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Diffusion in Copper and Copper Alloys
Part IV. Diffusion in Systems Involving Elements of Group VIII

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A survey, comparison, and critical analysis is presented of data compiled from the scientific literature concerning diffusion in copper alloy systems involving elements in Group VIII (Co, Fe, Ni, Pd, Pt, Rh, Ru). Here the term "copper alloy system" is interpreted in the broadest sense. For example, the review of diffusion in the Cu-M system reports all diffusion situations which involve both copper and element M, including diffusion of Cu in M or in any binary, ternary or multicomponent alloy containing M; diffusion of M in Cu or in any alloy containing Cu; and diffusion of any element in any alloy containing both Cu and M. Topics include volume diffusion, surface diffusion, grain boundary diffusion, tracer diffusion, alloy interdiffusion, electromigration, thermomigration, dislocation-pipe diffusion, and diffusion in molten metals. An extensive bibliography is presented along with figures, tabular presentation of data and discussion of results.

Key words: Alloys; cobalt; copper; diffusion; electromigration; iron; nickel; palladium; platinum; rhodium; ruthenium; thermomigration.

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1. Introduction

1.1. Organization of Review According to Alloy System

The present review is the fourth in a series designed to provide data on diffusion in copper and copper alloys. The first paper [1] in the series covered copper self-diffusion. The second paper [2] of the series dealt with diffusion in the copper-silver and copper-gold systems. The third paper [3] reviewed diffusion in copper alloy systems which involved the elements of the groups IA, IIA, IIIB, IVB, VB, VIB, and VIIB. The present paper continues the coverage of diffusion in copper alloy systems. Data on diffusion in systems which involve copper and elements of group VIII are presented in this paper. Succeeding papers in this series will cover the remaining copper alloys.

Each Cu-M alloy system (M = Co, Fe, Ni, Pd, Pt, Rh, Ru) will be reviewed independently as a unit; and each system is provided with an independently numbered list of references. The term "Copper alloy system" is interpreted in the broadest sense here. For example, the review of diffusion in the Cu-Fe system includes all diffusion situations which involve both copper and iron. This same format will be followed for all Cu-M systems. According to this format, the Cu-Fe review treats:

(1) Diffusion of iron in pure copper
(2) Diffusion of copper in pure iron
(3) Diffusion of copper or iron in Cu-Fe binary alloys
(4) Diffusion of impurities in Cu-Fe binary alloys
(5) Diffusion in any ternary alloy containing both copper and iron (or in any multicomponent alloy containing both copper and iron)
(6) Diffusion of copper in any alloy containing iron
(7) Diffusion of iron in any alloy containing copper.

For easy reference, a list of subsections is provided in the table of contents for each alloy system. Under the Cu-Fe system as an example, binary situations which involve only copper and iron (items 1, 2, and 3 in the above list) are discussed first and are presented in separate subsections under the Cu-Fe section. Then, ternary situations involving a third element in addition to copper and iron are presented. These ternary subsections appear in alphabetical order according to the chemical symbol of the third element. Data of types 4, 5, 6, and 7 all are included in each such subsection if available. If no diffusion data are available on a given three-component system, say Cu-Fe-M, then this system is simply not listed. Special diffusion effects, such as grain boundary diffusion, surface diffusion, electromigration, etc., are discussed in a final set of subsections.

Diffusion measurements in quaternary and other higher order multicomponent alloys are not common in copper alloy systems. General discussions of diffusion in these alloys are presented in a single subsection entitled, for example, Cu-Fe-X.

1.2. Methods Used to Present and Compare Data

The primary quantities of interest for diffusion are the diffusion coefficient, D, and the activation energy for diffusion, Q. The diffusion coefficient is defined by the equation

$$J=-D(\partial c/\partial x), \qquad (1)$$

where $\partial c/\partial x$ is the concentration gradient of the diffusing species along a direction x of interest, and the diffusion flux, J, is the amount of diffusing species crossing unit area normal to the x-axis per unit time. D, itself, is a constant of proportionality and usually is expressed in units of cm^2/s. Experimentally, D is usually found to depend exponentially on temperature according to an Arrhenius-type equation,

$$D=D_0 \exp(-Q/RT). \qquad (2)$$

Thus, a straight line is usually obtained when log D is plotted as a function of T^{-1}. Here, T is the absolute temperature, D_0 and Q are experimentally measured constants which can be determined from the intercept and the slope of that line, and R is the universal gas constant ($1.987\ cal \cdot K^{-1} \cdot mol^{-1} = 8.314\ J \cdot K^{-1} \cdot mol^{-1}$).

The quantity Q in eq (2) is usually found expressed in the literature in units of kcal/mol, or in units of kcal alone (with the mole understood). Usually Q can be determined to only two or three significant figures and has a value between 10,000 and 100,000 cal/mol. Thus, when Q is expressed directly in terms of cal/mol, as is sometimes found in the literature, the last few zeros before the decimal are not significant figures. A second type of unit for Q frequently found in the literature is the electron volt or electron volt per atom. When this unit is reported, it is understood that R in eq (2) is replaced by Boltzmann's constant, k (equal to $1.3806 \times 10^{-23}\ J \cdot K^{-1}$ or $8.617 \times 10^{-5}\ eV \cdot K^{-1}$).

In alloys, the dependence of D and Q on alloy composition provides another variable which must be considered in addition to those previously discussed for self-diffusion in pure copper [1]. Usually no consistent general equation can be written to express $D(c)$ at all concentrations, c. Thus, data on the composition dependence of D or Q is usually summarized in this review by displaying the measured values on graphs of D or Q versus composition, rather than by use of equations.

When the temperature dependence of D is considered, the best smooth line through the data often can be summarized by expressing D in the form of eq (2). In the present paper, the more reliable data usually are presented in display equations in the text in this form. In addition, individual D_0 and Q values may be quoted to provide information in summary form and expedite comparisons between differing measurements. Even for the temperature dependence of D, however, the most useful means of presenting and comparing data probably is by means of graphs, showing the diffusion coefficients themselves; in this case with log D plotted versus T^{-1}. A number of these graphs are shown in the present review.

The textual discussions provide commentary on the experiments reported and, wherever possible, a comparison and evaluation of the reliability of the experimental methods and results. An attempt has been made here to provide comprehensive coverage. In cases where very little good data are available on a system, even poor data will be presented and discussed as providing some indication of diffusion behavior in that system.

In choosing among various reported diffusion measurements for reliability, the internal consistency and reproducibility of the data are considered important. For example, it is expected that the experimental points, expressed as log D, should fall very nearly on a straight line when plotted as a function of T^{-1}, as given by eq (2). The degree of scatter from a line drawn through the experimental points is usually assumed to provide a good indication of the accuracy of the data. Such a line will not be well-established if only a few measurements in a limited temperature range are reported. For this reason, data taken at many different temperatures and over a wide temperature range normally are considered more reliable (in the absence of other considerations) and are more easily evaluated.

At temperatures near the melting point, volume diffusion through regions of good crystal structure is normally predominant. At lower temperatures, diffusion along the easy paths provided by grain boundaries often becomes important. Most data reported in the literature are for diffusion at moderately high temperatures, above two-thirds of the melting point, where volume diffusion usually dominates. Nevertheless, grain-boundary diffusion measurements also are reported in the review when available. A separate diffusion coefficient, D_{gb}, for diffusion in a grain-boundary can be defined from eq (1). A uniform D_{gb} value usually is assumed to apply to the entire grain-boundary volume, which is regarded as extending in two dimensions but having a finite width, δ. With the grain-boundary regarded as a plane, one can say that the plane envisioned in eq (1) normal to the concentration gradient will cut the grain-boundary plane along a line. Experimentally, the flux, J', crossing unit length of this line often is the quantity measured rather than the actual flux, J, per unit area, which is the quantity in eq (1). In such a case, taking the ratio $J'/-(\partial c/\partial x)$ yields $D_{gb} \cdot \delta$. Thus, where grain-boundary diffusion results are quoted, $D_{gb} \cdot \delta$ frequently is given instead of just D_{gb}, with δ being an unknown grain-boundary width, and $D_{gb} \cdot \delta$ then being expressed in units of cm^3/s.

A similar situation can arise in surface diffusion measurements if the surface is regarded as having a thickness, δ. More commonly though, the surface concentration is expressed in terms of the number of atoms, c', per unit area (rather than the number per unit volume). Then, the ratio, $J'/-(\partial c'/\partial x)$, yields a conventional surface diffusion coefficient, D_s, which can be expressed in the conventional units of cm^2/s.

For descriptions of standard experimental techniques of measuring volume, grain-boundary, and surface diffusion coefficients, and related diffusion quantities, the reader is referred to general review articles [4–8]. In addition, specific references and comments are provided at points in the textual commentary where results from some of the less-standard types of measurements are discussed.

1.3. Different Types of Diffusion Coefficients

For diffusion in alloys, one must be particularly careful to establish the type of diffusion coefficient that is reported. There are two main types of diffusion experiments in alloys frequently reported in the literature—tracer diffusion coefficients and interdiffusion coefficients.

