relation to the Matano method⁽²⁾, the equation has been used by many investigators in order to analyze the reaction diffusion or multi-phase diffusion phenomena. Because many investigators have found that each boundary concentration of two phases contacting at the interface is kept approximately constant during a period of reaction diffusion, the Matano method which needs employment of the Boltzmann variables may be applied to the reaction diffusion. At the same time continuity of the chemical potentials of diffusing species at the interface is assumed as a result of local equilibrium⁽³⁾. Recently, some authors⁽⁴⁾⁽⁵⁾ have tried to introduce intrinsic diffusion fluxes for analyzing reaction diffusion phenomena. The intrinsic fluxes yielding Kirkendall effect⁽⁶⁾ always links the vacancy flux which is characteristic of a nonequilibrium state. In the present paper a nonconservation phenomenon of the lattice planes as the sources or sinks of the vacancies at the interface and an interfacial reaction are intended to make clear from the standpoints of the frame of the reference for diffusion and from the experimental results on the Kirkendall effect and movement of the α/β interface in copper- β brass diffusion couples.

II. Frame of Reference

There are some frames of reference (coordinate systems) for diffusion. Among them Mass, mole and

volume fixed frames of reference are employed in order to obtain correct interdiffusion coefficients when volume change of a diffusion couple occurs as a result of mixing⁽⁷⁾. If mole fraction and molar volume of alloys and atomic weight for each component are known, a flux referred to one of the three types of the frames of reference is converted into the fluxes referred to the rest. For the three types of the frames of reference one can obtain the same value for the interdiffusion coefficients at a given concentration. The distinct frames of reference besides the above three types should be used in order to account for the interfacial reaction in reaction diffusion.

Darken⁽⁸⁾ has presented the following equation from a standpoint of the frame of references:

$$J_i = j_i + C_i v. \quad (1)$$

The first term on the right hand side is the intrinsic diffusion flux, $-D_i(\partial C_i/\partial X)$. The left hand side is the flux relative to the Matano coordinate system. For the system the mole or volume fixed frame of reference is used in general. Because Darken has set that the molar volumes of alloys are constant, the sum of J_i , i.e., $\sum J_i$, is identical to zero. Under this condition one obtains eq. (2),

$$v = -V(j_1 + j_2), \quad (2)$$

from summation of two equations as to species 1 and 2, where $V = 1/(C_1 + C_2)$. By way of eqs. (1) and (2) eq. (3),

$$\tilde{D} = N_1 D_2 + N_2 D_1, \quad (3)$$

has been derived by Darken, where N is the mole fraction. Darken has not intentionally described the diffusion mechanism for leading the Kirkendall effect. When the conceptions of the vacancy mechanism and vacancy flow have been introduced, eq. (4),

$$j_1 + j_2 + j_v = 0, \quad (4)$$

is presented as a condition for conservation of the lattice points⁽⁹⁾. Equation (4) is useful for accounting for the diffusion phenomena in terms of the ternary system in-

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cluding vacancies. Moreover, eq. (4) in relation to eq. (2) indicates that the marker movement is due to j_v and consequently the numbers of the lattice points should be conserved at the marker fixed plane. Because the eq. (4) does not hold in the entire region of a diffusion layer, it should be considered, in practice, that the marker fixed plane moves away from the place where the vacancies are non-conservative. Following the discovery of the Kirkendall effect Darken has established the conception that the diffusion coefficients of atoms may differ with each species.

Analysis of reaction diffusion deals with the problems including the movement of the two-phase boundary. Consider the diffusion couple consisting of the α and β phases in a binary system and the α/β interface moving at the rate of ω with respect to the Matano coordinate system. If the diffusion fluxes relative to the α and β phases at the interface are given by $(j'_i)_{\alpha\beta}$ and $(j'_i)_{\beta\alpha}$, the following equations hold between them and the fluxes relative to the Matano coordinate system:

$$(J_i)_{\alpha\beta} = (j'_i)_{\alpha\beta} + (C_i)_{\alpha\beta}\omega \quad (5)$$

and

$$(J_i)_{\beta\alpha} = (j'_i)_{\beta\alpha} + (C_i)_{\beta\alpha}\omega \quad (6)$$

where $(C_i)_{\alpha\beta}$ and $(C_i)_{\beta\alpha}$ are the concentrations of species i at the interface. Because $(j'_i)_{\alpha\beta}$ is equal to $(j'_i)_{\beta\alpha}$, subtraction of eq. (6) from eq. (5) yields

$$(J_i)_{\alpha\beta} - (J_i)_{\beta\alpha} = [(C_i)_{\alpha\beta} - (C_i)_{\beta\alpha}]\omega. \quad (7)$$

