STEADY STATE DIFFUSION IN Cu-Zn-Mn ALLOYS

by

J. D. Whittenberger and M. A. Dayananda

MASTER

ABSTRACT

Steady state substitutional diffusion was investigated in the copper-rich phase of the Cu-Zn-Mn system at 850°C with thin membranes of copper exposed to the vapors of zinc and manganese. For the four series of experiments studied, steady state concentration profiles that were invariant with time were established within four to six days. A simple mobility model was employed in the analysis of concentration profiles for the calculation of mobilities of zinc and manganese at various ternary compositions along the steady state composition paths. The isomobility lines of zinc and manganese generated from these calculations were consistent with the mobility data for the binary Cu-Zn and Cu-Mn systems.

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J. D. Whittenberger, formerly INCO Fellow in the School of Materials Science and Metallurgical Engineering, Purdue University, Lafayette, Indiana, is with NASA-Lewis Research Center, Cleveland, Ohio. M. A. Dayananda, Member AIME, is Associate Professor, School of Materials Science and Metallurgical Engineering, Purdue University.

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INTRODUCTION

Most of the diffusion studies in ternary solid solutions have been made under unsteady state conditions with infinite^(1,2) semi-infinite^(3,4), or finite⁽⁵⁾ diffusion couples. In particular, infinite solid-solid couples and semi-infinite vapor-solid couples have been employed for the determination of concentration-dependent interdiffusion coefficients as well as intrinsic diffusion coefficients in ternary alloys. The determination of these coefficients at a single ternary composition normally requires two independent experiments with diffusion couples having intersecting diffusion paths, as discussed by Kirkaldy⁽⁶⁾ and Philibert and Guy⁽⁷⁾. Alternatively, atomic mobilities of the diffusing species may be calculated from a single experiment on the basis of a simple mobility model, as shown by Dayananda⁽⁸⁾.

Substitutional diffusion under steady state conditions has not been experimentally investigated in ternary metallic systems. Even in binary systems, the main studies of the steady state have been limited to the interstitial diffusion^(9,10) of carbon in austenite and the substitutional diffusion of zinc in Cu-Zn alloys⁽¹¹⁾. The experimental set-up employed in these experiments corresponds to a thin membrane of a low vapor pressure component exposed on the one side to a vapor source of a high vapor pressure component and to a vapor sink on the other.

For a metallic membrane exposed to vapors which supply the diffusing components, the steady state refers to the condition when the profiles of all components become invariant with time. This requires that the fluxes referred to a coordinate system fixed relative to the membrane become constant. The steady state profiles are dependent on the constraints regarding flows and gradients imposed for any of the diffusing species.

It is the purpose of this paper to present steady state concentration profiles experimentally investigated at 850°C for diffusion of zinc and manganese through thin copper membranes exposed to the vapors of the diffusing species. These profiles are analyzed on the basis of a simple mobility model for the calculation of atomic mobilities of manganese and zinc over a wide range of composition along the steady state diffusion paths. For these calculations, use is made of the thermodynamic data⁽¹²⁾ as well as the data on mobilities⁽⁸⁾ available for the Cu-rich Cu-Zn-Mn alloys. The choice of the system is based on the earlier diffusion studies⁽³⁾ carried out with vapor-solid couples at 850°C in the Cu corner of the Cu-Zn-Mn isotherm⁽¹³⁾.

STEADY STATE DIFFUSION

The Coordinate System. Steady state diffusion in ternary alloys is analyzed on the basis of concentration profiles that are invariant with time. This analysis is confined to isothermal, unidimensional diffusion in a single phase membrane, which exhibits negligible change in its thickness and develops little porosity under steady state conditions.

Figure 1 shows schematic concentration profiles for ternary diffusion in a membrane exposed to two distinct vapor sources of the diffusing species, one on either side. These profiles correspond to the case when the high vapor pressure components 1 and 2 diffuse in opposite directions in a membrane of solvent 3 of negligible vapor pressure. During the initial unsteady state diffusion, the thickness of the membrane increases; however, after the steady state is established, the thickness becomes constant, since the net mass input becomes zero.

