MULTIPHASE DIFFUSION IN Cu-Ni-Zn SYSTEM

by

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ABSTRACT

Isothermal, multiphase diffusion was investigated with infinite diffusion couples in the Cu-Ni-Zn system at 775°C. The couples were assembled with disks of a β (bcc) ternary alloy sandwiched between disks of selected binary, Cu-Ni α (fcc) alloys and were annealed for 2 hours to 2 days. The diffusion structures were investigated metallographically and by electron probe analysis. The couples developed multiphase structures that showed transitions from planar interfaces to nonplanar morphologies with changes in composition of the α terminal alloys. The various structures are described by the aid of composition paths. The velocity of planar interfaces is discussed in terms of intrinsic fluxes in the adjacent phases.

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INTRODUCTION

The development of diffusion structures in multiphase, multicomponent alloys presents many features of metallurgical interest for study. One of these features is the morphology of interfaces between diffusion layers. Interfaces can be planar or nonplanar and affect not only the growth of layers but also the evolution of diffusion structure.

Diffusion structures displaying nonplanar morphologies have been developed by isothermal diffusion of multiphase couples in the Cu-Zn-Sn⁽¹⁾, Fe-Cr-Ni⁽²⁾ and Cu-Zn-Ni⁽³⁾ systems. Such studies have shown that the stability of planar interfaces is dependent on the terminal compositions of the couples.

Taylor et al.⁽³⁾ studied multiphase diffusion in the Cu-Ni-Zn system at 775°C with disks a β (bcc) ternary alloy joined to disks of pure copper or nickel (fcc) and observed the development of diffusion structures with two-phase layers and nonplanar interfaces. In this study multiphase diffusion in the Cu-Ni-Zn system is further investigated at 775°C with solid-solid couples in order to record the variation in diffusion structure as one of the two terminal compositions of the couples is varied. These couples are assembled with disks of a β (bcc) ternary alloy joined to disks of a series of α (fcc) Cu-Ni binary alloys of selected compositions. As the α composition is varied from a high Ni alloy to pure copper, the diffusion structures first exhibit a transition from two-phase layers to planar α/β interfaces and then a change from planar to nonplanar interfaces. These structures are related to the composition paths determined by electron microprobe analysis. In addition, the motion of planar interfaces in diffusion couples involving substitutional diffusion is analyzed in terms of intrinsic diffusion fluxes in the region of the interphase boundaries.

TWO-PHASE COUPLES WITH PLANAR INTERFACES

Interface Velocity

The velocity of motion of a planar interface can be described in terms of intrinsic fluxes of various components in the adjacent phases. In Fig. 1 are shown, schematically, the concentration profiles of a two-phase, ternary couple where β grows at the expense of α phase and inert markers initially placed at the weld-plane are found on the β side of the couple after diffusion.

If the velocity of the planar β/α interface is ϕ_I , the flux balance for component i at the interface can be written as:

$$(\tilde{J}_i^\beta)_I - (c_i^\beta)_I \phi_I = (\tilde{J}_i^\alpha)_I - (c_i^\alpha)_I \phi_I \quad [1]$$

where $(\tilde{J}_i^\beta)_I$ and $(\tilde{J}_i^\alpha)_I$ are the interdiffusion fluxes, and $(c_i^\beta)_I$ and $(c_i^\alpha)_I$ are the concentrations at the interface in the adjacent phases. Hence, ϕ_I is given by:

$$\phi_I = \frac{(\tilde{J}_i^\beta)_I - (\tilde{J}_i^\alpha)_I}{(c_i^\beta)_I - (c_i^\alpha)_I} \quad [2]$$

