TRANSPORT AND THERMODYNAMIC PROPERTIES OF SOLIDS

Final Report

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MASTER

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November 30, 1977

Prepared For

THE U. S. ENERGY RESEARCH AND DEVELOPMENT
ADMINISTRATION UNDER CONTRACT NO. E(11-1)-1436

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Final Technical Report C00-1436-48

Summary

This progress report covers the thirteenth and final year of operation under Contract E(11-1)-1436. A brief general review of research contributions by the principal investigators is given. All of the research was supported by AEC or ERDA through this contract or its immediate predecessor.

During the last year of operation the principal area of research has been ternary diffusion in solid solution alloys. Specific research projects deal with diffusion in the Cu-Ni-Zn and Fe-Ni-Al systems (two projects). Each of the projects is carried out by a graduate student, supervised by Professors R. E. Grace and/or M. A. Dayananda, as part of the Master's or Ph.D. requirements of Purdue University. This report concludes with a resume of each of the projects either recently completed or in progress.

Personnel

1. Richard E. Grace, Professor, School of Materials Engineering; Head Division of Interdisciplinary Engineering Studies; Principal Research Investigator.
2. M. A. Dayananda, Professor, School of Materials Engineering.
3. D. H. R. Sarma, Candidate for Ph.D. degree.
4. C. W. Kim, M.S. Met. E. to be completed by December, 1977.

November 30, 1977

General Review

Thirty students have received advanced degrees from Purdue University while receiving some type of research support through a series of contracts with AEC and ERDA. Twelve Ph.D. degrees and twenty-four Master's degrees have been awarded since 1956. All of the Master's degrees have been research-oriented with an accompanying thesis or equivalent report.

The list of students and degrees awarded are included as Table I. All of the research results have been published to date. Publication lists for Professors R. E. Grace and M. A. Dayananda are appended. Peer group review has been used explicitly in order to provide an independent assessment of the research results by the scientific and technical community.

The basic strength of the research over the years has been the systematic investigation of diffusion and its phenomenology in the following four research areas: A. Liquid metal diffusion and liquid metal corrosion, B. Formation and mobility of point defects in high temperature oxide semiconductors, C. Intrinsic and interdiffusion in multicomponent alloys, and D. Interfacial stability and development of diffusion structures in multiphase ternary systems.

The following comments summarize the results in each of the areas above:

- A. Darken's relations were found to be applicable to liquid metal diffusion; this observation was based on self and interdiffusion studies in zinc amalgams (paper by Schadler and Grace).
- B.1) The characterization of nonstoichiometric oxide semiconductors with regard to the formation and diffusion of point defects was explored by electrical conductivity and thermoelectric measure-

ments. The oxides studied included strontium titanate, calcium titanate, and calcium tungstate (papers by Walters, George, Rigdon, and Grace).

B.2) Mass transfer problems between oxides and metallic phases were investigated to explore both the kinetic and thermodynamic parameters governing the processes of oxidation and reduction and the development of oxide phases. Such studies were made in chromium oxide, wustite, and cupric oxide (papers by Kassner, Walters, Sailors, Edmiston, Rigdon, Liedl, and Grace). Kinetic parameters governing the sulfidation process in multicomponent oxides were also investigated and identified (paper by McCormick, Dayananda, and Grace).

C.1) Theoretical analysis of multicomponent diffusion and the experimental determination of intrinsic and interdiffusion data were carried out in several ternary systems such as Cu-Zn-Mn, Cu-Zn-Sn, Cu-Zn-Ni, Ag-Zn-Cd, and Fe-Ni-Al. These studies incorporated the analyses and use of both semi-infinite (vapor-solid) and infinite (solid-solid) types of diffusion couples and are among the first systematic investigations of ternary diffusion with inert markers. Also, the establishment of steady state diffusion was explored for the first time in a ternary alloy system (papers by Kirsch, Whittenberger, Carlson, Sisson, Moyer, Sarma, Kim, Dayananda, and Grace).