For a coordinate system whose origin is located at an external surface of the membrane, the steady state concentration profiles are fixed; thus

$$\left(\frac{\partial C_i}{\partial t}\right)_x = 0 \quad (i = 1, 2, 3) \quad [1]$$

for $0 \leq x \leq l$. From the continuity equation, it follows that

$$\left(\frac{\partial C_i}{\partial t}\right)_x = -\left(\frac{\partial \tilde{J}_i}{\partial x}\right)_t = 0 \quad [2]$$

where $\tilde{J}_i$ is the interdiffusion flux. Hence, the steady state implies constancy of fluxes referred to a coordinate system fixed relative to the membrane.

The Mobility Model. A simple phenomenological approach to multi-component diffusion is furnished by the mobility model^(14,8), where the intrinsic diffusion flux, J_i , of a diffusing component is considered to be proportional only to its own chemical potential gradient, $\partial \mu_i / \partial x$. In this model the intrinsic flux is given by

$$J_i = - \frac{C_i \beta_i}{N_0} \frac{\partial \mu_i}{\partial x} \quad (i = 1, 2 \dots n) \quad [3]$$

where C_i is the concentration in moles/cc; β_i is the mobility of component i ; and N_0 is Avogadro's number. The intrinsic flux which is referred to a fixed lattice is related to the interdiffusion flux, $\tilde{J}_i$, based on a reference frame fixed at the external surface of a diffusion membrane by:

$$\tilde{J}_i = J_i + C_i v \quad (i = 1, 2 \dots n) \quad [4]$$

where v is the velocity of the Kirkendall frame of reference relative to the external surface of the membrane. At steady state the fluxes are constant; hence,

$$\tilde{J}_i = K_i \quad [5]$$

for $0 \leq x \leq l$.

For the case of ternary diffusion shown in Fig. 1, where component 3 has negligible vapor pressure, $\tilde{J}_3$ is zero at the surfaces of the membrane for all time t . Hence, at the steady state

$$\tilde{J}_3 = K_3 = 0 \quad [6]$$

for $0 \leq x \leq l$. From Eqs. [4] and [6], one gets

$$v = \frac{\beta_3}{N_0} \frac{\partial \mu_3}{\partial x} \quad [7]$$

Substitution of Eqs. [5] and [7] in Eq. [4] for $i = 1, 2$ yields:

$$K_1 = -\frac{c_1}{N_0} \left(\beta_1 \frac{\partial \mu_1}{\partial x} - \beta_3 \frac{\partial \mu_3}{\partial x} \right) \quad [8]$$

and

$$K_2 = -\frac{c_2}{N_0} \left(\beta_2 \frac{\partial \mu_2}{\partial x} - \beta_3 \frac{\partial \mu_3}{\partial x} \right) \quad [9]$$

For the case where

$$\left| \beta_3 \frac{\partial \mu_3}{\partial x} \right| \ll \left| \beta_1 \frac{\partial \mu_1}{\partial x} \right| \quad [10]$$

and

$$\left| \beta_3 \frac{\partial \mu_3}{\partial x} \right| \ll \left| \beta_2 \frac{\partial \mu_2}{\partial x} \right| \quad [11]$$

Equations [8] and [9] can be simplified to:

$$K_1 = - \frac{C_1 \beta_1}{N_o} \frac{\partial \mu_1}{\partial x} \quad [12]$$

and

$$K_2 = - \frac{C_2 \beta_2}{N_o} \frac{\partial \mu_2}{\partial x} \quad [13]$$

Equations [12] and [13] may be employed for the calculation of β_1 and β_2 as functions of composition along the steady state path, provided steady state fluxes, K_1 and K_2 , can be determined by experiment. Alternatively, K_1 and K_2 can be evaluated, if data on mobilities are available at least for one composition on the steady state concentration profiles. Such data can be obtained from unsteady state diffusion experiments with marker motion studies as shown^(3,8) for the Cu-Zn-Mn alloys. Also, the application of the mobility model requires knowledge of the thermodynamics of the ternary system.

