Reaction-Diffusion in the Cu-Sn System

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The Cu-Sn binary diffusion couples were annealed in the temperature range of 190 to 220°C. Diffusion coefficients in the η and ϵ phases as well as the Kirkendall effect were measured. Kirkendall markers moved toward the Sn side and consequently the movement suggests the preferential diffusion of Sn atoms by a vacancy mechanism.

The Cu- η , α - η and δ - η couples were annealed in the temperature range of 357 to 404°C. There was only one ϵ phase layer in each diffusion zone of the three types of couples. The ϵ phase in the δ - η couple grew at the highest rate in spite of the fact that it had the smallest diffusion coefficient. It may be concluded that the concentration gaps between the ϵ and its neighboring phases are most effective on the growth of the ϵ . From this point of view, it was possible to predict what phase layer should preferentially grow in the reaction diffusion of five binary systems.

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I. Introduction

In reaction diffusion between two pure metals whose equilibrium phase diagram has some intermediate phases, the factors contributing to the preferential growth of a certain intermediate phase, say the j phase, have been summarized by Nishizawa and Chiba⁽¹⁾ as follows: (1) diffusivity of the j is larger than those of others, (2) formation energy of the j is larger than those of others, (3) crystal structures of neighbouring intermediate phases are similar to that of the j , (4) concentration gaps between the j and neighbouring phases are small, and (5) substances preventing diffusion, e.g., the oxide film, do not present at the interface between distinct intermediate phase layers. In actual cases, however, it may be difficult to appreciate to what extent these factors affect the preferential growth, consequently we cannot predict the phase which grows preferentially in the reaction diffusion of binary systems.

As for the η and ϵ phases in the equilibrium phase diagram of the Cu-Sn system⁽²⁾ which is shown in Fig. 1, the thickening rate of these phases has been measured from the standpoint of fundamental research of soldering⁽³⁾ and

Fig. 1 Equilibrium phase diagram of the Cu-Sn system.

reaction diffusion of copper with solid tin⁽⁴⁾. The purpose of this work is to determine diffusion coefficients in the η and ϵ phases which are formed between copper and solid tin and to confirm experimentally the effect of the fourth factor mentioned above on the growth of the ϵ phase layer using Cu- η , α - η and δ - η couples. From these results the possibility of the preferential growth in the reaction diffusion of several binary systems is discussed.

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II. Experimental Procedure

99.99%Cu and 99.9%Sn base metals which were weighed to have the compositions of the α , δ and η phases were sealed in silica capsules with 1/4 atom argon gas and kept in the homogeneous liquid state at 1120°C for 24 hr. After being cooled from 1120°C to 800, 500 and 350°C, the α , δ and η alloys were isothermally annealed for 10, 20 and 20 days at these temperatures respectively and then quenched into water. All the alloys thus obtained were homogeneous without concentration gradients. The compositions of the α , δ and η alloys which were chemically analyzed were 4.4, 20.6 and 43.8 at%Sn respectively. The couple halves were 10 mm ϕ $\times$ 2 mm size and their grain size were 1 to 2 mm ϕ .

After one side surfaces of the disks were metallographically polished, they were joined together across 5 $\mu\phi$ molybdenum wires as markers and kept in contact with stainless steel clumps at room temperature. The couple clumped was heated for the initial 1 or 2 hr annealing at a given temperature, the couple free from the clump underwent subsequent anneal at the same temperature. Anneal was carried out in argon gas atmosphere and the temperature was controlled within $\pm 1^\circ\text{C}$. The marker movements were measured in reference to the microhardness indentations in the semi-

infinite region according to a previous report⁽⁵⁾.

An electron probe microanalyzer (JXA-5) was used to determine concentration penetration curves by mainly counting tin L_α radiation. The conversion of the radiation intensity to chemical composition was made using the calibration curve as shown in Fig. 2.