C.2) A procedure was developed for the analysis of vacancy wind effects in multicomponent alloys. It was shown that vacancy wind effects as well as atomic mobilities could be determined in a multicomponent alloy with two experiments regardless of

the number of components (paper by Dayananda). This procedure was utilized in exploring the applicability of the diffusion models of Darken and Manning for relating tracer and intrinsic diffusion coefficients in selected binary and ternary metallic systems: Ag-Cd, Ag-Zn, Ag-Zn-Cd, and Cu-Zn-Ni (papers by Carlson, Iorio, Cheng, Dayananda, and Grace).

- D.1) The development of diffusion structures was systematically explored with selected series of multiphase diffusion couples characterized by gradual compositional changes in one of the terminal alloys. These studies allowed the indexing of the onset of instabilities at initially planar interfaces. The formation of nonplanar interfaces has been recorded as a function of time to study the time evolution of structures. The systems studied are Cu-Zn-Ni and Fe-Ni-Al (papers by Cheng, Sisson, Taylor, Wirtz, Dayananda, and Grace).
- D.2) An analysis of the development of nonplanar instabilities has been made in terms of individual fluxes of each of the diffusing species at an interphase boundary. SEM analysis of interfacial regions has shown that nonequilibrium compositions can develop in the vicinity of nonplanar interfaces (papers by Wirtz, Sisson, and Dayananda). Current work deals with an analysis of zero-flux planes in ternary interdiffusion in Cu-Ni-Zn alloys. A major objective is to describe the diffusive flows in terms of thermodynamic and kinetic interactions among the diffusing species.

Table I. Degrees Awarded Through AEC and/or ERDA Contracts, 1956-1977

A. M.S. Met. E. Degrees Awarded	
W. C. Phelps	June 1956
T. F. Archbold	June 1957
J. K. Jackson	January 1959
T. L. Sri Krishna	June 1961
R. J. Russell	June, 1962
E. A. Mizikar	August 1962
R. H. Sailors	January 1964
W. A. Edmiston	January 1965
P. F. Kirsch	June 1966
C. W. Taylor	January 1969
A. L. Hurley	June 1969
D. A. DiLeo	August 1970
N. R. Iorio	January 1972
W. C. Robertson	May 1974
T. D. Moyer	December 1974
L. E. Wirtz	August 1975
D. H. R. Sarma	August 1976
C. W. Kim	December 1977 (Expected)

B. Ph.D. Degrees Awarded	
H. W. Schadler	August 1957
W. D. Forgeng	June 1962
W. L. George	June 1968
J. D. Whittenberger	August 1969
P. T. Carlson	January 1971
E. S. McCormick	August 1972

Table I Cont'd.

C. M.S. Met.E. and Ph.D. Degrees Awarded		
	M.S.Met.E	Ph.D.
T. F. Kassner	January 1960	January 1963
M. A. Dayananda	January 1961	January 1965
L. C. Walters	January 1963	June 1966
M. A. Rigdon	January 1967	June 1971
R. D. Sisson, Jr.	January 1971	May 1975
G. H. Cheng	May 1973	August 1976

Projects

TERNARY DIFFUSION IN SOLID SOLUTION ALLOYS

Interdiffusion Fluxes and Local Mean Velocities in Cu-Ni-Zn Alloys

Investigator: C. W. Kim

Over the past few years of this contract, investigation of multi-component diffusion was carried out with α (fcc) and β (bcc) Cu-Ni-Zn alloys for the determination of both intrinsic and interdiffusion coefficients and the development of diffusion paths at 775°C. Also, thermodynamic activities of the various components were calculated by appropriate procedures of Gibbs-Duhem integration from binary and ternary activity data available in literature. A major objective of these studies was to describe the diffusive flows in a multicomponent system in the light of thermodynamic and kinetic interactions among the diffusing species.