THERMODYNAMICS OF THE Cu-Mn-Zn SYSTEM

Data on Zinc Activity. The vapor pressures of zinc determined by Chadwick and Argent⁽¹²⁾ for various Cu-Zn-Mn alloys were employed in the calculation of activity of zinc at 850°C over a wide range of compositions. The measured zinc vapor pressure P at $T^\circ K$ was expressed by

$$\log_{10} P = a + \frac{b}{T} \quad [14]$$

where a and b are constants dependent on the alloy composition. The vapor pressure of pure zinc, P^o , was calculated from⁽¹⁵⁾

$$\log_{10} P^o = - \frac{6670}{T} - 1.126 \log_{10} T + 12.0 \quad [15]$$

With the reported values⁽¹²⁾ of a and b , zinc activities were calculated from Eqs. [14] and [15] at 850°C. Figure 2 shows these data and the isoactivity lines of zinc drawn from them. Pertinent data on the activity of zinc for Cu-Zn binary alloys calculated by Birchenall and Mehl⁽¹⁶⁾ from the vapor pressure measurements of Hargreaves⁽¹⁷⁾ are also shown in Fig. 2.

Calculation of Activities of Manganese and Copper. Values of excess free energy, G^x , were calculated for various Cu-Zn-Mn alloys from the relation⁽¹⁸⁾

$$G^x = (1-N_{Zn}) \left[RT \int_0^{N_{Zn}} \frac{\ln \gamma_{Zn}}{(1-N_{Zn})^2} dN_{Zn} + G_{Cu-Mn}^x \right]_{N_{Cu}/N_{Mn}} \quad [16]$$

where γ_{Zn} is the activity coefficient of zinc and the path of integration is along lines of constant copper to manganese ratio, N_{Cu}/N_{Mn} . G_{Cu-Mn}^x corresponds to the binary Cu-Mn alloy on the line of integration with N_{Zn} equal to zero. G_{Cu-Mn}^x was determined from the activity data of Krenzer and Pool⁽¹⁹⁾ at 850°C summarized by:

$$a_{Zn} = 1.3 N_{Mn} \quad [17]$$

$$a_{Cu} = 1 - N_{Mn} \quad [18]$$

for $0 \leq N_{Mn} \leq 0.13$.

From the evaluated G^x the partial molar excess free energy of manganese $\bar{G}_{Mn}^x$ and hence its thermodynamic activity were calculated for various compositions from the relations⁽¹⁸⁾:

$$\bar{G}_{Mn}^x = G^x + (1 - N_{Mn}) \left(\frac{\partial G^x}{\partial N_{Mn}} \right)_{N_{Cu}/N_{Zn}} \quad [19]$$

and

$$\bar{G}_{Mn}^x = RT \ln (a_{Mn}/N_{Mn}) \quad [20]$$

Activity of copper could then be evaluated from

$$\ln(a_{Cu}/N_{Cu}) = \frac{1}{N_{Cu} RT} \left[G^x - N_{Zn} \bar{G}_{Zn}^x - N_{Mn} \bar{G}_{Mn}^x \right] \quad [21]$$

The results of these calculations are shown in Figs. 3 and 4 in the form of isoactivity lines of manganese and copper, respectively.

EXPERIMENTAL PROCEDURE

Cu-Zn-Mn alloys of various compositions were made by induction melting OFHC copper, high purity zinc (99.999 pct.), and electrolytic manganese (99.98 pct.) in zirconia crucibles under argon atmosphere. These alloys were chill cast into a copper mold, and the resulting ingots were machined to fine chips less than 0.003 in. thick with acetone as a coolant. The chips were outgassed in vacuum for 12 hours at 200°C. Table 1 lists the composition of various alloys used as vapor sources.

The diffusion assembly essentially consisted of a 0.010 in. thick OFHC copper membrane exposed on either side to alloy chips of chosen compositions serving as vapor sources, as shown in Fig. 5. To ensure the separation of the two vapor sources, a copper diffusion cell was constructed by diffusion bonding the membrane to an end of an OFHC copper tubing (3/4 in. O.D. - 1/16 in. wall thickness) which had been metallographically polished through lapping with 0.05 μ alumina. The

bonding was carried out by assembling the tubing and the membrane together in a stainless steel clamp and annealing the assembly in an evacuated vycor tube for 12 hours at 900°C .