An understanding of why tracer and interdiffusion experiments, which both define their diffusion coefficients, D, by means of eq (1), yield different diffusion coefficient values can be gained by considering the physical arrangement of these measurements and the basic diffusion equations. The basic kinetic diffusion equation for the atom flux, J, of a diffusing species with respect to the end of a specimen can be written as

$$J = -D^* \frac{\partial c}{\partial x} + \langle v \rangle_F \, c + v_k c. \tag{3}$$

Here, D^* is a quantity related to the atom jump frequencies of the diffusing species; $\langle v \rangle_F$ is the atom drift velocity from atomic driving forces; c is the concentration; and v_k is the velocity of the local lattice plane with respect to the ends of the specimen. It may be noted that eq (3) is similar to eq (1) but differs in two respects: (1) eq (3) contains two velocity-concentration terms, $\langle v \rangle_F \, c$ *and* $v_k c$, and (2) the coefficient of $\partial c/\partial x$ in eq (3) is the specific quantity, D^*, rather than a general diffusion coefficient, D.

In a typical tracer diffusion experiment, a very thin layer of tracer atoms is deposited on the surface of a homogeneous alloy, and diffusion is carried out in the absence of driving forces. Here, the tracer atoms diffuse into an essentially unchanging homogeneous matrix, and $\langle v \rangle_F$ and v_k are zero. Consequently, D^* is the measured diffusion coefficient in this type of experiment, which results in D^* being called the "tracer diffusion coefficient."

By contrast, in an interdiffusion experiment, two bulk specimens of different alloy composition are brought into contact, and atoms diffuse in both directions across the interface. These alloys usually have positive or negative energies of mixing, and atom drift velocities $\langle v \rangle_F$ can arise from forces created by gradients in these energies. Also, the D^* values of the various constituents usually are unequal. This inequality produces a net atom flux across the interface toward one end of the specimen and makes v_k differ from zero. In simple interdiffusion experiments, where other driving forces are absent, $\langle v \rangle_F$ and v_k are proportional to $\partial c/\partial x$, and J still is found to be directly proportional to $\partial c/\partial x$. However, if one calculates an interdiffusion coefficient, $\tilde{D}$, from the ratio $-J/(\partial c/\partial x)$, as in eq (1), one should expect to find $\tilde{D} \neq D^*$.

For a binary alloy, $\tilde{D}$ is the same for both constituents. Thus, there are two, different tracer diffusion coefficients for the two constituents in a binary alloy (one for each constituent), but only one interdiffusion coefficient. The interdiffusion coefficient in some references is called the "chemical diffusion coefficient," or the "chemical interdiffusion coefficient."

The interdiffusion coefficient, $\tilde{D}$, in a binary alloy containing constituents A and B can be related to the tracer diffusion coefficients, $D_A{}^*$ and $D_B{}^*$, for A and B atoms in that alloy by the equation

$$\tilde{D} = (N_A D_B{}^* + N_B D_A{}^*) \Phi S, \tag{4}$$

where N_A and N_B are the mole fractions of species A and B in the alloy, Φ is the thermodynamic factor, and S is the vacancy wind factor. When either N_A or N_B goes to zero, both Φ and S go to unity; so in the limit of a very dilute binary alloy, $\tilde{D}$ should equal the tracer diffusion coefficient of the dilute constituent. In non-dilute alloys, ΦS can differ appreciably from unity, say by a factor of four. In these alloys, additional information (which is usually not available) on thermodynamic activity coefficients is needed to determine $\tilde{D}$ from $D_A{}^*$ and $D_B{}^*$.

A third type of diffusion coefficient in alloys is the intrinsic diffusion coefficient, D_i^I. This coefficient is defined by eq (1) when J in that equation is defined as the atom flux of species i with respect to a local lattice plane. Equations relating D_i^I to other diffusion coefficients are given, for example, in reference [9]. When v_k differs from zero, D_i^I will differ from $\tilde{D}$. When $\langle v \rangle_F$ differs from zero, D_i^I will differ from D_i^*.

In the discussion of D_i^I and $\tilde{D}$ given above, it was assumed that the only atomic driving force was that from the heat of mixing. If other driving forces of unknown magnitude are present in an experiment or if other lattice distortions contribute to v_k, the measured diffusion coefficient, $[-J/(\partial c/\partial x)]$, will, of course, be affected. Usually in these cases, one refers to an "effective diffusion coefficient" obtained from eq (1).

In situations where the measured J or $\partial c/\partial x$ values are believed to contain significant unknown errors, an "apparent diffusion coefficient" may still be defined based on the apparent values of J and $\partial c/\partial x$ (or of the other related quantities) which the particular experiment provides.

Diffusion coefficients may show a strong dependence on alloy composition. This composition dependence can lead to very nonsymmetric concentration-versus-distance profiles in some interdiffusion experiments. If a nonsymmetric profile is assumed to be symmetric, a single "average diffusion coefficient" can be calculated for the experiment. Other methods of finding an average diffusion coefficient applicable to a given concentration range may give somewhat different results, since the types of averaging may differ.

In ternary and higher-order multicomponent alloys, there will be more than one dependent concentration gradient. Then, instead of defining a single diffusion coefficient as in eq (1), it often is convenient to define a set of partial diffusion coeficients, D_{ij}, where

$$J_i = -\sum_j D_{ij} \frac{\partial c_j}{\partial x}, \tag{5}$$

Here, J_i is the flux of species i, and $\partial c_j / \partial x$ is the concentration gradient of species j. Since the sum of the concentration gradients of all species in the crystal must equal zero, one of the concentration gradients must be eliminated from the general expression if one wishes to obtain independent, partial diffusion coefficients. This gradient can arbitrarily be chosen to be any one of the gradients, $\partial c_n/\partial x$. Then,

$$J_i = -\sum_{j \neq n} D_{ij}^n \frac{\partial c_j}{\partial x}, \tag{6}$$

where

$$D_{ij}^n = D_{ij} - D_{in} \cdot \tag{7}$$

For an n-component alloy, there are $n-1$ independent partial diffusion coefficients, D_{ij}^n. for each species i.

In multicomponent alloys, partial diffusion coefficients can be either intrinsic diffusion coefficients or interdiffusion coefficients. Here again, the distinction is that the intrinsic diffusion coefficients are related to the fluxes with respect to local lattice planes, whereas the interdiffusion coefficients are related to fluxes measured relative to the undiffused ends of the specimen.

Further discussion of the physical meaning of D^*, D^I and $\tilde{D}$ can be found in references [2], [3], and [10].

1.4. Other Diffusion Related Quantities

In this review, the emphasis is on direct measurements of diffusion coefficients. There are, however, a number of diffusion-related phenomena, such as sintering, creep, gas-permeation rates, measurements of interface motion, and a variety of relaxation-time measurements, from which estimates of diffusion rates can be made. These data are reported when it appears that significant diffusion information can be obtained from them. For example, diffusion activation energies often can be estimated from these diffusion-related phenomena.

Temperature and alloy composition are the major variables usually considered in reporting diffusion data. Nevertheless, diffusion rates also can be influenced by a number of other factors, such as pressure, electric fields, temperature gradients, ultrasonic vibration, and strain rates. When appropriate data are available, separate descriptions are provided in the reviews which report on these special effects.

For diffusion as a function of pressure, p, it usually is possible to write

$$D = D(p=0) \exp\left(-p\Delta V/kT\right), \tag{8}$$

where $D(p=0)$ is the value of the diffusion coefficient at zero pressure, and ΔV is called the measured activation volume. For hydrostatic pressures on metals, very high pressures usually are required before D changes appreciably, since ΔV is usually of the order of an atomic volume.

In the case of diffusion in an electric field, a critical quantity in determining the diffusion rates is the measured effective charge, q^{**}, of the diffusing species, since the field E affects the drift velocity in eq (3) according to the equation

$$\langle v \rangle_F / D^* = q^{**} E (kT)^{-1}. \tag{9}$$

Here q^{**} may differ appreciably, however, from the actual charge of the diffusing species. For diffusion in a temperature gradient, the measured heat of transport, Q^{**}, serves a similar function, with

$$\langle v \rangle_F / D^* = -Q^{**} \nabla T / kT^2. \tag{10}$$

These quantities are discussed more fully, for example, in reference [3] and in other earlier reviews in this series.