Interdiffusion fluxes are related⁽⁴⁾ to intrinsic fluxes by:

$$(\tilde{J}_i^\beta)_I = (J_i^\beta)_I + (c_i^\beta)_I v_I^\beta \quad [3]$$

and

$$(\tilde{J}_i^\alpha)_I = (J_i^\alpha)_I + (c_i^\alpha)_I v_I^\alpha \quad [4]$$

where $(J_i^\beta)_I$ and $(J_i^\alpha)_I$ are the intrinsic fluxes of component i , and v_I^β and v_I^α are the Kirkendall velocities in the two phases at the interface. For substitutional diffusion, these velocities are expressed in terms of intrinsic fluxes by:

$$v_I^\beta = - \sum_{i=1}^n (J_i^\beta)_I / \rho^\beta \quad [5]$$

and

$$v_I^\alpha = - \sum_{i=1}^n (J_i^\alpha)_I / \rho^\alpha \quad [6]$$

where n is the number of components, and ρ^β and ρ^α are, respectively, the densities of the β and α phases assumed as constant. Substituting Eqs. [3], [4], [5], and [6] into Eq. [2] one finds:

$$\phi_I = \frac{(J_i^\beta)_I - (N_i^\beta)_I \sum_{i=1}^n (J_i^\beta)_I - (J_i^\alpha)_I + (N_i^\alpha)_I \sum_{i=1}^n (J_i^\alpha)_I}{C_{iI}^\beta - C_{iI}^\alpha} \quad [7]$$

where $(N_i^\beta)_I$ and $(N_i^\alpha)_I$ are concentrations expressed as fraction. Since the vacancy flux J_v is related to the intrinsic fluxes by:

$$J_v = - \sum_{i=1}^n J_i \quad [8]$$

Eq. [7] may be rewritten as:

$$\phi_I = \frac{[(J_i^\beta)_I - (J_i^\alpha)_I] + [(N_i^\beta)_I (J_v^\beta)_I - (N_i^\alpha)_I (J_v^\alpha)_I]}{(C_{iI}^\beta) - (C_{iI}^\alpha)} \quad [9]$$

From Eq. [9] it is apparent that the difference in vacancy fluxes on either side of the interface affects the interface motion and the greater this difference, the larger the influence on the magnitude of ϕ_I .

Position of Marker Plane

Inert markers initially placed at the weld-plane are found either on the α side or the β side of the interface after diffusion. The location of the marker plane depends on the velocity of the interface relative to the Kirkendall

velocities in the two phases in the region of the interface. Two cases of interest are presented below.

(a) For the β phase to grow at the expense of α with markers remaining on the β side of the interface, ϕ_I must be greater than v_I^β ;

$$\phi_I - v_I^\beta > 0. \quad [10]$$

Substituting Eqs. [2], [3], and [4] in Eq. [10], one finds:

$$(j_i^\beta - j_i^\alpha)_I > (c_i^\alpha)_I (v_I^\alpha - v_I^\beta). \quad [11]$$

With the aid of Eqs. [5] and [6], Eq. [11] may be rewritten in terms of intrinsic fluxes as:

$$\rho^\alpha \rho^\beta (j_i^\beta - j_i^\alpha)_I > (c_i^\alpha)_I \left[\rho^\alpha \sum_{i=1}^n j_i^\beta - \rho^\beta \sum_{i=1}^n j_i^\alpha \right]_I. \quad [12]$$

(b) If α grows into β with the markers remaining in the α phase, the inequality to be satisfied is:

$$\phi_I - v_I^\alpha < 0 \quad [13]$$

or:

$$(j_i^\beta - j_i^\alpha)_I < (c_i^\beta)_I (v_I^\beta - v_I^\alpha). \quad [14]$$

In terms of intrinsic fluxes, Eq. [14] may be written as

$$\rho^\alpha \rho^\beta (j_i^\beta - j_i^\alpha)_I < (c_i^\beta)_I \left[\rho^\beta \sum_{i=1}^n j_i^\alpha - \rho^\alpha \sum_{i=1}^n j_i^\beta \right]_I \quad [15]$$

Inequalities of the type expressed in Eqs. [12] and [15] are satisfied by intrinsic fluxes of various components on either side of a planar interface.

EXPERIMENTAL

Five Cu-Ni binary (α) alloys and one Cu-Ni-Zn ternary (β) alloy were prepared from OFHC copper, high purity nickel, and high purity zinc by induction melting in alumina crucibles under an argon atmosphere and quenching the melts in water. The binary alloy slugs were cold rolled to 40% reduction and given a homogenizing anneal for one week at 950°C. Table I lists the composition of various alloys. The five binary alloys are designated as A, B, C, D and E and the ternary alloy as T.