III. Experimental Results

1. Cu-Sn couples

In this series anneal was carried out in the temperature range of 190 to 220°C. A typical photomicrograph of a diffusion zone and a scanning profile by E.P.M.A. are shown in Photo. 1 and Fig. 3 respectively. The η and ϵ phase layers appeared in the diffusion zone according to the equilibrium phase diagram, but α solid solution of Sn in Cu was not detected at all. After anneal the markers were always presented in the η layer as shown in Photo. 1. The markers moved toward the Sn side, although the shift of the markers was less than 5 μ even after annealing for 900 hr at 220°C. The direction of the marker movement is in agreement with the result obtained by Bhedwar et al.⁽⁶⁾ who ascribed that Sn atoms were more mobile than Cu atoms.

Figure 4 shows parabolic growth of the total

Fig. 2 Relative intensity-concentration curve of Sn L_α radiation for electron probe analysis.

Photo. 1 Photomicrograph of the Cu-Sn couple annealed at 220°C for 900 hr. There is a marker in the η phase layer.

Fig. 3 E.P.M.A. line analysis curve of the Cu-Sn couple annealed at 220°C for 900 hr.

Fig. 4 Parabolic relation between the width of the total, η and ϵ phases and diffusion time. The Cu-Sn couples were annealed at 220°C.

diffusion layer as well as the η and ϵ phases at 220°C. A rate constant k for the parabolic growth of an intermediate phase layer is defined as

Fig. 5 Temperature dependence of square of the parabolic rate constants for the total, η and ϵ phases in the Cu-Sn couples.

$$W = kt^{1/2} \quad (1)$$

where W is the width of an intermediate layer and t is the time of anneal. Figure 5 shows the temperature dependence of the square of the rate constants of the total layer as well as the η and ϵ layers. The linear relationship was set up between the square of the rate constant and the reciprocal of the absolute temperature. From the relation, eqs. (2) to (4) were obtained by using the least squares method.

$$\text{Total layers : } k_{\text{total}} = 6.23 \times 10^{-6} \exp(-13800/RT), \quad (2)$$

$$\eta \text{ phase layer : } k_{\eta}^2 = 8.06 \times 10^{-7} \exp(-12700/RT), \quad (3)$$

$$\epsilon \text{ phase layer : } k_{\epsilon}^2 = 2.14 \times 10^{-6} \exp(-14600/RT). \quad (4)$$

In the reaction of Cu with the molten Sn saturated with Cu in the temperature range of 320 to 410°C, the apparent activation energies for the growth of the η and ϵ phases have been estimated to be 8.7 and 11 kcal/mol respectively⁽³⁾. Starke et al. have measured k_{η}^2 and k_{ϵ}^2 for the Cu-Sn couples annealed at 180 and 210°C⁽⁴⁾. These values are considerably larger than those obtained in this experiment. Using the two values obtained by Starke et al. we estimated the apparent activation energies for

Table 1 Boundary concentration and k^2 of the η and ε phases in the Cu-Sn couples.

Anneal		Phase boundary concentration (at % Sn)				Square of parabolic rate constants (cm ² /sec)	
Temp. (°C)	Time (hr)	$C_{\varepsilon\text{Cu}}$	$C_{\varepsilon\eta}$	$C_{\eta\varepsilon}$	$C_{\eta\text{Sn}}$	k_{η}^2	k_{ε}^2
190	400	24.8	26.2	45.4	47.7	8.82×10^{-13}	2.72×10^{-13}
	625	24.8	26.3	45.4	47.1		
	900	24.9	26.2	45.2	46.5		
200	400	24.7	25.9	45.3	47.4	1.12×10^{-12}	3.84×10^{-13}
	625	24.5	25.8	45.1	46.6		
	900	24.3	25.7	45.2	47.2		
210	400	24.3	26.1	44.8	47.0	1.42×10^{-12}	5.21×10^{-13}
	625	24.3	25.9	44.7	45.7		
	900	24.5	25.5	44.8	46.3		
220	400	24.5	25.5	44.5	46.2	2.04×10^{-12}	7.41×10^{-13}
	625	24.2	25.3	44.8	45.9		
	900	24.2	25.7	44.7	46.4		