Discussions also are given there of the relation between gas permeation rates and diffusion. For example, if K is the permeation rate through an alloy, S is the solubility, and D the diffusion coefficient, one can write for diffusion-controlled permeation [11, 12]

$$K = DS. \qquad (11)$$

In an interdiffusion experiment, the net shift with respect to the ends of the specimen in the position of the original interface lattice plane is called the Kirkendall shift, x_k. This shift, which results from unequal intrinsic diffusion of components across the plane, can be measured, for example, by placing inert wires or other markers at this plane. For normal parabolic diffusion at constant temperature for diffusion time τ, the Kirkendall shift will be proportional to $\tau^{1/2}$, since $x_k = \int_0^\tau v_k \, dt$, and v_k is proportional to $\tau^{-1/2}$. Here, v_k is the same velocity which appears in eq (3). For simple interdiffusion in a binary A-B alloy, v_k is proportional to $D^I_A - D^I_B$, and

$$x_k = 2\tau (D^I_A - D^I_B) \quad (\partial N_A/\partial x)_\tau . \qquad (12)$$

In parabolic diffusion, $\partial N_A/\partial x$ is proportional to $\tau^{-1/2}$, so eq (12) yields $x_k \propto \tau^{1/2}$, as expected

In binary alloys, $\tilde{D}$ is related to the intrinsic diffusion coefficients by

$$\tilde{D} = N_A D^I_B + N_B D^I_A . \qquad (13)$$

If $\tilde{D}$ and x_k are measured at a binary alloy interface of known composition and concentration gradient, D^I_A and D^I_B can be found from eqs (12) and (13).

1.5. Note on References

Many references are in non-English languages. Where English translations are available, it has been so noted in brackets following the original citation. The bulk of these translations are available from the National Technical Information Service (NTIS), Springfield, Va. 22151. Others are available from Henry Brutcher Technical Translations (HB), P.O. Box 157, Altadena, Calif. 91001; the British Iron and Steel Industry Translation Service (BISI), The Iron and Steel Institute, 39 Victoria Street, London, S.W. 1, England; or the National Translation Center (NTC), 35 West 33rd Street, Chicago, Illinois 61606.

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2. Copper-Cobalt

2.1. Co* → Cu

The rates of diffusion of the radioactive tracer-impurity ^{60}Co into single crystals of high purity copper have been reported by Mackliet [1] and Sakamoto [2], both over reasonably large temperature ranges. Their results are in disagreement with each other as is seen from the plots of the temperature dependence of the diffusion coefficients obtained in their experiments. Mackliet's high temperature data can be represented by the expression:

$$D^*_{\mathrm{Co} \to \mathrm{Cu}} = 1.93 \exp(-54.1 \text{ kcal} \cdot \text{mol}^{-1}/RT) \text{ cm}^2/\text{s},$$

whereas Sakamoto's data can be represented by the expression:

$$D^*_{\mathrm{Co} \to \mathrm{Cu}} = 5.7 \exp(-55.2 \text{ kcal} \cdot \text{mol}^{-1}/\mathrm{RT}) \text{ cm}^2/\text{s}.$$

Despite the nonlinear plot, Mackliet's data appear to be the more reliable since they were obtained from a more careful experiment which resulted in greater accuracy and precision.

Mackliet used high purity copper (99.998$^+$ %) versus Sakamoto's copper of unspecified purity.

After careful surface preparation, Mackliet annealed his single crystals and then electrodeposited his tracer ^{60}Co. Sakamoto did not anneal his drum-shaped samples

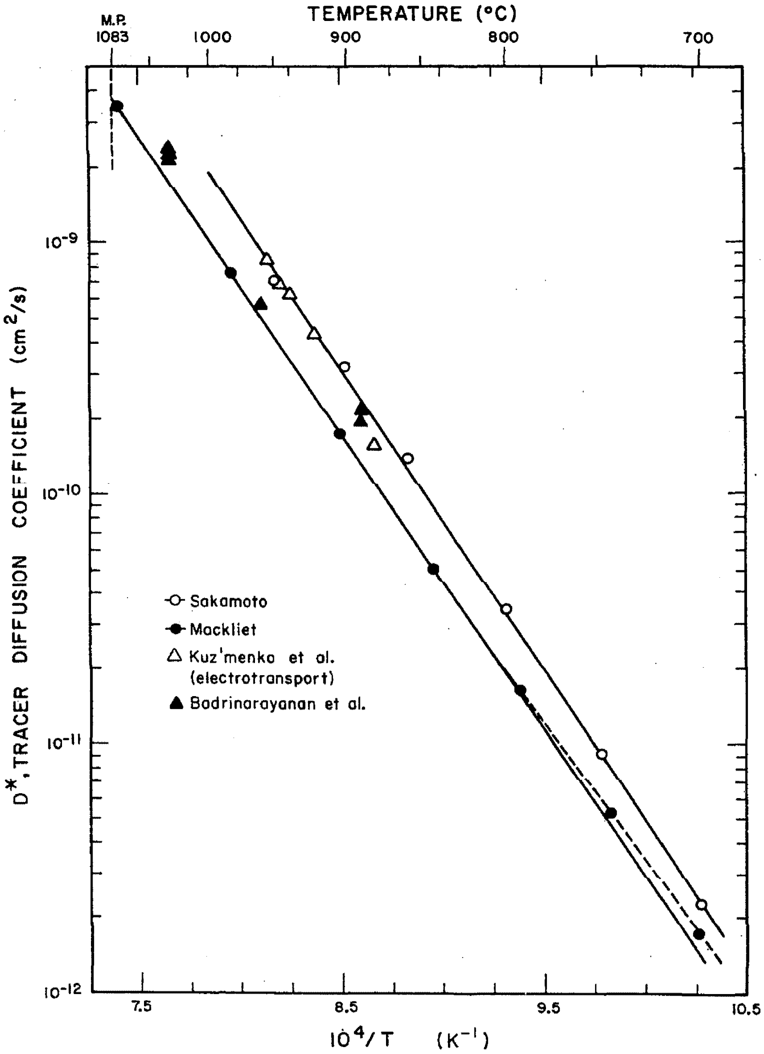

Figure 1. The tracer diffusion coefficient of ^{60}Co in single crystals of pure copper as a function of reciprocal absolute temperature.

Data taken from Sakamoto [2], Mackliet [1], and Badrinarayanan et al. [4]. The electrotransport data of Kuzmenko et al. [23] are shown for comparison.

after cutting and machining, or before electrodeposition. It is conceivable that the newly exposed surfaces of Sakamoto's specimens contained a worked layer, causing recrystallization and polycrystallinity during the diffusion anneals, which resulted in higher diffusion rates.

Mackliet deposited a ^{60}Co layer of 7.5 Å or less, whereas Sakamoto's layer was considerably thicker (approximately 20 Å).

The temperatures in Mackliet's experiments ranged from 700 to 1077 °C (with furnace temperature excursions of 1 °C at the higher temperatures, and 1.5 °C at most other temperatures), and diffusion times of 4 hours to 40 days. Sakamoto's diffusion runs extended over the smaller temperature range of 700 to 950 °C (the furnace temperature being held constant to within ± 2 °C) for periods of several hours to 20 days.

Although the penetration curves of both authors indicated a strict proportionality between the logarithm of the specific activity and the square of the penetration depth, Sakamoto's possessed considerably more scatter. Taking these penetration plots, calculating from them the logarithms of the diffusion coefficients, and plotting log D versus the reciprocal of the absolute temperature, one obtains a straight line from Sakamoto's data and a non-linear plot from Mackliet's data. (See figure 1). Because of the non-linearity of Mackliet's plot, D_0 and Q were calculated for both the initial and final portions of the curve with the aim of showing that the differences in slope and intercept for the two portions are much greater than the statistical errors in the individual values. The values of D_0 and Q appear in table 1. The unexpectedly large diffusion coefficients observed at the low temperature may be attributed to the randomly distributed dislocations ordinarily found in a metal. The contribution of such dislocations to "apparent" volume diffusion have been pointed out by Hart [3].

Subsequent isotope effect measurements for the diffusion of cobalt in polycrystalline copper by Badrinarayanan and Mathur [4] yielded coefficients which are in good agreement with those of Mackliet [1]. Their results are plotted in figure 1 and listed in table 2.

TABLE 1. Tracer diffusion parameters of ^{60}Co in copper. Data taken from Mackliet [1].

T (°C)	D_0 (cm^2/s)	Q (kcal/mol)
840-1077	1.93 ± 3%	54.1 ± 0.14%
700-800	0.39 ± 0.2%	50.6 ± 0.01%

TABLE 2. Tracer diffusion coefficients of ^{60}Co in copper. Data taken from Badrinarayanan and Mathur [4].

T (°C)	D* (cm^2/s)
1033	2.43×10^{-9} 2.26×10^{-9} 2.14×10^{-9}
960	5.75×10^{-10} 5.71×10^{-10}
890	2.15×10^{-10} 1.95×10^{-10}

2.2. Cu-Co Interdiffusion

Interdiffusion coefficients have been measured as a function of composition in dilute, single-phase, Cu-Co alloys (containing as much as 2 wt% Co) [5, 6]. The diffusion couples were constructed of spectroscopically pure, polycrystalline copper and cobalt specimens and annealed at temperatures varying from 800 to 1073 °C. The degree of interpenetration in the α-phase was determined with an electron-probe micoanalyzer. Interdiffusion coefficients were calculated with the aid of the Matano method [7] and a modified Hall analysis. Hall's analytical evaluation of interdiffusion coefficient at low solute concentrations [8] was reanalyzed, taking into consideration the nonlinear behavior exhibited by the probability plots of their experimental data in these regions. Measurements were made at eight different temperatures (±2 °C), and the interdiffusion coefficients calculated at compositions up to 2 wt% cobalt (see fig. 2) appear to increase very rapidly at the more dilute cobalt concentrations. When the coefficients are plotted as a function of the reciprocal absolute temperature, an Arrhenius expression can be obtained. Figure 3 gives the activation energy for interdiffusion as a function of cobalt concentration. The variation of the pre-exponential factor with cobalt composition is shown in figure 4. Also plotted (for comparison) in figures 3 and 4 are the activation energy and pre-exponential factor obtained by Mackliet [1] in his radioactive tracer experiments.