One micron alumina markers were placed on the surfaces of the bonded membrane with a thin slurry of alumina in ethyl alcohol. The copper cell was then filled with about 50 grams of chips of one of the vapor source alloys. The cell was evacuated, flushed with hydrogen and finally sealed under vacuum of less than $1\ \mu$ pressure by cold welding with the aid of a hydraulic press. The operation of cold welding consisted of collapsing the copper tube and shearing it by means of a hardened steel wedge placed in the frame of the press.

The sealed copper cell was then introduced into a 12 in. long quartz capsule, 1.3 in. in diameter. The capsule was packed with about 50 grams of chips of a second alloy and its open end was closed under a stream of argon which prevented the oxidation of the chips. The capsule was flushed with hydrogen, evacuated and sealed at a pressure of less than $1\ \mu$.

The diffusion capsule was then annealed in a tube furnace at 850°C for a diffusion time of 4, 6, or 9 days. The temperature gradient was less than 2°C over the length of the capsule (about 10 in.) and the temperature was controlled to $\pm 0.5^{\circ}\text{C}$. The annealed capsules were air cooled.

The copper cell was then cut open and the surfaces of the diffused membrane were photomicrographed. The membrane was sectioned in half with an acid saw employing a mixture 2:1:1 nitric acid, orthophosphoric acid, and acetic acid as the solvent with the surfaces of the membrane protected by stop-off lacquer. One-half of the membrane was copper

plated, cold mounted, metallographically polished, and electropolished⁽²⁰⁾ in orthophosphoric acid at room temperature. The polished section was examined for markers and any possible pore development. The membrane was then repolished with 1 μ diamond paste and analyzed for concentration profiles with an ARL-AMX electron microprobe by point-to-point counting techniques. Simultaneous analyses were made for zinc and manganese by monitoring and measuring the intensities of Zn K_{α} and Mn K_{α} radiations with at least 2 probe traces recorded for each membrane. The measured intensities were converted into compositions on the basis of Ziebold's empirical method⁽²¹⁾ with conversion parameters experimentally determined with both binary and ternary alloy standards.

EXPERIMENTAL RESULTS

Four series of experiments that resulted in steady state diffusion are listed in Table 2 along with the data on the thickness of the diffused membranes and the burial of markers. These data show that the thickness of the membranes in each series changed little under steady state diffusion and that measurable marker burial was observed only on that side of the membrane exposed to the zinc-rich vapor source.

Typical photomicrographs of the surfaces of a diffused membrane are shown in Figs. 6(a) and 6(b). These show the delineation of grains as well as the formation of shallow surface pits on both surfaces of the membrane. Figs. 7(a), 7(b), and 7(c) are photomicrographs of the cross-sections of the diffused membranes in one of the series of experiments.

The microprobe analysis of each of the diffused membranes by repeated traces yielded reproducible concentration profiles of zinc and manganese.

The diffusion profiles obtained for the various series of experiments are presented in Figs. 8, 9, 10, and 11. The composition paths corresponding to these profiles are shown on the copper-zinc-manganese isotherm at 850°C in Fig. 12.

An additional observation made in the region of markers and pores on the high zinc side of the membranes in series I, II, and IV was a local enrichment in manganese concentration recorded as a peak or hump in the manganese profile. A fall or dip in zinc concentration was also observed in these regions. Since these peaks and dips appeared very close to the surface of the membranes, they were not shown in the concentration profiles presented in Figs. 8-11. The observed enrichment of manganese and depletion of zinc in the region of pores of the membranes have been presented and discussed⁽²²⁾ in terms of the concepts of solute segregation by vacancy drag and the reverse solute atom flow which can occur around vacancy sinks in substitutional alloys.