The above equation means mass balance⁽¹⁰⁾ and no accumulation at the interface. The equation also indicates that J_i is not continuous at the interface and for validity of the equation j'_i should be continuous. Continuity of j'_i is represented in terms of the relation, $(j'_i)_{\alpha\beta} = (j'_i)_{\beta\alpha}$. The relation is proved with the aid of Fig. 1. Summation of two eqs. (5) as to species 1 and 2 gives

$$\omega = -V(j'_1 + j'_2)_{\alpha\beta}. \quad (8)$$

The above equation is the same type as eq. (2). The parenthesized term in eq. (2) indicates the net atomic flow or the vacancy flow by way of eq. (4). On the contrary, the parenthesized term in eq. (8) contains not only the net atomic flow but distinct fluxes arising from the interfacial reaction. The reaction and the fluxes will be illustrated later.

Representing the intrinsic fluxes at the α/β interface by $(j_i)_{\alpha\beta}$ and $(j_i)_{\beta\alpha}$, one obtains the following relation between them and the fluxes relative to the interface:

$$(j_i)_{\alpha\beta} - (j'_i)_{\alpha\beta} = (C_i)_{\alpha\beta}u \quad (9)$$

and

$$(j_i)_{\beta\alpha} - (j'_i)_{\beta\alpha} = (C_i)_{\beta\alpha}u', \quad (10)$$

where u and u' are relative moving velocities between two types of the frame of reference. Subtraction of eq. (10) from eq. (9) yields

$$(j_i)_{\alpha\beta} - (j_i)_{\beta\alpha} = (C_i)_{\alpha\beta}u - (C_i)_{\beta\alpha}u'. \quad (11)$$

Fig. 1 Schematic concentration $-\lambda(x/\sqrt{t})$ curve to account for the relation, $(j_i)_{\alpha\beta} - (j_i)_{\beta\alpha} = 0$. Matano interface is identical with a weld interface of the α and β phases at $t=0$. $(j_i)_{\alpha\beta} = (j_i)_{\beta\alpha} = -\{1/2\sqrt{t}\} \{\text{area } [H(C_i)_{\alpha\beta}G]\}$.

Equation (11) corresponds to eq. (1) or eq. (2) in Ref. (5) and denotes that the markers deviate from the interface if the markers are inserted into the interface moving, except for the special case where eq. (11) equals zero. Summation of two eqs. (11) as to species 1 and 2 is expressed by

$$\Sigma[(j_i)_{\alpha\beta} - (j_i)_{\beta\alpha}] = (1/V)_{\alpha\beta}u - (1/V)_{\beta\alpha}u'. \quad (12)$$

Even if $(1/V)_{\alpha\beta}$ is equivalent to $(1/V)_{\beta\alpha}$, u never equals u' as long as the vacancies are created or annihilated corresponding to the formation or disappearance of the lattice planes at the interface.

III. Experimental Procedure

Pure Cu-45 at%Zn β brass diffusion couples were used in the present experiment. Pure copper specimens were made according to a procedure described previously⁽¹¹⁾. The 45 at%Zn specimens were made by melting a copper block of 99.99% purity together with a zinc block of 99.99% purity in a quartz capsule under the purified argon gas. The alloy rods 10 mm in diameter were rolled at about 600 K to a thickness of about 7 mm. For each specimen of the pure copper and the 45 at%Zn β brass, molybdenum powder with about 1 μ mm in average diameter was inserted as the multiple markers according to a procedure described in previous papers⁽¹¹⁾. The molybdenum powder was also used for the Kirkendall markers in the Cu-45 at%Zn β brass diffusion couples. The diffusion couples with the multiple and Kirkendall markers were annealed at 1023 K during various periods of anneal time.

After diffusion the couple was cut parallel to the diffusion direction and the section was polished metallographically on a buff. An electron probe microanalyzer (JEOL JXA-733) was used for determining the concentration distribution in the annealed couple. The operating conditions of the microanalyzer were as follows: accelerating voltage 25 kV, the take off angle of Zn $K\alpha$ X rays, 0.222 rad; the specimen current, about 5×10^{-6} A; the line scanning speed 0.833 or 1.667×10^{-6} m/s. The intensity of the Zn $K\alpha$ X ray was translated to the concentration of Zn by use of a calibration curve.