There are no other qualitative investigations of interdiffusion with which to compare the composition dependencies found in these experiments.

There has been a very brief and qualitative study of interdiffusion in the Cu-Co binary system reported [9]. The authors employed an x-ray microradiographic technique [10, 11] based on the use of an x-ray monochromatic focusing technique of high resolution, using low order reflections in order to avoid the difficulty inherent in the K_α-splitting of reflections of high orders. Copper was electrodeposited onto polycrystalline (of unspecified grain size) alloy foils of composition 32.6 at.% cobalt, balance copper. The diffusion couples were annealed at 800, 900, and 1000 °C (±5 °C) for 4 hours. Analysis by the combined diffraction microradiography technique revealed that cobalt diffuses along grain boundaries in copper between 800 and 900 °C. At 1000 °C, the dominant diffusion mechanism was volume diffusion.

Solid cobalt has been interdiffused with pure molten copper in the temperature range 1100 to 1300 °C for times as long as 1800 seconds [12]. Examination of the interface revealed that the molten copper moved into the solid cobalt principally by lattice diffusion.

2.3. Cu-Co-Au

The diffusion of radioactive ^{57}Co into a Cu_3Au alloy has been studied [13]. The diffusion coefficients were determined over the temperature range 650–900 °C. A thin layer (100 atomic layers) of ^{57}Co was electrodeposited on large grained polycrystalline alloy specimens (the alloys were made of components of an unspecified purity). After the diffusion anneals, the ^{57}Co concentration gradient was determined through the use of a "self-absorption method" [14–18]. The calculated tracer diffusion coefficients are listed in table 3.

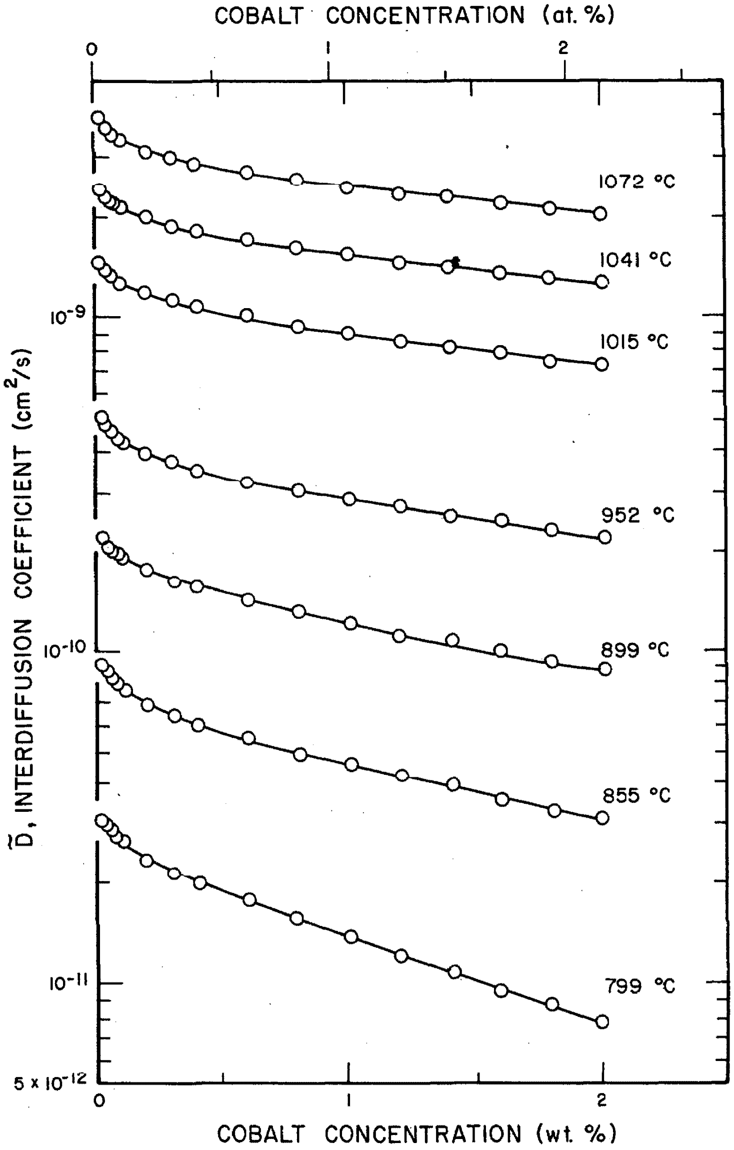

FIGURE 2. Interdiffusion coefficients as a function of cobalt concentration in the α-phase Cu-Co system.

Coefficients calculated (using a modified Hall method) by Bruni and Christian [6].

A plot of the temperature dependence of these data is shown in figure 5. A least-squares analysis of the data over the considered temperature range can be described by the following Arrhenius equation:

$$D^*_{Co \rightarrow Cu_3Au} = (4.2 \pm 0.5) \times 10^{-2} \exp\left[-(2.00 \pm 0.04)\ \text{eV} \cdot \text{atom}^{-1}/kT\right]\ \text{cm}^2/\text{s}.$$

In addition to the given error in the value of the pre-exponential factor, D_0, there is a source of further uncertainty of ±10% to be considered. This additional uncertainty in the value of D_0 arises because of the pre-exponential factor's dependence on the geometry adopted for the activity measurements, as well as the choice of the absorption coefficient used in the calculations.

2.4. Cu-Co-O

The interdiffusion of Co and Cu_2O at 800 and 1000 °C has been studied [19, 20], with special attention given to the reaction products (their rate of formation and their morphology) formed in the interdiffusion zone.

2.5. Cu-Co-Ti-X

Qualitative interdiffusion studies in the Cu-Co-Ti systems have been performed [21]. These studies were undertaken with regard to the diffusion soldering of

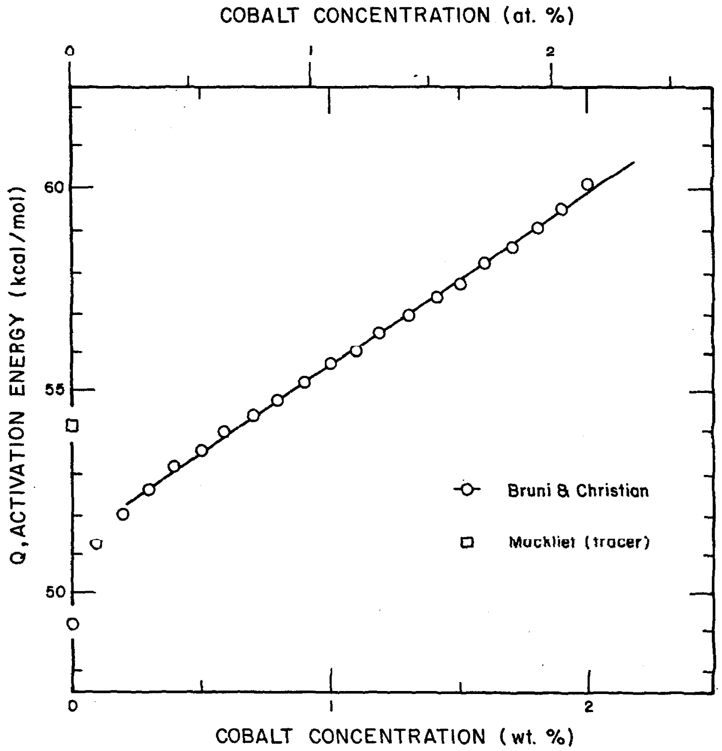

FIGURE 3. Activation energy for interdiffusion in the α-phase of Cu-Co system as a function of cobalt concentration.

Data taken from Bruni and Christian [6]. The activation energy obtained in radioactive tracer diffusion experiments by Mackliet [1] is also shown for comparison.

TABLE 3. Tracer diffusion coefficients of ^{57}Co in Cu_3Au. Data taken from Benci et al. [13].

T (°C)^a	D* (cm^2/s)
900	1.08×10^{-10}
850	4.77×10^{-11}
800	1.78×10^{-11}
750	6.62×10^{-12}
700	1.83×10^{-12}
650	5.40×10^{-13}

^{a}Temperatures measured to ±2 °C.

titanium and titanium alloys. No useful quantitative interdiffusion data were reported.

2.6. Cu-Co-Zn

The impurity diffusion of radioactive ^{60}Co into the ordered super-lattice of CuZn (β-brass) has been reported [22]. The experiments were performed in the temperature range 320–700 °C. The tracer was electrodeposited on coarse-grained, polycrystalline, alloy (47.2 at.% Zn) specimens of unspecified purity.