With the aid of the thermodynamic data for Zn and Mn presented in Figs. 2 and 3, the mobilities, β_{Zn} and β_{Mn} , were calculated at various compositions along the steady state profiles in Figs. 8, 9, 10, and 11 after an initial evaluation of the steady state fluxes K_i . For the calculation of β_{Zn} , $K_{\text{Zn}}^{\text{III}}$ was first computed with Eq. [8] for the composition path III; values of mobilities used in this calculation were determined near the composition point S (Fig. 12) from the work of Dayananda⁽⁸⁾ reevaluated with the aid of thermodynamic data and reported in Fig. 13. From $K_{\text{Zn}}^{\text{III}}$ values of β_{Zn} were determined at compositions H and T from Eq. [12], since Eq. [10] was found to be valid on the basis of data in Fig. 13. Hence, the fluxes $K_{\text{Zn}}^{\text{IV}}$ and K_{Zn}^{I} for paths IV and I could be

determined with the subsequent evaluation of β_{Zn} at compositions Q and R and the value of K_{Zn}^{II} . From the steady state fluxes, β_{Zn} was calculated for compositions along all the steady state paths from Eq. [12]. Similar calculations were made for β_{Mn} along paths II, IV, and I after an initial evaluation of the flux, K_{Mn}^{II} . Mobilities required for the calculation of K_{Mn}^{II} were determined⁽²³⁾ at a composition close to point P with Cu-Mn binary diffusion couples. Calculations of β_{Mn} were not possible along path III due to negligible manganese gradients in the concentration profiles. The magnitudes of the steady state fluxes of Zn and Mn for all the paths are listed in Table 3. Figs. 14 and 15 show the results of the mobility calculations in the form of isomobility lines for zinc and manganese, respectively, on the ternary isotherm at 850°C.

DISCUSSION

The experimental realization of the steady state diffusion in a finite membrane requires that the concentration profiles of all the diffusing species become invariant with time. Vapor-solid couples with a membrane exposed on either side to vapor sources supplying the diffusing species may be employed provided: (a) the vapor sources undergo negligible depletion during diffusion, (b) any mass exchange between sources occurs by diffusion only through the membrane, (c) the formation of pores is negligible in the membrane, and (d) the thickness of the membrane remains constant under steady state diffusion.

The concentration profiles of zinc and manganese for the four series of experiments presented in Figs. 8, 9, 10, and 11, indicate that the profiles were stationary after about four days of diffusion at 850°C. This is consistent with the fact that the membranes in each series changed little in thickness under steady state conditions, as indicated in Table 2.

The steady state profiles show that the concentrations of both zinc and manganese developed at the surfaces of the membranes were invariably lower than those of the alloys used as vapor sources. Similar observations were made by Dayananda and Grace⁽³⁾ for unsteady state diffusion with vapor-solid couples in the copper-zinc-manganese system. The present steady state experiments seem to indicate that the composition developed at a solid-vapor interface for a given vapor source may also depend on the diffusive flows within the membrane. This is illustrated by the experiments in series II and III where alloy 2 (Cu-5.6 at. pct. Mn) was employed as one of the vapor sources. The surface concentrations of manganese developed by this alloy were 3.1 and 4.9 at. pct. for the couples in series II and III, respectively. The main difference in these couples is that the flux of manganese in series III experiments was negligibly small unlike that for experiments in series II.

The formation of surface pits shown in Figs. 6(a) and 6(b) indicates the condensation of vacancies at the external surfaces of the membranes. Such pits or pores were also observed by Yue and Guy⁽¹¹⁾ for copper membranes exposed to zinc vapor.

The cross-sections of the diffused membranes shown in Figs. 7(a), 7(b), and 7(c) indicate little or no porosity except in the region of the markers imbedded only on the high zinc side. These regions appear broad due to the dissolution caused during electropolishing. Enhancement of porosity in these regions can occur with time, as they constitute internal vacancy sinks.

With diffusion time the depth of burial of markers on the high Zn side appeared to increase slightly for membranes in series I, II, and IV, while it became immeasurably small for those in series III.

Experiments in series III differed from those of the other series in that the flux of manganese was negligibly small at the steady state, as given in Table 3. The imbedding of markers was negligible on the high Mn side for all membranes. The extent of marker burial is related⁽³⁾ to the magnitude of the intrinsic flow of copper to the vapor-solid interface.

