Diffusional and Thermodynamic Interactions
in the Cu-Ni-Zn System at 775°C

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Diffusion was investigated in both α(fcc) and β(bcc) phase regions of the Cu-Ni-Zn system at 775°C with solid-solid diffusion couples and interdiffusion coefficients were determined at several compositions. Intrinsic and interdiffusion coefficients were also estimated from available data on thermodynamic activities and tracer diffusivities for α Cu-Ni-Zn alloys; and the estimated coefficients were consistent with those experimentally determined.

Large off-diagonal coefficients indicating strong interactions among the diffusing species were observed and could be appreciated in terms of the compositional dependence of the thermodynamic activities of the components.

THE phenomenological description of multicomponent diffusion as formulated originally by Onsager1 has served as an adequate basis for both theoretical and experimental analysis of diffusion in ternary systems. In substitutional alloys, the interactions among the diffusing components have been considered as arising from thermodynamic2-5 and/or kinetic6-8 effects. Experimental studies of ternary diffusion in substitutional alloys are many in literature and include those that deal with the determination of diffusion data, such as intrinsic diffusion coefficients,9-13 interdiffusion coefficients,14-16 atomic mobilities15,16 and vacancy wind parameters17 and tracer diffusion coefficients.18 Expressions have also been derived to interrelate6,18 intrinsic and interdiffusion coefficients, and to relate14,19,20 these coefficients with atomic mobilities or tracer diffusion data for multicomponent alloys.

In this study, ternary diffusion was investigated in both α(fcc) and β(bcc) phase regions of the Cu-Ni-Zn isotherm21 at 775°C. Single phase diffusion couples were set up with α as well as β alloys and ternary interdiffusion coefficients were determined at several compositions. Also, there exist in literature appreciable data on thermodynamic activities22 as well as on tracer diffusivities17 for α Cu-Ni-Zn alloys; these data were used in estimating interdiffusion coefficients on the basis of relations among interdiffusion, intrinsic diffusion and tracer diffusion coefficients. These estimated coefficients were consistent with those experimentally determined. The present results were also consistent with interdiffusion data for α Cu-Zn-Ni alloys available at 900°C.23

As part of the thermodynamic calculations, isoactivity lines were determined for Zn, Ni, and Cu in both α and β regions of the Cu-Ni-Zn isotherm21 at 775°C through procedures involving ternary Gibbs-Duhem integration. For these calculations use was made of the available thermodynamic data for the Cu-Ni-Zn,25 Cu-Zn,26-28 Ni-Zn29,30 and Cu-Ni31 alloys.

DIFFUSIONAL INTERACTIONS
IN TERNARY ALLOYS

The theoretical basis for the interactions of elements during diffusion is found in the phenomenological description of multicomponent diffusion. The interactions among the various diffusing species are taken into account in an extended form of Fick's law as proposed by Onsager.3 For unidirectional diffusion in an n-component system, the interdiffusion flux \( \tilde{J}_i \) of component \( j \) referred to a laboratory fixed frame of reference is defined by:

\[
\tilde{J}_i = -\sum_{j=1}^{n-1} D_{ij} \frac{\partial C_j}{\partial x} \quad (i = 1, 2, \ldots, n - 1)
\]

where the \( D_{ij}'s \) are the interdiffusion coefficients, \( \partial C_j/\partial x \) is the concentration gradient of component \( j \), and \( n - 1 \) refers to the number of independent concentrations. Similarly, on the lattice-fixed frame of reference, also called Kirkendall frame, Fick's law may be written as

\[
\tilde{J}_i = -\sum_{j=1}^{n} D_{ij} \frac{\partial C_j}{\partial x} \quad (i = 1, 2, \ldots, n),
\]

where \( J_i \) is the intrinsic flux of component \( i \) and the \( D_{ij}'s \) are the intrinsic diffusion coefficients. The relationship between the interdiffusion and intrinsic fluxes is given by

\[
\tilde{J}_i = J_i + C_i V_m
\]

where \( C_i \) is the molar concentration of component \( i \) and \( V_m \) is the velocity of the lattice-fixed frame relative to the laboratory fixed frame.

The intrinsic flux based on the Kirkendall frame is often expressed in terms of atomic mobility and chemical potential gradients.2 If the interactions among the various species are ignored on this frame, \( J_i \) becomes proportional to the chemical potential gradient, \( \partial \mu_i/\partial x \) and is given by

\[
J_i = -C_i \beta_i \frac{1}{N_o} \frac{\partial \mu_i}{\partial x}
\]

where \( \beta_i \) is the atomic mobility and \( N_o \) is Avogadro's number. On the basis of Eqs. [2] and [4], the intrinsic diffusion coefficients can be expressed18,20 in terms of atomic mobilities by

\[
D_{ij} = C_i \beta_j \frac{1}{N_o} \frac{\partial \mu_i}{\partial C_j}
\]