Disks, approximately 1 cm in diameter and 1 cm in thickness, were cut from the alloys, and their surfaces were metallographically polished by lapping through 0.05 μ alumina. Inert markers were placed on the disks by immersing them in a thin slurry of 1 μ alumina in absolute alcohol. Diffusion couples were assembled with disks of the β alloy sandwiched between disks of the α alloys; the disks were held together by means of clamps made of Kovar. The assembled couple was placed in a quartz tube along with chips of the β alloy to minimize the zinc loss from the disks during the initial stages of the diffusion-anneal. The capsule was flushed with hydrogen, evacuated and sealed.

The diffusion-anneal of all couples was carried out at 775°C in a Lindberg Heavy-duty tube furnace. The temperature gradient across the diffusion capsule was less than 1°C and the temperature was controlled to $\pm 0.5^\circ\text{C}$. Annealing time was 2, 12, or 48 hours. The annealed capsules were quenched in ice-brine to retain the high temperature structure of the diffusion zone and to prevent decomposition of the β alloy.

The diffused couples were cold-mounted and ground to expose sections parallel to the direction of diffusion. The sections were metallographically prepared and etched with a solution of potassium dichromate⁽⁵⁾. The diffusion

Table I: Composition of Alloys

Alloy Designation	Composition (wt. pct.)		
	Copper	Nickel	Zinc
T (β)	30.3	20.4	49.3
A (α)	21.1	78.9	--
B (α)	43.0	57.0	--
C (α)	61.6	38.4	--
D (α)	79.2	20.8	--
E (α)	90.1	9.9	--

structures were then photomicrographed at appropriate magnifications. The couples were then analyzed for phase identification and concentration profiles with an ARL-AMX electron microprobe. For this analysis the samples were repolished with $1/4 \mu$ diamond paste to remove the etched layer with care taken to prevent smearing. Analyses were made for zinc and copper by monitoring and measuring the intensities of ZnK_{α} ($\lambda = 1.436 \text{ \AA}$) and CuK_{α} ($\lambda = 1.542 \text{ \AA}$) X-radiations, and the concentration profiles were determined by point-to-point counting techniques. The measured intensities were converted to compositions by means of Ziebold's⁽⁶⁾ conversion procedure with the alloys in Table I employed as standards.

METALLOGRAPHIC STUDIES

Diffusion Structure

The six series of diffusion couples investigated in this study are designated by A/T, B/T, C/T, D/T, E/T and Cu/T on the basis of alloy designations given in Table I.

- (a) A/T Couples: A typical diffusion structure developed in the A/T couple annealed for 12 hr. is shown in Fig. 2. There are three distinct regions within the diffusion zone. Region a consists of a two-phase layer with nonisolated growth of α in β . This can be better seen in Fig. 3. Region b consists of a layer of β phase striated in appearance due to a martensitic type transformation that occurs during quenching. Region c consists of isolated, acicular precipitates of α growing in β matrix. These precipitates become less acicular and more rounded with further diffusion as can be seen in Fig. 4 showing the diffusion structure of the A/T couple diffused for 48 hr.

- (b) B/T couples: The diffusion structure of a B/T couple diffused for 12 hr. is shown in Fig. 5. The diffusion zone essentially consists of a two-phase layer (designated d) with interpenetration of α and β phases into each other, and no singular crystallographic orientation dependence in the growth morphology appears evident in this zone. Similar diffusion zones were observed in B/T couples annealed for 2 and 48 hr.
- (c) C/T Couples: Fig. 6 shows the planar α/β interface developed in the C/T couple diffused for 12 hr. Region e corresponds to the depth of diffusion on the α side of the interface. The planar morphology of the interface was also observed in a couple annealed for 2 hr.
- (d) D/T Couples: For diffusion times of 2 and 12 hr., D/T couples also developed planar α/β interfaces. In Fig. 7 is shown the diffusion zone of a couple diffused for 2 hr; the region f corresponds to the depth of diffusion on the α side of the α/β interface.
- (e) E/T Couple: The diffusion zone of a E/T couple diffused for 2 hr. is presented in Fig. 8, which shows the nonplanar morphology developed at the α/β interface. This break-down of the planar interface shows an apparent periodicity in certain segments of the diffusion zone. Region g refers to the average diffusion depth on the α side of the interface.
- (f) Cu/T Couple: The nonplanar morphology observed in the diffusion zone of a Cu/T couple diffused for 12 hr. is shown in Fig. 9. The diffusion structure shows the orientation-dependent growth of columnar precipitates of α within the β phase in the region h and is similar to those presented by Taylor et al.⁽³⁾