After the diffusion anneals, the specimens were sectioned on a lathe and the concentration gradients determined. From these data, the diffusion coefficients were calculated, and these are plotted in figure 6. A significant break was found in the curve at the transition temperature of 468 °C, as has been noted for self-diffusion in β-brass. In the disordered region above the transition temperature, the D versus $(1/T)$ plot is linear, and the data follow the Arrhenius law:

$$D = 0.047 \exp\left(-26.90\,\text{kcal}\cdot\text{mol}^{-1}/RT\right)\text{cm}^2/\text{s},$$

obtained from a least-squares fit of the data. Very near, and just above the transition temperature, there is a departure from linearity.

At the transition temperature, where long-range order begins, the D versus $(1/T)$ curve begins decreasing more rapidly.

In the ordered region (below 468 °C), the logarithmic plot of D versus $(1/T)$ has a finite curvature. Since

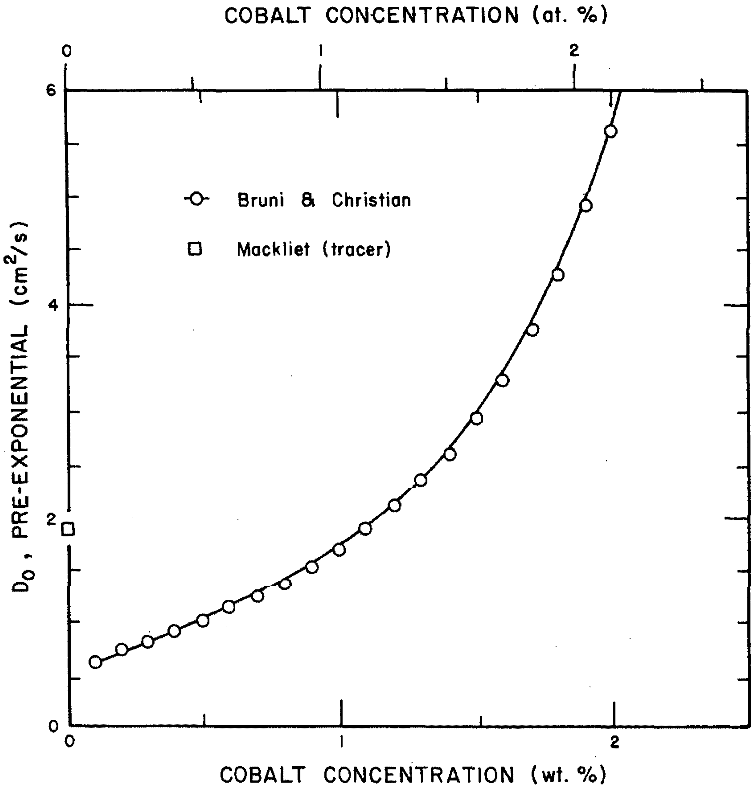

FIGURE 4. The pre-exponential factor, D_0, for interdiffusion in the α-phase of the Cu-Co alloy system as a function of cobalt concentration.

Data taken from Bruni and Christian [6]. and the radioactive tracer diffusion experiments of Mackliet [1].

the data do not fit a straight line, no frequency factor or activation energy is calculated for diffusion in the ordered super-lattice.

The authors do relate by means of numerical and graphical interpolations their empirical curves of $D(T)$ to a function of the long-range order parameter.

2.7. Electromigration

The electrotransport of ^{60}Co in copper has been studied [23]. The authors used an isothermal tracer technique [24, 25]. Using this method, a thin layer of less than one micron of the radioactive tracer was electrolytically deposited on the end faces of two identical specimens. The active surfaces were then placed in contact with each other and inserted between the electrodes. A direct current of 2000 A was passed through the specimens under vacuum. The current density was approximately 150 to 250 A/mm. After the experiment, the specimen was removed from the apparatus and separated at the plane of contact. The Gruzin residual-activity method [26] was employed to determine the distribution depth of the active material in the anode and cathode halves of the specimen. The diffusion coefficients determined in these experiments are listed in table 4. These D values are larger than those of Mackliet, being approximately the same as those of Sakamoto (see figure 1). Because of the restricted temperature range and scatter in the data, no activation energy was calculated.

TABLE 4. Diffusion coefficients of ^{60}Co in copper from electrotransport experiments. Data taken from Kuzmenko et al. [23].

T (°C)	D^* (cm^2/s)
956	8.7×10^{-10}
945	7.0×10^{-10}
939	6.3×10^{-10}
922	4.4×10^{-10}
882	1.6×10^{-10}

In all the experiments the transport of the ^{60}Co was in the direction of the anode, thus indicating that the electron wind is the predominant force determining the mobility of the ^{60}Co ion in the copper lattice. Scattering cross sections and "effective charge numbers" were also calculated from these data. The authors did not report

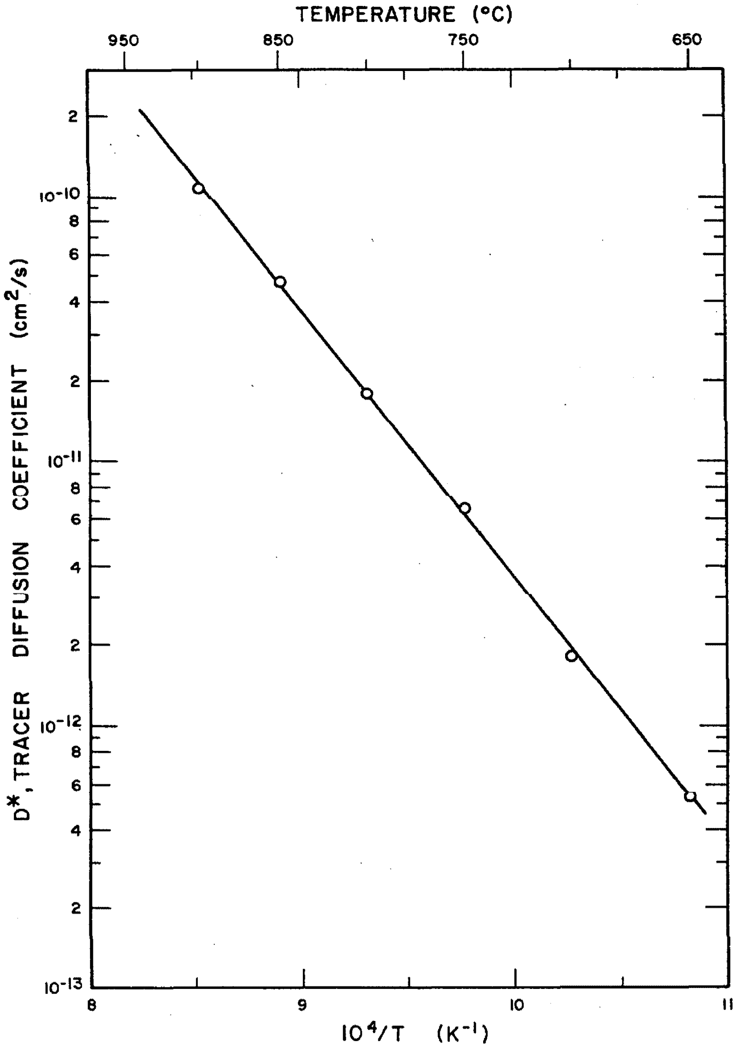

FIGURE 5. The tracer diffusion coefficients of ^{57}Co in a Cu$_3$Au alloy as a function of reciprocal absolute temperature.

Data taken from Benci et al. [13].

the details of their specimen preparation, the precision of their data, or discuss possible error sources in their experiments, although the isothermal isotope technique utilized in the experiment has since been improved upon [27].

The electromigration of ^{58}Co has been investigated by Guilmin and coworkers [28] who employed a thin-layer technique (see e.g., refs. 29–31) in their experiments at 1015 °C. The radioactive cobalt impurities migrated towards the anode. An effective valency of -34 ± 5 was calculated from the data.

2.8. Thermomigration

The thermomigration of cobalt in dilute solid Cu-Co alloys has been reported [32, 33]. In both studies, a steady-state technique utilizing radioactive tracers was used to study the migration of the ^{60}Co impurities. Spectrographically pure copper (99.999%) was used as the starting material in preparation of specimens containing a uniform concentration of the ^{60}Co impurity. After removing the samples from the furnace, they were sectioned on a lathe and the radioactivity counted.

Unfortunately, the results are conflicting. In the earlier investigation [32], the cobalt was found to migrate towards the cold side of all the specimens, whereas in the most recent study [33], the opposite was found.