IV. Results

The Cu-45 at%Zn β brass diffusion couples were annealed at 1023 K for 14.4, 21.6, 32.4 and 43.2 ks. The relation between zinc concentration and the Boltzmann variable ($\lambda_\xi = \xi/\sqrt{t}$) obtained from the couples annealed is shown in Fig. 2, where ξ means the mole fixed frame of reference. The zinc concentrations of the α and β phases at the α/β interface were respectively 35 and 40 at%Zn. They did not depend on anneal time. Matano interface lies between the α/β and Kirkendall interfaces. Figure 3 shows a composition image by E.P.M.A. obtained from the Cu-45 at%Zn β brass diffusion couple annealed at 1013 K for 14.4 ks. The α phase layer adjoining the pure Cu region contacts with the β phase layer. The β phase layer is divided by the Kirkendall interface. The β phase layer lying between the α/β interface and the Kirkendall interface is newly formed by diffusion. The multiple markers embedded in a pure Cu region before diffusion

Fig. 2 $N_{Zn}-\lambda_\xi$ curve for the Cu-45 at%Zn β brass diffusion couples annealed at 1013 K.

Fig. 3 Composition image by E.P.M.A. Rearrangement of multiple markers in the Cu-45 at%Zn β brass diffusion couple annealed at 1013 K for 14.4 ks, where the multiple markers were buried in the pure copper region before diffusion.

Fig. 4 Schematic accounting for rearrangement of the multiple markers.

Fig. 5 Interdiffusion coefficients estimated from the Cu-45 at%Zn β brass diffusion couples.

are arranged in a curved form in the diffusion layer of the α phase region and in a straight form in the β phase layer newly formed. The curved multiple markers are in the same situation as Fig. 5 in a previous paper⁽¹¹⁾. This indicates that the newly formed lattice planes distribute over the entire diffusion layer in the α phase region. The straight multiple markers in the β phase layer indicate that there is no lattice formation in an inner part of the layer. The most remarkable feature in Fig. 3 is a bend of the multiple markers at the α/β interface.

Figure 4 schematically shows the mechanism for formation of the bend, where $\circ$ marks denote the atoms which

compose the α phase, $\bullet$ marks denote the multiple markers and $\odot$ marks denote the atoms which compose the β phase. At the interface the $\circ$ atoms shift from the α phase to the β phase along with the marker. At the same time $\odot$ atoms come from the inner part of the β phase to construct a new lattice plane belonging to the β phase together with the $\circ$ atoms. Arrival of the $\odot$ atoms yields the vacancy flow toward an opposite direction and only the arrived $\odot$ atoms contribute to net increase of the lattice points at the interface. Thus, formation of the extra lattice plane at the interface makes the bend of the multiple markers. In the Cu-45 at%Zn β brass diffusion couple the Zn atoms which come from the β brass side of the Kirkendall interface behave as the $\odot$ atoms. A matter of course, the $\circ$ and $\odot$ atoms may be arranged in disorder in place of the ordered arrangement shown in Fig. 4. In eq. (12) one among two factors controlling the bend is difference between the molar volumes of the α and β phases. The molar volume of the 45 at%Zn β brass is only 3% larger than that of the 35 at%Zn α brass, as a result of calculation with the aid of a handbook⁽¹²⁾.

The vacancies created in the α region and at the α/β interface ought to be annihilated in the diffusion layer of the β phase after passing through Kirkendall interface. However, void formation and the bend arrangement of the multiple markers were not observed. Figure 5 shows the interdiffusion coefficients in the α and β phases estimated by the Matano method. The coefficients in the α phase is in good accordance with the coefficients previously reported⁽¹¹⁾. The diffusion layer is very wide as shown in Fig. 2 and correct concentration gradient is hard to determine, so that the coefficients in the β phase are more inaccurate than those in the α phase. Hence, the coefficients are given by many spots in comparison with the data by Mehl *et al.*⁽¹³⁾. The coefficients in the β phase are more than 100 times as large as that at 30 at%Zn in the α phase. They scarcely depend on the zinc concentration. That D_{Zn}/D_{Cu} is larger than unity is also valid in the β phase because the Kirkendall markers move to the β brass side. The vacancies are sunk by disappearance of the lattice planes in the β phase, accordingly arrangement of the multiple markers should be in a curved form. Because of the large diffusion coefficients and the wide diffusion layer, it seems unable to detect the bend.