the growth of the η and ε phases to be 32 kcal/mol for the η and 31 kcal/mol for the ε . The marked difference of the activation energies obtained by the investigators may be due to the difficulty of measuring the accurate layer thickness, because of the very thin layer and the extremely uneven interface between the layers. Using Cu-Sn couples consisting of evaporated films of both metals, Tu⁽⁷⁾ detected the η' phase layer existing as a single intermediate layer in the couple kept at room temperature and found that $k_{\eta'}^2$ is at least 10^{-17} cm²/sec. Assuming that the η to η' transformation did not significantly affect the diffusion coefficient, he compared the k_{η}^2 obtained by extrapolating straightforward the result of Starke et al. to 20°C with the $k_{\eta'}^2$ at 20°C. Because the extrapolated k_{η}^2 , 10^{-20} cm²/sec, was much smaller than the $k_{\eta'}^2$, Tu concluded that the growth of the η' at 20°C might be controlled by boundary diffusion. However, the k_{η}^2 estimated by extrapolating the result of this experiment to 20°C is about 10^{-16} cm²/sec, being clearly larger than the $k_{\eta'}^2$ at 20°C. This is contradictory to Tu's conclusion, but this meaning is obscure.

Table 1 summarizes the concentration of each interface between intermediate phases as well as the k_{η}^2 and k_{ε}^2 , from which it is evident that each boundary concentration, C_{ij} , is independent of anneal time. From the master curve at 190°C as shown in Fig. 6, we can estimate D_{η} and D_{ε} by use of Heumann's method⁽⁸⁾. Temperature dependence of the

Fig. 6 Master concentration-penetration curve of the Cu-Sn couples annealed at 190°C.

D_{η} and D_{ε} is shown in Fig. 7, and represented by eqs. (5) and (6).

$$D_{\eta} = 1.55 \times 10^{-4} \exp(-15500/RT) \quad (5)$$

$$D_{\varepsilon} = 1.43 \times 10^{-4} \exp(-16900/RT) \quad (6)$$

2. Cu- η , α - η and δ - η couples

According to the equilibrium phase diagram of the Cu-Sn system the η phase is formed by the peritectic reaction of the ε phase with the liquid at 415°C, the δ phase eutectoidically dissociates into the α and ε phases at about 350°C. On account of avoiding these transformation, the Cu- η , α - η and δ - η couples

Fig. 7 Temperature dependence of diffusion coefficients for the η and ϵ phases in the Cu-Sn couples.

were annealed in the temperature range of 357 to 404°C. The δ layers in diffusion zones of the three types of couples were not detected, despite the fact that this phase is stable in the equilibrium diagram. Hence, there was only the ϵ layer in each diffusion zone of three kinds of the couples, no concentration gradients in all couple halves which were adjacent to the ϵ could be observed. Photograph 2 shows photomicrographs of the three types of couples

annealed at 404°C. Variation of the marker position with the couples is not related to the marker shift but to the position of original or the Matano interface. The markers in all couples annealed moved toward the Sn side within a distance of 5 μ .

The parabolic growth and its temperature dependence for the ϵ phases in the three types of couples are shown in Figs. 8 and 9 respectively. It appears from these figures that the growth rate of the ϵ phase increases in the

Fig. 8 Parabolic relation between the width of the ϵ phases and diffusion time. The Cu- η , α - η and δ - η couples were annealed at 404°C.

Photo. 2 Photomicrographs of the Cu- η , α - η and δ - η couples annealed at 404°C for 4 hr. The η couple halves situate in the upper parts of all the photomicrographs. (a): Cu- η couple (b): α - η couple (c): δ - η couple

Fig. 9 Temperature dependence of square of the parabolic rate constants for the ϵ phases in the Cu- η , α - η and δ - η couples.

order of the δ - η , α - η and Cu- η couples. The straight lines in Fig. 9 can be represented by the following equations:

$$\text{Cu-}\eta \text{ couples: } k_e^2 = 8.07 \times 10^{-4} (-18700/RT), \quad (7)$$

$$\alpha\text{-}\eta \text{ couples: } k_e^2 = 1.07 \times 10^{-3} (-18900/RT), \quad (8)$$

$$\delta\text{-}\eta \text{ couples: } k_e^2 = 2.97 \times 10^{-3} (-19800/RT). \quad (9)$$

Figure 10 shows the E.P.M.A. line analysis curve of the Cu- η couple annealed at 404°C

Fig. 10 E.P.M.A. line analysis curve for the Cu- η couple annealed at 404°C for 39 hr.

for 39 hr, in which the concentration gradient in the ϵ phase layer can be approximately drawn by a straight line. The linear concentration gradient in the ϵ phase layer was always observed in the α - η and δ - η couples. Table 2 summarizes the boundary concentration at both sides in the ϵ layers in the three types of the couples and k_e^2 . Because the layer grew according to the parabolic law and each boundary concentration in the ϵ was kept constant independent of the anneal time, the concentration penetration curves obtained from one kind of the couples annealed at a given temperature for various periods of time can be represented by one master curve.