2.9. Molten Metals

The impurity diffusion coefficient of cobalt in liquid copper has been measured over the temperature range 1100–1300 °C [34]. A modified capillary-reservoir technique was employed. The data will fit an Arrhenius-type equation within the limits of the experimental errors. For the liquid Cu-Co system:

$$D = (2.3_5 \pm 0.02_2) \times 10^{-3} \exp\,[-(11.39 \pm 0.26)\ \text{kcal}\cdot\text{mol}^{-1}/RT]\ \text{cm}^2/\text{s}.$$

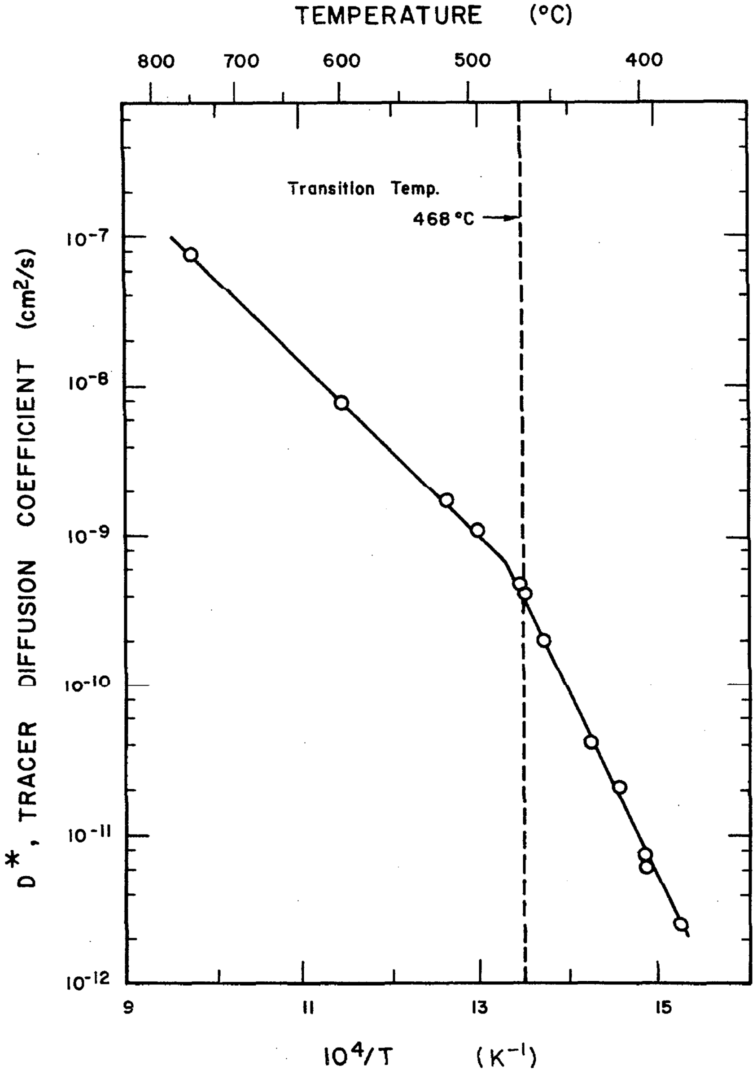

FIGURE 6. The tracer diffusion coefficient of ^{60}Co in ordered and disordered Cu-Zn (47.2 at.%) (β-brass).

After Bassani et al. [22]

These diffusion parameters are in contrast to those obtained from dissolution experiments [35] where the activation energy was determined to be 8.98 kcal/mol and pre-exponential factor, 2.4×10^{-4} cm^2/s.

Solid cobalt has been interdiffused with molten copper [12] and is discussed in section 2.2, Cu-Co Interdiffusion.

2.10. Cu-Co References

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3. Copper-Iron

3.1. Fe*→ Cu

The rate of diffusion of radioactive iron in pure copper has been reported by a number of authors [1–9]. Their results are shown in figure 7. The isotope effect measurements of Mullen [5–7] appear to be the best values of all those reported. Mackliet's results [1, 2] were confirmed by Mullen's careful experiments. Barreau et al. [8] obtained results which are in excellent agreement with Mullen and Mackliet. The experiments of Bernardini and Cabane [9] are also in good agreement with Mackliet. The only disagreement is in work published by Tomono and Ikushima [4] who later [10] conceded that poor experimental technique and control in their experiments were responsible for the discrepancy.

Mullen in his experiments plated ^{55}Fe and ^{59}Fe isotopes onto single crystals of pure copper and diffused them at temperatures ranging from near the melting point down to 716 °C. The specimens were sectioned after diffusion and the relative diffusivity of the two iron isotopes determined (see table 5). The tracer diffusion parameters, D_0 and Q, in the Arrhenius equation were determined by a least-squares fit of Mullen's data and most of Mackliet's data. The resulting Arrhenius-expression with estimated errors is:

$$D^*_{\mathrm{Fe}} = (1.01 \pm 0.23) \exp\left[-(50.95 \pm 0.46)\ \mathrm{kcal \cdot mol^{-1}}/RT\right]\ \mathrm{cm^2/s},$$

and should accurately indicate the rate of diffusion of iron tracers in copper in the temperature range 700–1050 °C. This temperature dependence obtained from tracer-sectioning techniques has been confirmed in experiments where the Mössbauer effect was the tool employed [11–15].

Sotskov et al. [3] studied the motion of phase boundaries in the Fe-Cu system with radioactive isotopes. Assuming that the phase boundary motion is determined by diffusion processes occurring within the adjacent phases, they were able to calculate diffusion coefficients (approximately 10^{-10} cm²/s) for radioactive iron diffusing into pure copper in the temperature range 925–1050 °C (see fig. 7). Although the resultant coefficients are of the right order of magnitude, they are somewhat less reliable than the above-mentioned studies because of the additional factors introduced by the accompanying phase transformations.

3.2. Cu*→ Fe

The diffusion of radioactive ^{64}Cu has been measured by Lazarev and Golikov [16–19], Anand and Agarwala

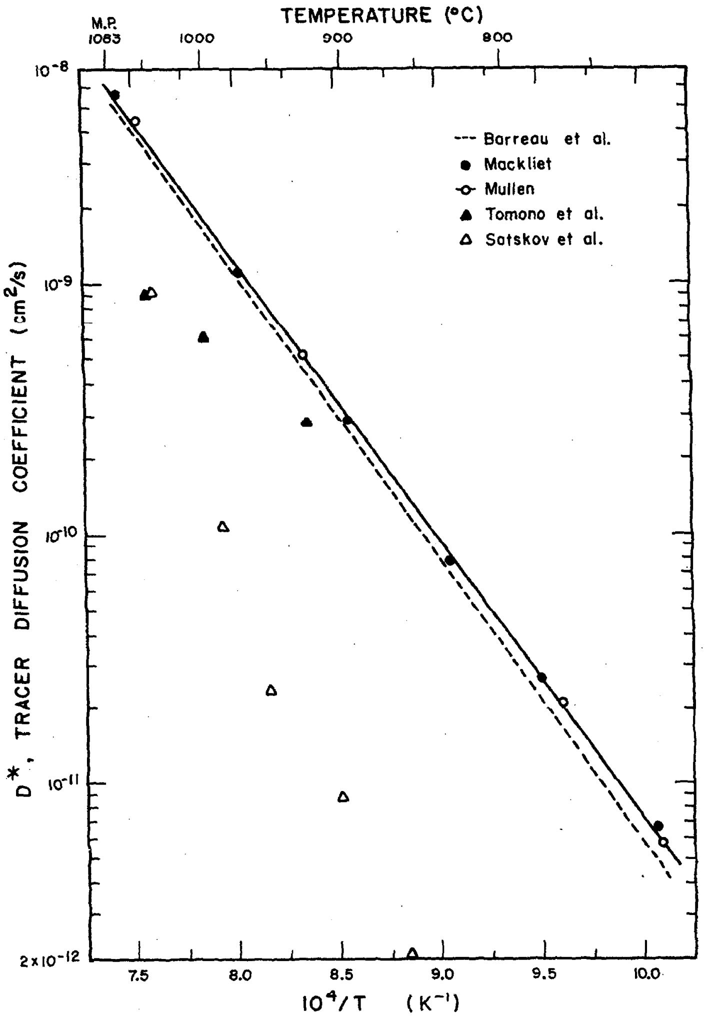

FIGURE 7. The tracer diffusion coefficient of iron in pure copper as a function of reciprocal absolute temperature.

Data extracted from the investigations of [2–4, 6, 8].

[20], and by Rothman and coworkers [21]. The results are not in agreement (see fig. 8). The data of Rothman et al. show a large discontinuity in the Arrhenius plot of the tracer diffusion coefficient at the α/γ transformation temperature, whereas the data of the other two groups do not.

As was demonstrated in the paper of Rothman et al., the major discrepancy between the results probably was due to grain boundary contributions which strongly affected the γ-phase measurements of Anand and Agarwala. Trapping of the diffusing copper by inclusions or impurities also possibly occurred in these experiments of Anand and Agarwala. The same may be said of the Soviet investigation.