The phenomenological basis for studies of multicomponent diffusion has been Onsager's formalism of Fick's law extended to multicomponent alloys. However, the determination of interdiffusion fluxes in such alloys can be made without invoking Fick's law. In this report, an analysis is presented whereby interdiffusion fluxes can be calculated directly from the concentration profiles of diffusion couples without the need for a prior knowledge of interdiffusion coefficients. This procedure is applied for the determination of fluxes of each component at various sections of selected diffusion couples investigated in the Cu-Ni-Zn system. In addition, local mean velocities of the diffusing species are also calculated from the knowledge of fluxes. A major outcome of these calculations is the recognition that the interdiffusion flux as well as the local mean velocity of a component can become zero at a plane within the diffusion

zone and can have opposite signs on either side of such a zero-flux plane. Concentration profiles of Cu-Ni-Zn ternary couples are analyzed for the identification of sections characterized by zero interdiffusion flux of either Ni or Cu.

Interdiffusion flux $\tilde{J}_i$ of component i referred to a fixed laboratory coordinate can be evaluated at any section x directly from the concentration profiles. The variation of concentration C_i with t at any x is expressed by the continuity equation:

$$\left(\frac{\partial C_i}{\partial t} \right)_x = - \left(\frac{\partial \tilde{J}_i}{\partial x} \right)_t \quad (1)$$

or

$$- \left(\frac{\partial x}{\partial t} \right)_{C_i} \left(\frac{\partial C_i}{\partial x} \right)_t = - \left(\frac{\partial \tilde{J}_i}{\partial x} \right)_t$$

$$v(C_i) \left(\frac{\partial C_i}{\partial x} \right)_t = \left(\frac{\partial \tilde{J}_i}{\partial x} \right)_t \quad (2)$$

where $v(C_i)$ refers to the velocity of propagation of a concentration level identified with concentration C_i . Since for solid-solid diffusion couples C_i is a function of the parameter λ where $\lambda = x/\sqrt{t}$,

$$v(C_i) = \left(\frac{\partial x}{\partial t} \right)_{C_i} = \frac{1}{2} \frac{\lambda}{\sqrt{t}} \quad (3)$$

Hence, at constant t , Eq. (2) becomes:

$$\left(\frac{\partial \tilde{J}_i}{\partial x} \right)_t = \frac{1}{2} \frac{\lambda}{\sqrt{t}} \left(\frac{\partial C_i}{\partial x} \right)_t$$

or

$$\begin{aligned}
 \int d\tilde{J}_i &= \int \frac{1}{2} \frac{\lambda}{\sqrt{t}} \left(\frac{\partial C_i}{\partial x} \right)_t dx \\
 &= \int \frac{1}{2} \frac{\lambda}{\sqrt{t}} \frac{dC_i}{d\lambda} \frac{1}{\sqrt{t}} \sqrt{t} \cdot d\lambda \\
 &= \int \frac{\lambda}{2\sqrt{t}} dC_i \\
 &= \frac{1}{2t} \int x dC_i
 \end{aligned} \tag{4}$$

Hence,

$$\int_{\tilde{J}_i(\infty)}^{\tilde{J}_i(x)} d\tilde{J}_i = \frac{1}{2t} \int_{C_i(\infty)}^{C_i} x dC_i \tag{5}$$

Since $\tilde{J}_i(\infty)$ is zero,

$$\tilde{J}_i(x) = \frac{1}{2t} \int_{C_i(\infty)}^{C_i} x dC_i \tag{6}$$

The integral in Eq. (6) can be obtained from the concentration profile of component i with $x = 0$ located at the Matano plane.

The flux $\tilde{J}_i$ at any section x is related to the local mean velocity u_i by

$$\tilde{J}_i = C_i u_i \tag{7}$$

Hence, u_i can be evaluated as a function of x for a diffusion couple.