In the case where there is only one intermediate phase layer having a linear concentration gradient in a diffusion zone and no concentration gradient exists in both couple halves adjacent to the intermediate layer, we can easily measure the diffusion coefficients in the layer by assuming that the diffusion coefficient is constant independent of the concentration. When two concentration gaps at the interfaces on the both sides of the j intermediate phase are denoted by ΔC_a and ΔC_c respectively, the concentration difference in the j layer is denoted by ΔC_b , as shown in Fig. 11, the diffusion coefficient in the j layer is given by the following equation⁽⁹⁾⁽¹⁰⁾:

$$k_j^2 = 2\Delta C_b(1/\Delta C_a + 1/\Delta C_c)D_j \quad (10)$$

where k_j is a parabolic rate constant of the j phase. The temperature dependence of the diffusion coefficient in the ϵ layer is shown in

Fig. 11 Schematic concentration-penetration curve of the i - k couple.

Table 2 Boundary concentration and k_e^2 of the ϵ phases in the Cu- η , α - η and δ - η couples.

Couples	Anneal		C_{IJ} (at % Sn)		k_e^2 (cm ² /sec)
	Temp. (°C)	Time (hr)	$C_{\epsilon\text{Cu}}$	$C_{\epsilon\text{Sn}}$	
Cu- η	357	16	23.3	23.8	2.69×10^{-10}
		25	23.5	23.7	
		36	23.3	23.9	
	372	17.5	23.3	23.8	3.76×10^{-10}
		25	23.5	23.7	
		36	23.3	23.8	
	378	16	23.4	23.8	4.24×10^{-10}
		25	23.5	23.8	
		36	23.3	23.8	
	388	16	23.5	23.7	5.34×10^{-10}
		25	23.4	23.8	
		38	23.4	23.8	
	404	16	23.4	23.8	7.67×10^{-10}
		25	23.4	23.8	
		39	23.4	23.7	
α - η	357	4~38	23.4	23.8	2.97×10^{-10}
	372	4~38	23.4	23.8	4.24×10^{-10}
	388	4~38	23.4	23.8	6.06×10^{-10}
	404	4~38	23.4	23.8	8.47×10^{-10}
δ - η	357	4~36	23.1	23.6	4.00×10^{-10}
	372	4~36	23.1	23.6	5.81×10^{-10}
	378	4~36	23.1	23.6	6.92×10^{-10}
	388	4~38	23.1	23.6	8.41×10^{-10}
	404	4~39	23.1	23.6	1.18×10^{-9}

Fig. 12 Temperature dependence of diffusion coefficients for the ϵ phases in the Cu- η , α - η and δ - η couples.

Fig. 12, from which the following equations were obtained:

$$\text{Cu-}\eta \text{ couples: } D_e = 1.09 \times 10^{-2} \times \exp(-18700/RT), \quad (11)$$

$$\alpha\text{-}\eta \text{ couples: } D_e = 1.30 \times 10^{-2} \times \exp(-18900/RT), \quad (12)$$

$$\delta\text{-}\eta \text{ couples: } D_e = 6.59 \times 10^{-3} \times \exp(-19800/RT). \quad (13)$$

In the temperature range of Fig. 12, the diffusion coefficients in the ϵ phases increase in the order of the α - η , Cu- η and δ - η couples and the diffusion coefficients for the δ - η couples are appreciably smaller than those for the two other types of couples.