Location and Motion of Markers

The location of markers after diffusion varied considerably for couples A/T through Cu/T. For the A/T couples the marker plane lies in the β phase

layer of region b, as can be seen in Fig. 2. In the case of B/T couples, the marker plane passes through the ($\alpha + \beta$) two-phase region shown in Fig. 5 and markers are found both in the α and β grains. For both the C/T and D/T couples, the marker plane is located on the α -side of the α/β planar interface, as indicated in Figs. 6 and 7. From Figs. 8 and 9 markers are found on the α -side of the nonplanar α/β interface for couples, E/T and Cu/T.

The motion of markers relative to the planar α/β interface in C/T and D/T couples was parabolic with time. This is shown in Fig. 10 where the distance of the marker plane from the interface is plotted as a function of square-root of diffusion time.

Growth Kinetics

The average widths of diffusion layers and regions developed in the diffusion zone of the various couples are given in Table II. These data are plotted against square-root of time in Figs. 11 and 12.

The widths of regions a and b of the A/T couple varied parabolically with time, as shown in Fig. 11. However, as shown in Fig. 12, appreciable deviation from the parabolic growth was exhibited by the cumulative width (a + b + c) of the various layers for diffusion times greater than 12 hr. due to the nonparabolic growth of the region c. Parabolic growth with time was observed for layer d of the B/T couple and regions e, f and g of couples, C/T, D/T and E/T, respectively, as shown in Fig. 12. The region h of the Cu/T couple showed nonparabolic growth for times greater than 12 hrs. Parabolic growth rates of diffusion layers with nonplanar morphologies have been reported in Al-Zn-Mg⁽⁷⁾ and Cu-Zn-Sn⁽⁸⁾ diffusion couples.

COMPOSITION PATHS

Composition paths determined by electron probe analysis of the various couples are presented in Fig. 13. These paths are drawn on the Cu-Ni-Zn

Table II. Growth of Diffusion Layers with Time

Couple	Layer or Region	Diffusion Time, hr.	Width, μ
A/T	<u>a</u>	2	7
		12	17
		48	35
	<u>b</u>	2	34
		12	87
		48	152
	<u>a + b + c</u>	2	112
		12	263
		48	840
B/T	<u>d</u>	2	54
		12	120
		48	256
C/T	<u>e</u>	2	51
		12	115
D/T	<u>f</u>	2	66
		12	170
E/T	<u>g</u>	2	78
		12	187
Cu/T	<u>h</u>	2	190
		12	440
		48	1080

ternary isotherm at 775°C . The tie-lines within of the $(\alpha + \beta)$ two-phase region of the isotherm are schematically shown by dotted lines, and their direction is based on the analysis of an equilibrated two-phase alloy.

The diffusion path of the A/T couples shows three apparent crossings of the $(\alpha + \beta)$ two-phase region. The segment i-l of the path refers to the region c containing α needles in the β matrix, while the path segment l-m indicates a traverse from region c to region b of the diffusion structure. The segments m-n and n-p correspond, respectively, to the b and a layers of the diffusion zone. The couple B/T exhibits a path that crosses the two-phase region at an angle to the tie-lines. This crossing is indicated by the i-k segment of the diffusion path corresponding to the traverse across the two-phase layer d of the couple. The paths for the C/T and D/T diffusion couples are similar in their crossing of the $(\alpha + \beta)$ two-phase region. The segment i-j of the paths that represents this crossing appears parallel to a tie-line that corresponds to a local equilibrium between α and β phases. The diffusion path for the E/T couple crosses the $(\alpha + \beta)$ two-phase region nearly parallel to a tie-line and differs little from the crossing represented by the segment i-j. The diffusion path for the Cu/T has been reported by Taylor et al.⁽³⁾

DISCUSSION

The diffusion couples investigated in this study have shown that changes in one of their terminal compositions can give rise to considerable variation in the development of diffusion structure. As the α terminal composition was varied from alloy A through alloy C, a transition from two-phase layers to single phase layers with planar interfaces was observed in the diffusion structure. The α/β interface remained planar for the change in α alloy from alloy C

to alloy D, but became nonplanar with further change of the terminal composition to alloy E or pure Cu.