In the experiments of Rothman et al., two grades of iron were utilized, Armco iron and a higher purity grade, Ferrovac E. The ^{64}Cu isotope was evaporated onto the surfaces of these iron specimens and diffused at temperatures in the range 850–1368 °C. The copper tracer diffusion coefficients obtained from Gaussian or near-Gaussian penetration plots are listed in table 6. The results indicated that the grain boundary diffusion of copper was predominent at temperatures $\leqq 815$ °C in the α-phase. In the γ-phase, grain boundary diffusion predominated at temperatures $\leqq 1250$ °C. Autoradiographs confirmed the diffusion of copper in the grain boundaries. Additionally, autoradiographs from the less pure iron specimens indicated the agglomeration of ^{64}Cu near the grain boundaries, leading the authors to speculate on the trapping of ^{64}Cu by inclusions or a

TABLE 5. Tracer diffusion coefficients of ^{55}Fe in copper. Data taken from Mullen [6].

T (°C)	$D^*_{^{59}Fe}$ (cm^2/s)	1-$D_{^{59}Fe}/D_{^{55}Fe}$	Isotope Effect (E)
1056.1[a]	4.38×10^{-9}	0.0256 ± 0.0018[b]	0.742 ± 0.052[b]
1056.1	4.46×10^{-9}	0.0235 ± 0.0012	0.681 ± 0.036
927.4	5.16×10^{-10}		
927.4	5.11×10^{-10}	0.0234 ± 0.0015	0.679 ± 0.043
767.3	2.10×10^{-11}	0.0224 ± 0.0010	0.650 ± 0.028
716.8	5.76×10^{-12}	0.0203 ± 0.0018	0.590 ± 0.053

[a] All temperatures ±1 °C.

[b] Errors shown are least-squares standard error.

TABLE 6. Tracer diffusion coefficients of ^{64}Cu in pure iron. Data taken from Rothman et al. [21].

T (°C)	Phase	D* (cm^2/s)
1368[a]	γ	5.20×10^{-10}
1368	γ	5.03×10^{-10}
1315	γ	2.56×10^{-10}
1315	γ	2.45×10^{-10}
1285	γ	1.55×10^{-10}
1285	γ	1.52×10^{-10}
901.6[b]	α	5.1×10^{-11}
867.0	α	2.2×10^{-11}
854.5	α	1.8×10^{-11}

[a] Temperatures in the γ-phase measured to ±3 °C.

[b] Temperatures in the α-phase measured to ±1 °C.

precipitation process connected with impurities in solution.

These results of Rothman et al. are consistent with the interdiffusion results of Speich and coworkers [22] who also found a discontinuity in the interdiffusion coefficient in the α/γ transformation (see fig. 8). Since Speich et al. measured interdiffusion in dilute Fe-Cu (0–2 wt%) alloys, their measured interdiffusion coefficients should be nearly equal to $D^*_{Cu\rightarrow Fe}$. In the γ-phase, they report $D_0 = 1.8$ cm^2/s and $Q = 70.5$ kcal/mol. In the α-phase above the Curie temperature, $D_0 = 8.6$ cm^2/s and $Q = 59.7$ kcal/mol. Below the Curie temperature (759 °C), an anomalous decrease in D occurs. This work is discussed more thoroughly in section 3.5, on interdiffusion in Cu-Fe.

The effect of minor alloying additions to iron (such as is found in mild steels) on the copper tracer diffusion coefficient was investigated by Lindner and Karnik [23], and by Rassoul and coworkers [24]. In the experiments by Lindner and Karnik, the iron contained 0.13% carbon (as well as 0.63% Mn, 0.16% Ca, < 0.1% Si, Ni, Cr, S and P). The tracer diffusion coefficients (see fig. 9) were determined by measuring the decrease in surface activity resulting from diffusion and absorption. Their measurements, made over a temperature range of 800 to 1200 °C, yielded diffusion coefficients which can be described by a single Arrhenius expression, with $D_0 = 3$ cm^2/s and $Q = 61$ kcal/mol. On a D vs $1/T$ plot, the line from this Arrhenius equation is comparable to that of Anand and Agarwala, showing no discontinuities and lying about midway between the separate lines describing diffusion of copper in pure α-iron and copper in pure γ-iron, as determined by Speich et al. and Rothman et al.

Rassoul and coworkers (also working with a mild steel) made their measurements over a broad temperature range so as to encompass both the α- and γ-phases and the two-phase region between them. Their iron (steel 1020) specimens contained 0.20% carbon, and a thin-layer method [25, 26] of determining the copper tracer diffusion coefficient was employed. Figure 9 contains the Arrhenius plots of these data. The diffusion coefficients are several orders of magnitude higher than

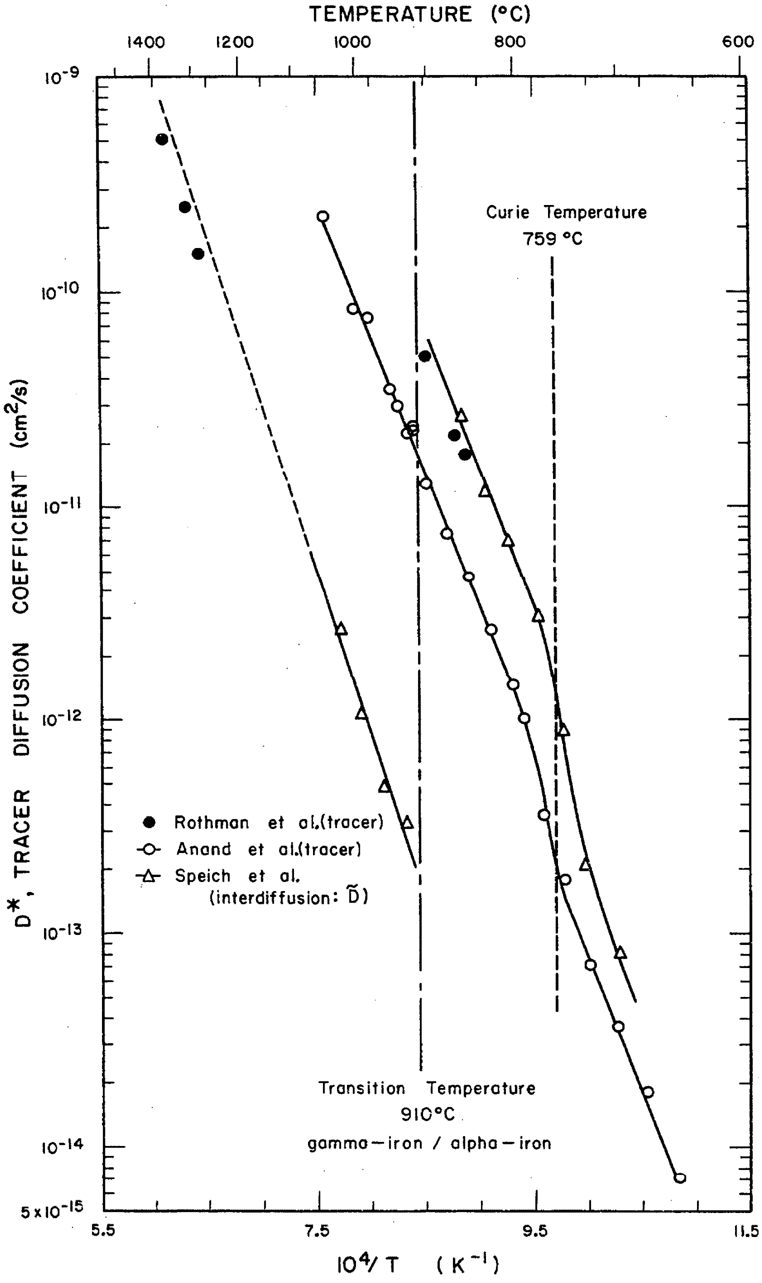

FIGURE 8. The tracer diffusion coefficient of copper in pure iron as a function of reciprocal absolute temperature.

The effect of the Curie temperature and the α/γ phase transition on the rate of tracer diffusion is readily apparent. Data excerpted from the studies of Anand and Agarwala [20], and Rothman and coworkers [21]. The interdiffusion coefficients as determined by Speich and coworkers [22] are also shown for comparison.

other results reported above, which is surprising. Nevertheless, a pronounced discontinuity in diffusion coefficient values is found at each phase boundary. Reliable activation energies probably should not be expected from this data because of the small number of measurements in each phase. The authors' published D_0 and Q values appear to be in error and are inconsistent with their published diffusion coefficient values.

3.3. Fe* → Fe-Cu

Self-diffusion studies of radioactive iron isotopes in Fe-Cu alloys (containing 0.6 at.% Cu) in the narrow temperature range of 840 to 880 °C were inconclusive [27]. The copper alloying addition apparently did not cause a change in the value of the iron self-diffusion rate when in pure α-iron. Values of the coefficients were

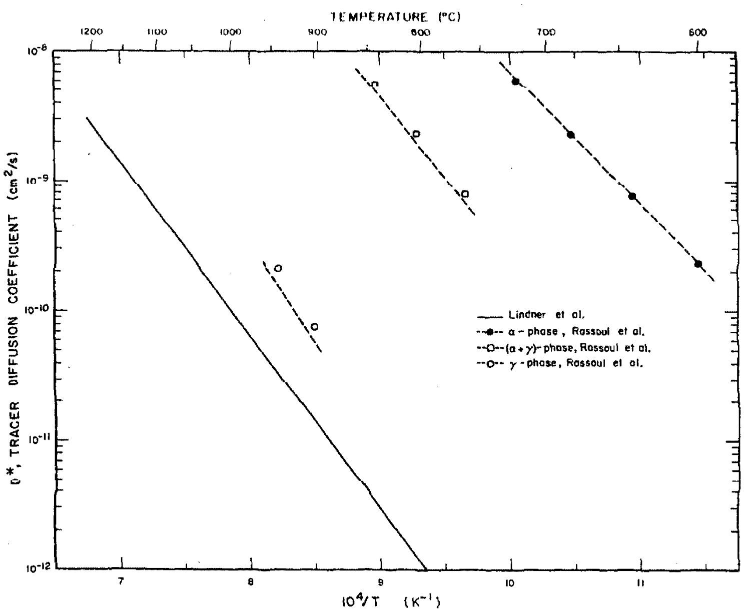

FIGURE 9. The copper tracer diffusion coefficient in mild steels as a function of reciprocal absolute temperature.