IV. Discussion

When a diffusion couple consists of two metals with greatly different molar volumes, the concentration should be measured in moles per unit volume for the purpose of obtaining more accurate diffusion coefficients, as exemplified by Hirano and Ipposhi⁽¹¹⁾. Because the molar volumes of Cu and Sn are 7.09 and

16.29 cm³/mol respectively, it is desirable to use moles per unit volume instead of mole fractions. Using lattice parameters of the $\alpha^{(12)}$, $\epsilon^{(13)}$, η and $\delta^{(14)}$ phases, we calculated molar volumes of these phases and then determined diffusion coefficients of the phase layers in the Cu–Sn, Cu– η , α – η and δ – η couples. In all cases, however, the results showed that the diffusion coefficients calculated by using Cu mol/cm³ were about two times larger than those calculated by using Sn mol/cm³, and the mean values of the two types of the diffusion coefficients were nearly equal to the diffusion coefficients estimated by employing mole fraction.

In Fig. 12, the diffusion coefficients of the ϵ layer in the δ – η couples were appreciably smaller than those in the Cu– η and α – η couples. Some investigators⁽¹⁵⁾⁽¹⁶⁾ have reported that the diffusion coefficient at a certain concentration depends on the type of couples, but this fact remains unclarified at the present time. Apart from this problem, we should remark the fact that the ϵ phases in the δ – η couples grow at the fastest rate although they have the smallest diffusion coefficients. In eq. (10), it is suitable to consider that the concentration gaps between the j and its neighbouring phases have effects on the growth rate of the j phase. It can be said that the fourth factor in introduction of this paper, which was first cited by Seith⁽¹⁷⁾, was experimentally confirmed. In the reaction diffusion of the Au–Al⁽⁵⁾, Cu–Al⁽¹⁸⁾, Ti–Ni⁽¹⁹⁾ and Ni–Zn⁽²⁰⁾ systems, Au₅Al₂, δ , TiNi and γ phases preferentially grow respectively. There is no definite rule between the crystal structures of these phases and their neighbouring phases. In view of the melting points or decompose temperatures of the above four phases, they do not always have larger formation energies than those of their neighbouring phases. Hence, the second and third factors may not be responsible to the preferential growth. Exclusive of the fifth factor, we should eventually pay attention to the first and fourth factors. All the four phases are situated at positions to satisfy the fourth factor in each phase diagram. Since it has been well known that diffusion coefficients in metals and alloys increase with approach to melting

point, diffusivities in the intermediate phases of a binary couple at a given temperature may not differ greatly if the melting points do not significantly vary with the phase. In this case, therefore, it can be considered that the preferential growth can be brought out by the fourth alone even if the first is not satisfied. As for the reaction diffusion of the Fe–Zn system⁽²¹⁾, palisade δ_1 begins to grow rapidly after δ_1 layer is divided into compact and palisade δ_1 layers. This may be due to the effect of the fourth, but the effect of the third may not possibly be neglected because of the analogy between the crystal structure of the palisade and that of the compact⁽²²⁾⁽²³⁾. It has been frequently reported that one or more intermediate phase layers which are seen in an equilibrium phase diagram of a certain binary system do not appear, but a particular phase layer preferentially grows in a diffusion zone of the corresponding binary couple⁽²⁴⁾⁽²⁵⁾. In these cases, of course, the phases which preferentially grow, can not be predicted from the equilibrium phase diagrams.

V. Conclusion

The Cu–Sn binary diffusion couples were annealed in the temperature range of 190 to 200°C. Diffusion coefficients in the η and ϵ phases as well as the Kirkendall effect were measured. The movement of Kirkendall markers toward the Sn side suggests the preferential diffusion of Sn atoms by a vacancy mechanism. The diffusion coefficients of the η and ϵ phases were represented by the following equations:

$$D_{\eta} = 1.55 \times 10^{-4} \exp(-15500/RT),$$

$$D_{\epsilon} = 1.43 \times 10^{-4} \exp(-16900/RT).$$

The Cu– η , α – η and δ – η couples were annealed in the temperature range of 357 to 404°C. There was only one ϵ phase layer in each diffusion zone of the three types of couples. The ϵ phase in the δ – η couple grew at the highest rate despite the fact that it had the smallest diffusion coefficients. It can be concluded that the concentration gaps between the ϵ and its neighbouring phases may be most effective on the growth of the ϵ . From this point of view, the phase layers which preferentially grow in

each reaction diffusion of the Au-Al, Cu-Al, Ti-Ni, Ni-Zn and Fe-Zn systems can be predicted.

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