The development of nonplanar interfaces and two-phase layers in ternary multiphase couples is normally associated^(1,3) with composition paths that pass through two-phase regions of the isotherm across tie-lines. This implies that a range of two-phase equilibria characterizes a two-phase layer or a nonplanar interphase boundary. On the other hand, a planar interface between two phases is described by a diffusion path parallel to a tie-line within the two-phase region of the ternary isotherm. The composition paths of the various couples in Fig. 13 appear consistent with these concepts.

From the position of the marker planes in the diffused couples, it is apparent that β grows into the α side for couples, A/T and B/T, while β is consumed by α for couples, C/T, D/T, E/T and Cu/T. This change in the direction of transformation seems to occur with the observed transition in the diffusion structure from two-phase layers to planar interfaces.

For couples exhibiting the same direction of transformation it is apparent from Fig. 12 that couples with planar α/β interfaces exhibit slower growth rates than those with two-phase layers or with nonplanar interfaces. The instability of planar interfaces may, therefore, be related to critical rates of transformation as dictated by atomic transport in adjacent phases. This would imply that the relative magnitudes of the terms in Eq. [9] for ϕ_I may affect the stability of interfaces and that the inequalities of the type given in Eqs. [12] and [15] in terms of intrinsic fluxes may not be satisfied for all components in the case of unstable interfaces. Eqs. [12] and [15] are considered valid for planar interfaces in multiphase couples involving one dimensional diffusion with negligible lateral fluxes.

Hence, an analysis of the problem of planar versus nonplanar morphology in multiphase couples needs to consider the relative magnitudes of diffusive flows of the various components in adjacent phases. Accordingly, the kinetic description of the onset of interfacial instability requires a knowledge of intrinsic diffusivities and the associated vacancy flows on either side of an interphase boundary.

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FIGURE CAPTIONS

- Fig. 1. Schematic concentration profiles of a ternary solid-solid diffusion couple; M.P.-Marker plane; O.W.P.-Original weld plane.
- Fig. 2. Diffusion structure of A/T couple diffused for 12 hours at 775°C; 256 X.
- Fig. 3. Diffusion structure of A/T couple diffused for 12 hours at 775°C; region a; 1280 X.
- Fig. 4. Diffusion structure of A/T couple diffused for 48 hours at 775°C; 256 X.
- Fig. 5. Diffusion structure of B/T couple diffused for 12 hours at 775°C; 256 X.
- Fig. 6. Diffusion structure of C/T couple diffused for 12 hours at 775°C; 256 X.
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- Fig. 8. Diffusion structure of E/T couple diffused for 2 hours at 775°C; 640 X.
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520 X.
- Fig. 2. Diffusion coefficients of C/L couple diffused for 15 hours at 1120°C:
520 X.
- Fig. 2. Diffusion coefficients of B/L couple diffused for 15 hours at 1120°C:
520 X.
- Fig. 4. Diffusion coefficients of V/L couple diffused for 18 hours at 1120°C:
region 5: 1580 X.
- Fig. 3. Diffusion coefficients of V/L couple diffused for 15 hours at 1120°C:
520 X.
- Fig. 5. Diffusion coefficients of V/L couple diffused for 15 hours at 1120°C:
couple: M.B.-marker bands: O.M.B.-original metal bands.
- Fig. 1. Schematic concentration profiles of a binary solid-solid diffusion

FIGURE CAPTIONS

CONCENTRATION OF COMPONENT 1 OR 2

$x=0$

$t=0$

x (DISTANCE)

Figure 1

Figure 2

Figure 3

c

b

Figure 4

β

d

α

MARKER
PLANE

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

MARKER DISTANCE FROM β/α INTERFACE
(MICRONS)

Figure 100

Figure 11

Figure 12

Figure 13