All steady state profiles presented in this study correspond to countercurrent flows of Zn and Mn through the copper membranes. Countercurrent fluxes of the solutes help minimize the net vacancy flux through the membrane and the concomitant Kirkendall shifts within the diffusion zone. On the other hand, solutes diffusing through the membrane in the same direction can give rise to large vacancy flows which may cause distortion⁽¹¹⁾ of the membrane.

The composition loop, T H Q R T, formed by the diffusion paths in Fig. 12 provides a check for the internal consistency of the mobility calculations. Mobility calculations initiated with β_{Zn} at point T and extended along the loop T H Q R T with Eq. [12] are found to regenerate the initial β_{Zn} . Also, the isomobility lines for zinc in Fig. 14 are consistent with the mobility data of Horne and Mehl⁽²⁴⁾ for the Cu-Zn binary system. β_{Zn} appears most sensitive to composition at high zinc and low manganese concentrations. Values of β_{Mn} agree with those of Cu-Mn alloys⁽²³⁾ for concentrations up to 7 at. pct. Mn.

The composition paths in Fig. 12 show variations in shape ranging from a straight line to a S-shaped curve and resemble diffusion paths of vapor-solid or solid-solid diffusion couples of the unsteady state. But, they differ from the unsteady state diffusion paths, since they are subject

to the experimental constraint that at the steady state the copper flux, K_{Cu} , is virtually zero in the membranes. In terms of thermodynamics of the steady state, the paths may be dictated by a variational principle involving minimum entropy production or a similar dissipation function. However, the test of such a criterion in this study requires further information on both concentration profiles and fluxes for the diffusion membranes prior to the establishment of the steady state.

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FIGURE CAPTIONS

- Fig. 1 Schematic Concentration Profiles at Steady State
- Fig. 2 Isoactivity Lines of Zinc from Zinc Activity Data of Chadwick and Argent⁽¹²⁾ for Cu-Zn-Mn Alloys at 850°C
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Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

(a)

(b)

Figure 6

SIDE EXPOSED TO ALLOY 13

SIDE EXPOSED TO ALLOY 12

(a)

(b)

(c)

Figure 7

Figure 8

Figure 9

Figure 10

Figure 11

Figure 12

Figure 13

Figure 14

Figure 15

TABLE CAPTIONS

Table 1	Analyses of Cu-Zn-Mn Alloys
Table 2	Steady State Diffusion Experiments in Cu-Zn-Mn Alloys at 850°C
Table 3	Magnitudes of Steady State Fluxes

Table 1. Analyses of Cu-Zn-Mn Alloys

Alloy Number	Composition (in at. pct.)		
	Mn	Zn	Cu
1	5.7	14.9	79.4
2	5.6	—	94.4
7	—	10.9	89.1
8	—	11.9	88.1
9	10.5	2.8	86.7
12	17.1	2.2	80.7
13	—	7.4	92.6

Table 2. Steady State Diffusion Experiments in Cu-Zn-Mn Alloys at 850°C.

Series	Run	Time (Days)	Vapor Source I (Alloy Number)	Vapor Source II (Alloy Number)	Thickness of Diffused Membrane (microns)	Marker Burial on the side of Vapor-Source II (microns)
I	17	4	9	7	277	4.7
	16	6	9	7	275	4.85
	18	9	9	7	274	8.1
II	20	4	2	8	275	2.85
	22	9	2	8	277	5.65
III	23	4	2	1	275	3.8
	24	6	2	1	273	—
	25	9	2	1	280	—
IV	34	4	12	13	275	4.7
	35	6	12	13	273	5.5
	36	9	12	13	276	< 10.0

Table 3. Magnitudes of Steady State Fluxes

Series	$[K_i]^*$ (moles/cm ² /sec) $\times 10^{10}$	
	Zn	Mn
I	8.2	5.0
II	5.9	1.2
III	20.0	—
IV	4.8	4.2

* K_{Cu} is taken to be zero at steady state