The calculation of interdiffusion fluxes by means of Eq. (6) has been carried out for several single phase Cu-Ni-Zn diffusion couples annealed at 775°C. On the ternary isotherm in Fig. 1 are shown diffusion paths for four couples along with isoactivity lines for Cu, Ni, and Zn passing through

the composition points of the terminal alloys designated by α_3 , α_5 , α_7 , and α_9 . The couples correspond to the series, α_5 , vs. α_7 , α_9 , Cu, α_3 . The concentration profiles as well as activity profiles for these couples are presented in Figs. 2, 3, 4, and 5. In these figures x_0 refers to the Matano plane and x_M corresponds to the location of inert markers after diffusion. From the concentration profiles the interdiffusion fluxes $\tilde{J}_{Zn}$, $\tilde{J}_{Ni}$, and $\tilde{J}_{Cu}$ have been calculated as functions of x for each couple and are presented in Figs. 6, 7, 8, and 9. The directions of interdiffusion fluxes for the various components in each couple are indicated on the corresponding composition paths in Fig. 10.

The couple α_5/α_7 in Fig. 2 corresponds to a couple with Ni concentration almost identical in the terminal alloys. However, it can be seen that the activity a_{Ni} of Ni in alloy α_7 is higher than that in α_5 . Hence, Ni can be expected to diffuse from α_7 to α_5 . This observation is confirmed by the calculated $\tilde{J}_{Ni}$ presented in Fig. 6. The positive direction is taken to be the direction of increasing x and both $\tilde{J}_{Ni}$ and $\tilde{J}_{Cu}$ are found to be negative, while $\tilde{J}_{Zn}$ is positive in the direction of α_5 to α_7 .

The couple α_5/α_9 in Fig. 3 may be looked upon as a Ni isoactivity couple, i.e., a couple with almost identical Ni activities in the terminal alloys. It is interesting to note that after diffusion the a_{Ni} profile for the couple develops a maximum and a minimum, as indicated in Fig. 3 and the direction of interdiffusion flux of Ni is not quite apparent. However, the interdiffusion fluxes as calculated from Eq. (6) and plotted against x in Fig. 7 clearly show that $\tilde{J}_{Ni}$ is not unidirectional but has different signs on different sides of a plane corresponding to an x of about 105. In addition $\tilde{J}_{Ni}$ goes to zero at the section or plane where the

flux reversal occurs. Such a plane may be referred to as the zero-flux plane for Ni. With regard to flows of zinc and copper, $\tilde{J}_{Zn}$ is positive in the direction of α_5 to α_9 , while $\tilde{J}_{Cu}$ has the opposite direction over the entire diffusion zone.

For the couple α_5/Cu shown in Fig. 4 there exist maxima in the profiles of concentration and activity of Ni similar to those observed for the couple α_5/α_9 . Correspondingly, the calculated values of $\tilde{J}_{Ni}$ presented in Fig. 8 indicate a zero-flux plane for Ni and a reversal of direction for the interdiffusion flux of Ni. In addition, a zero-flux plane for copper is also observed and its presence may be appreciated in the light of the activity minimum developed in the Cu activity profile as can be seen in Fig. 4.

The couple α_5/α_3 in Fig. 5 is characterized by terminal alloys with similar concentrations of Zn and maxima and minima are developed in both the concentration profile and activity profile of Zn. In addition, maxima and minima are developed in the concentration and activity profiles of Cu during diffusion, although the terminal alloys of the couple differ appreciably in their initial Cu concentrations and activities. The calculated values of interdiffusion fluxes presented in Fig. 9 show the presence of two zero-flux planes for copper but no zero-flux planes for Zn or Ni.

The directions of interdiffusion fluxes as well as the compositions corresponding to the zero-flux planes developed in the various couples for the couple series, $\alpha_5/\alpha_7, \alpha_9, Cu, \alpha_3$, are indicated on the composition paths in Fig. 10. For the couple α_5/α_7 , there exists no zero-flux composition points. As one of the terminal alloys is changed to α_9 , a zero-flux plane for Ni is developed corresponding to the composition represented by point

a. With further change of the terminal composition to pure Cu, the couple α_5/Cu exhibits a zero-flux plane for Ni at the composition indicated by point b; in addition, a zero-flux plane for Cu is developed at the composition point c. The zero-flux planes for Ni disappear for the couple α_5/α_3 , where two zero-flux planes for Cu with compositions corresponding to points d and e form.