The interfacial reaction and the fluxes referred to the α/β interface are illustrated with the aid of Fig. 4. The reaction consists of the $\circ$ atom shift and the arrival of the $\odot$ atoms, corresponding to transformation reaction from the α phase to the β phase at only the interface. The $\circ$ atom shift is regarded as the atom flow whose reference plane is given by a line distinguishing the α and β phases in Fig. 4. Because of equivalence of $(j'_i)_{\alpha\beta}$ with $(j'_i)_{\beta\alpha}$ and no accumulation of atoms between the reference planes of the fluxes, an only plane may be considered in place of the reference planes.

V. Discussion

The bend of the multiple markers at the interface and

extremely large Kirkendall effect were observed in reaction diffusion between silver and antimony, where only one Ag_3Sb diffusion layer was detected⁽¹⁴⁾. Only one Cu_3Si diffusion layer and the large Kirkendall effect were also detected in the reaction diffusion between copper and silicon⁽¹⁵⁾. The extremely fast diffusion velocity of the Cu atoms was explained in terms of the vacancy flow from the Cu_3Si/Si interface as the source to the Cu/Cu_3Si interface as the sink. The vacancy flow arising from creation and annihilation of the vacancies in a diffusion layer may be characteristic of a nonequilibrium state. Nevertheless the plural phases are seen in the equilibrium phase diagram, the case where only one phase is formed by the diffusion may be closely linked together the interfacial reaction in a strong nonequilibrium state. The bending degree of the multiple marker arrangement in this experiment is smaller than that in the silver-antimony system. The degree seems to depend on amount of the vacancies created at the two-phase boundary.

By employing the β brass specimens having various zinc contents Itoh⁽¹⁶⁾ has investigated dependence of distance between the Kirkendall and α/β interfaces in the Cu- β brass diffusion couples on the zinc content. In the range from 51.15 at (52 mass) to 43.30 at (44 mass)%Zn the distance decreased with decrease of the zinc content in the β brass couple half. Both interfaces were overlapped each other at about 43.30 at (44 mass)%Zn. Up to this content the α/β interface moved away from the Kirkendall interface due to α phase growth. It is clear from his results that the opposite movement of the Kirkendall and α/β interfaces as shown in Fig. 2, i.e., the β phase growth by consuming the α phase at the interface, does not always occur by reaction diffusion between the α and β phases. It should be understood that the α phase growth by consuming the β phase may also occur as a result of the same reaction diffusion, accompanying annihilation of the vacancies. Moreover, Itoh's result shows that there is a special case where the Kirkendall markers always stay at the interface and move along with the interface. If it is so, $(j_i)_{\alpha\beta}$, $(j_i)_{\beta\alpha}$, $(j'_i)_{\alpha\beta}$ and $(j'_i)_{\beta\alpha}$ as to the same component are equal to each other, accordingly both j_i and j'_i are continuous at the interface. In this situation there is no interfacial reaction and $(D_i)_{\alpha\beta}/(D_i)_{\beta\alpha}$ is equal to $(\partial C_i/\partial X)_{\beta\alpha}/(\partial C_i/\partial X)_{\alpha\beta}$, so that we can easily image continuity of the chemical potential and the local equilibrium at the interface.

Nonconservation of the vacancies at the interface means accumulation⁽⁵⁾ and relates to the interfacial reaction. Therefore, the nonconservation phenomenon is a important problem for analyzing reaction diffusion. For application of the Matano method to a diffusion couple after anneal, many investigators have considered aftereffect of the vacancy flow, apart from the phenomenon. Equation (7) has been also employed by many authors⁽¹⁷⁾⁻⁽²⁰⁾. Furthermore, the equation in a simple form is very useful to express movement of the interface under a practical concentration gradient. However, one must consider that the diffusion fluxes in the

equation are affected by many factors in relation to the interfacial reaction.

VI. Summary

Reaction diffusion between the α and β phases in the Cu-Zn system were investigated. The α/β interface in the Cu-45 at%Zn β brass diffusion couple moves toward an opposite direction of the Kirkendall marker shift. The extra lattice plane formation accompanying creation of the vacancies at the α/β interface was proved experimentally. Generally, the intrinsic diffusion fluxes of i component are not continuous at the interface.

The equation, $(-\tilde{D}\partial C_i/\partial X)_{\alpha\beta} - (-\tilde{D}\partial C_i/\partial X)_{\beta\alpha} = [(C_i)_{\alpha\beta} - (C_i)_{\beta\alpha}]\omega$, has been used by many investigators on reaction diffusion. The moving velocity, ω , of the α/β interface in the present experiment mainly depends on the number of the atoms shifting from the α phase to the β phase in the interface. Interfacial reaction on reaction diffusion consists of such atom shift and the atom arrival due to creation of the vacancies at the interface and their subsequent movement.

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