The general method of experimentally determining interdiffusion coefficients is based on the procedure adopted by Matano32 utilizing Boltzmann's analysis. In the extension of Matano's procedure to multicomponent alloys33 the diffusion coefficients as functions of composition are determined from a solution to
Fick's second law,
\[ \frac{\partial C_i}{\partial t} = \frac{\partial}{\partial x} \left( \sum_{j=1}^{n-1} D_{ij} \frac{\partial C_j}{\partial x} \right) \quad (i = 1, 2, \ldots, n-1). \] \[ \text{[6]} \]
on obtained in terms of Boltzmann parameter, \( \lambda \), where \( \lambda = \frac{x}{\sqrt{T}} \). For a single phase ternary diffusion couple of the semiinfinite or infinite type, the solution to Eq. \[ \text{[6]} \], in terms of \( x \) and \( t \) becomes
\[ C_i(x, \alpha C, \alpha C) = -2t \left( D_{11} \frac{\partial C_1}{\partial x} + D_{12} \frac{\partial C_2}{\partial x} \right) C_i \quad (i = 1, 2). \] \[ \text{[7]} \]
In order to solve Eq. \[ \text{[7]} \] for the interdiffusion coefficients in a ternary system, two independent diffusion couples having a common composition point \( C_i \) on their experimental diffusion paths are necessary. Eq. \[ \text{[7]} \] may then be employed for each couple and the \( D_{11} \) and \( D_{12} \) may be determined from the pair of simultaneous equations obtained for each \( i \).

A method for experimentally determining intrinsic diffusion coefficients in binary alloys was originally presented by Heumann. In an extension of this method applicable to multicomponent couples, Eq. \[ \text{[2]} \] is integrated with respect to time to obtain an expression for the total cumulative flux past a marker plane. For a ternary system this becomes
\[ \int_0^t J_i \, dt = A_i = \int_0^t \left( D_{11} \frac{\partial C_1}{\partial x} + D_{12} \frac{\partial C_2}{\partial x} \right) \, dt \quad (i = 1, 2, 3). \] \[ \text{[8]} \]
For a marker plane of constant composition moving parabolically with time, Eq. \[ \text{[8]} \] can be integrated to obtain
\[ A_i = -2t \left( D_{11} \frac{\partial C_1}{\partial x} + D_{12} \frac{\partial C_2}{\partial x} \right) \text{ marker plane} \quad (i = 1, 2, 3). \] \[ \text{[9]} \]

In order to calculate the intrinsic diffusion coefficients from Eq. \[ \text{[9]} \] two independent diffusion couples with identical marker compositions are required; then for each component two equations, one from each couple, can be set up with Eq. \[ \text{[9]} \] and solved for the six \( D_{ij} \)'s. This procedure has been adopted in the experimental determination of intrinsic diffusion coefficients in several ternary systems.

THERMODYNAMICS OF Cu-Ni-Zn ALLOYS

Thermodynamic Data and Calculations

Chadwick and Argent measured the vapor pressure of zinc for several \( \alpha \) Cu-Ni-Zn ternary alloys in the vicinity of 1000 K. Their data on the zinc vapor for each alloy as a function of temperature, \( T \) (K), are given by
\[ \log_{10} P = a + b \left( \frac{1}{T} \right) \] \[ \text{[10]} \]
where \( P \) is the zinc vapor pressure in mm Hg, and \( a \) and \( b \) are constants dependent on the alloy composition. The vapor pressure of pure zinc, \( P^* \), is given as a function of temperature by
\[ \log_{10} P^* = -6670 \frac{T}{T} - 1.126 \log_{10} T + 12.0. \] \[ \text{[11]} \]
From the experimental values of \( a \) and \( b \), the zinc activities were calculated at 775°C from Eqs. \[ \text{[10]} \] and \[ \text{[11]} \] with liquid Zn as the standard state. Based on these activities, isoaicity lines for zinc were drawn within the \( \alpha \) phase region of the isotherm as shown in Fig. 1. It can be seen that these lines are almost parallel to lines of constant Zn concentration except in the Cu-rich region of the isotherm.

The dashed lines within the \( (\alpha + \beta) \) region of the isotherm correspond to tie-lines experimentally determined from two-phase alloys equilibrated at 775°C. The isoaicity lines for Zn in the \( \beta \) phase have been drawn with the aid of tie-lines in the \( (\alpha + \beta) \) region and the thermodynamic data of Davies for \( \beta \) Cu-Zn alloys and the data of Liang, et al., for \( \beta \) Ni-Zn alloys.

The thermodynamics of the Cu-Zn system have been investigated by Hargreaves, Schneider and Schmid, Argent and Wakeman, and most recently by Davies by measurements of vapor pressure of zinc over the binary alloys at various temperatures. The data of Davies are in good agreement with the others and were used to calculate the activity of zinc as a function of composition in the \( \alpha \) and \( \beta \) phases of the Cu-Zn system. With the data on activity of zinc at 775°C a binary Gibbs-Duhem integration was carried out to calculate the activity of copper as a function of composition. Both Cu and Zn exhibit a negative deviation from Raoult's law. These data for the Cu-Zn system are plotted as a function of composition in Fig. 2.

The thermodynamics of the Ni-Zn system were in...