The composition points a and b for zero-flux of Ni are similar in the fact that the Ni fluxes are divergent from the points along the diffusion paths. In other words, the Ni fluxes are in opposite directions away from the zero-flux planes in the diffusion zones of the couples. Similarly, composition points c and d for zero-flux planes for Cu are characterized by the fact that the Cu fluxes are directed towards the zero-flux planes. On the other hand, the point e has outward directed Cu fluxes along the diffusion path.

The composition points a, b, c, d, and e for the zero-flux planes do not correspond to either the minima or maxima developed in concentration profiles or activity profiles. However, they can be identified with the help of isoactivity lines for the components drawn through the terminal alloys as shown in Fig. 1. It can be seen that points a and b for zero-flux of Ni correspond to points of intersection of the composition paths of couples α_5/α_9 and α_5/Cu with the Ni isoactivity line passing through the terminal alloy composition point α_5 . Similarly, the points c and d are the points of intersection of the Cu isoactivity line passing through α_5 with the diffusion paths for the couples, α_5/Cu and α_5/α_3 , respectively. Point e lies at the intersection of the path for the couple α_5/α_3 with the Cu isoactivity line through α_3 . It may be noted that none of the couples in this study developed zero-flux planes for zinc in spite of the maxima

and minima in Zn activities that were observed in Fig. 5. This is consistent with the fact that the Zn isoactivity lines passing through the terminal alloys are not intersected by the diffusion paths of the couples. Hence, it is apparent that the development of a zero-flux plane for a component can be expected within the diffusion zone of a couple, provided the isoactivity line for the component drawn through either of the terminal alloy compositions for the couple intersects the diffusion path.

Since the interdiffusion flux of one of the components is zero at a zero-flux plane, the sum of the interdiffusion fluxes of the remaining components is also zero at such planes. For example, in Fig. 7 $\tilde{J}_{Ni}$ equal to $-(\tilde{J}_{Zn} + \tilde{J}_{Cu})$ is zero at the zero-flux plane for Ni. Similarly, in Fig. 9 there are two zero-flux planes for Cu where $(\tilde{J}_{Ni} + \tilde{J}_{Zn})$ is zero.

The presence of zero-flux planes in diffusion couples does not violate the continuity equation given by Eq. (1). From Figs. 7-9, it is obvious the $\tilde{J}$ is a continuous function of x for each component and that $\partial J/\partial x$ is also continuous at all x including the zero-flux planes.

Another important observation of this study is that the interdiffusion flux of a component is not zero at the maxima and minima in its activity profile. This can be easily seen from Figs. 3 and 7 for the couple α_5/α_9 where $\tilde{J}_{Ni}$ is negative across the a_{Ni} hill and is positive across the a_{Ni} valley. This observation substantiates the fact that interactions among the diffusing components cannot be ignored in the description of interdiffusion fluxes in terms of thermodynamic activity gradients.

The zero-flux plane for a component also corresponds to the plane of zero local mean velocity for the component as can be expected on the basis of Eq. (7). In Fig. 11 is presented the variation of the local mean

velocity with distance for the couple α_5/α_9 . It can be seen that u_{Ni} can be zero, negative or positive depending on the section x . Also, the maximum values of local mean velocities for the components are not observed at the Matano plane x_0 in contrast to the maxima for $\tilde{J}_i$ expected to occur at x_0 (see Figs. 6-9).

A major objective of this study of ternary diffusion in Cu-Zn-Ni alloys was to answer the following questions on the basis of experimental observations:

1. Can a component show an apparent flow up its own activity gradient in a multicomponent alloy?
2. Can a component interdiffuse in opposite directions in a single phase multicomponent couple?

The answer to both these questions is in the affirmative on the basis of the experimental findings of this study. In addition, the formation of zero-flux planes for individual components within diffusion couples has been reported for the first time and related to the intersections of diffusion paths and isoactivity lines through terminal compositions on an isotherm.

Ternary Diffusion in Fe-Ni-Al System

Investigator: D. H. R. Sarma

This research involves the investigation of both single phase and multiphase diffusion with solid-solid diffusion couples assembled with β (bcc) and γ (fcc) Fe-Ni-Al alloys at 1000°C. One of the objectives of this study is to describe the diffusional interactions among the components in terms of thermodynamic or kinetic parameters. A second objective is to study the stability of interfaces and the development of diffusion

structures in multiphase couples as influenced by their terminal compositions.

The current studies with selected β vs γ couples have shown that the development of instabilities at the β/γ interface is always associated with the nonequilibrium compositions on either side of the interface. Such nonequilibrium compositions indicate apparent steps in the thermodynamic activities of Al, Ni, and Fe at the interface. In addition, maxima and minima in the Fe activity vs distance profiles have been observed in the vicinity of interfaces.

The development of such inflections in the activity vs distance profiles in both single and multiphase couples are being further explored with the aid of "isoactivity couples." These couples are set up with terminal β and γ alloys characterized by a similar thermodynamic activity of one of the components, so that the couples have their terminal compositions along isoactivity lines of Fe, Ni, or Al. The couples are annealed at 1000°C and analyzed for concentration profiles and diffusion paths by electron microprobe analysis. Interdiffusion fluxes are calculated directly from the concentration profiles. The calculated fluxes are analyzed in terms of gradients in thermodynamic activities of the individual components for the determination of interactions among the diffusing species.

Several alloys have been prepared for use in the assembly of diffusion couples. These alloys are listed in Table II. Some of the couples of the isoactivity type that have been planned are presented in Table III along with the couple characteristics. Some of these couples have been diffusion annealed and are currently being analyzed.

This is on-going Ph.D. project and is expected to continue for the next two years.

Table II. Compositions of Alloys

Alloy Designation	Phase Region	Composition (atom percent)		
		Fe	Ni	Al
1	β	16.0	49.7	34.3
2	β	--	56.0	44.0
3	γ	61.0	32.0	7.0
4	γ	77.0	23.0	--
5	β	65.3	--	34.7
6	β	35.0	34.0	31.0
7	γ	10.3	79.9	9.8
8	γ	19.2	80.8	--
9	γ	28.1	71.9	--
10	γ	--	86.7	13.3
11	γ	50.4	49.6	

Table III. Diffusion Couples

Couple Designation	Characteristics of Terminal Alloys
1 vs 2	β phase, similar Ni activity
3 vs 4	γ phase, similar Ni activity
1 vs 3	β vs γ , similar Ni and Al activities
10 vs 9	γ phase, similar Ni activity
5 vs 6	β phase, similar Fe activity
7 vs 8	γ phase, similar Fe activity
6 vs 11	β vs γ , similar Fe activity

Fig. 1 Diffusion Paths for the Couple Series α_5 vs α_7 , α_9 , Cu, and α_3 Annealed at 775°C for 2 Days. Isoactivity lines for Cu, Zn, and Ni passing through the terminal composition points are shown by dashed lines.

Fig. 2 Concentration Profiles and Activity Profiles for the Couple α_5/α_7 Annealed at 775°C for 2 Days.

Fig. 3 Concentration Profiles and Activity Profiles for the Couple α_5/α_9 Annealed at 775°C for 2 Days.

Fig. 4 Concentration Profiles and Activity Profiles for the Couple α_5 /Cu Annealed at 775°C for 2 Days.

Fig. 5 Concentration Profiles and Activity Profiles for the Couple α_5/α_3 Annealed at 775°C for 2 Days.

Fig. 6 Calculated Interdiffusion Fluxes for the Couple α_5/α_7

Fig. 7 Calculated Interdiffusion Fluxes for the Couple α_5/α_9 .

Fig. 8 Calculated Interdiffusion Fluxes for the Couple α_5/Cu .

Fig. 9 Calculated Interdiffusion Fluxes for the Couple α_5/α_3 .

Fig. 10 Flow Directions for Interdiffusion Fluxes of Cu, Ni, and Zn Indicated on the Diffusion Paths. Points a, b, c, d, and e correspond to compositions of zero flux planes of one of the components for the various couples.

Fig. 11 Variation of Local Mean Velocities of Cu, Zn, and Ni for the Couple α_5/α_9 .

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