The effect of minor alloying additions and phase transformations is readily apparent. Data excerpted from the papers of Lindner and Karnik [23], and Rassoul and coworkers [24].

of the order of 10^{-12} cm²/s in the temperature range investigated. Although an isotope effect was looked for, none was found.

Zhukhovitskii and coworkers [28] measured iron self-diffusion rates in two-phase Cu-Fe alloys. In their experiments, thick layers of ^{59}Fe were electrolytically deposited on a number of alloys (see table 7). The diffusion temperatures were 900 and 1000 °C. After diffusion anneals of 100 to 150 hours in vacuum, the loss in β-activity was measured, and an effective iron self-diffusion coefficient determined using the analysis described by Zhukhovitskii, Kryukov, and Geodakyan [29, 30]. The coefficients are termed "effective" diffusion coefficients since the measurement encompasses the mobilities in two different phases as well as grain boundaries. The results of the calculations are listed in table 7. Figure 10 shows how the iron mobility varies with copper concentration. The authors compared their results to those predicted by several theoretical models [31, 32]. Meeting with little success, they instead offered a new mathematical treatment.

TABLE 7. Effective diffusion coefficients of ^{59}Fe in Fe-Cu alloys. Data taken from Zhukhovitskii et al. [28].

Fe-Cu Alloy (wt% Cu)	D* (cm²/s) 900 °C	1000 °C
5.0	5.0×10^{-13}	3.37×10^{-12}
9.9		4.29×10^{-12}
19.1	7.5×10^{-13}	5.84×10^{-12}
40.9	1.08×10^{-12}	6.45×10^{-12}
50.4	1.63×10^{-12}	
60.8	2.37×10^{-12}	9.28×10^{-12}
79.8	4.75×10^{-12}	1.89×10^{-11}
90.0	8.35×10^{-12}	3.40×10^{-11}
97.6	2.24×10^{-11}	6.13×10^{-11}

Iron self-diffusion coefficients were shown to be affected by the presence of copper (0.27 at.%) in α-iron single crystals [33]. Measurements made in the temperature range 778–901 °C revealed a dehancement in the iron-tracer mobility relative to pure iron crystals (see table 8). Although the temperature range of the investigation was rather narrow and measurements were made at only three temperatures, a curvature was found in the Arrhenius plot and did not allow an activation energy to be determined.

An isotope effect for iron self-diffsuion in single crystals of α-iron containing 0.27 at.% copper did not differ (within experimental error) from those measurements made with pure iron specimens [34]. The isotope effect values (0.39 at 778.3 °C, and 0.45 at 901 °C) are close to those obtained in earlier experiments [35] by other workers.

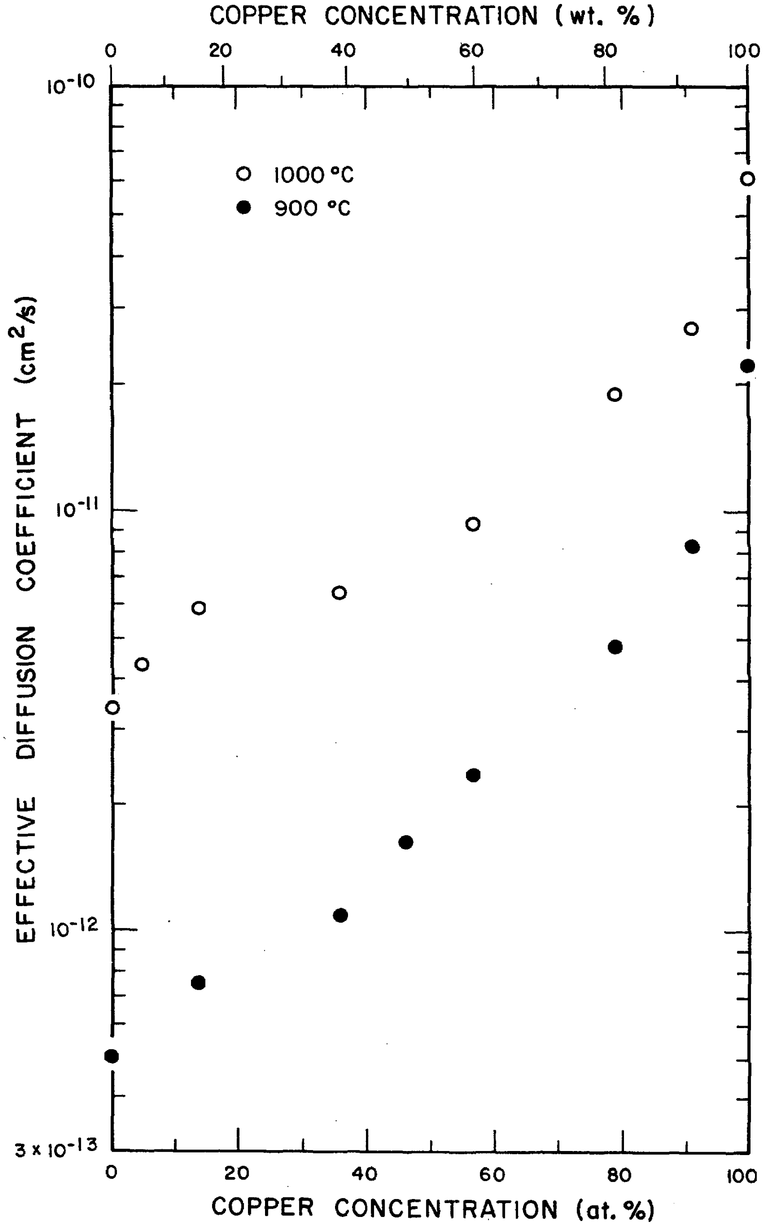

FIGURE 10. Effective diffusion coefficients of ^{59}Fe as a function of copper concentration in Fe-Cu alloys at 900 and 1000 °C.

Data taken from Hsin et al. [28].

3.4. $Cu^* \rightarrow$ Cu-Fe

Dilute alloying additions or iron to pure copper have been found to decrease the rate of copper self-diffusion in the neighborhood of 1020 °C [36]. Utilized in the serial-sectioning experiments were polycrystalline and single crystal alloy specimens. Alloy compositions, temperatures, and tracer diffusion coefficients are listed in table 9. The results can be expressed mathematically by the relation:

$$D^*_{Cu\rightarrow Cu\text{-}Fe} = D^*_{Cu\rightarrow Cu}(1 + b \cdot C_{Fe}),$$

where $b = (-5 \pm 1.5)$ and C_{Fe} = atom fraction of iron solute.

Lazarev and Golikov [16, 18] investigated both the volume and grain boundary diffusion coefficients of ^{64}Cu, not only in pure iron, but also iron alloys containing 0.18 and 1.2 wt% Cu. Since the results they obtained in their pure iron specimens are in conflict with more reliable investigations, some strong doubts must be cast upon these tracer studies in Fe-Cu alloys.

3.5. Cu-Fe Interdiffusion

Although a variety of interdiffusion studies have been

TABLE 8. Tracer diffusion coefficients of ^{59}Fe in single crystals of Fe-Cu (0.27 at.%). Data from Irmer et al. [33].

T (°C)	D* (cm^2/s)
901	4.7×10^{-12}
809	5.24×10^{-13}
778.3	2.07×10^{-13}

TABLE 9. Tracer diffusion coefficients of ^{64}Cu in Cu-Fe alloys. Data taken from Bocquet [36].

T (°C)^a	Cu-Fe Alloy (at.% Fe)	D* (cm^2/s)
1078	1.44 ± 0.04	4.68×10^{-9}
1021	0 (pure Cu)	2.30×10^{-9}
1023	0.2 ± 0.01	2.08×10^{-9}
	0.5 ± 0.02	2.04×10^{-9}
1020	1.38 ± 0.04	2.12×10^{-9}
	1.45 ± 0.04	1.95×10^{-9}
	2.40 ± 0.05	1.98×10^{-9}
992	1.82 ± 0.04	1.26×10^{-9}

performed in the Cu-Fe system (with a variety of results), the two most definitive investigations [22, 37] are in disagreement with each other. Speich and coworkers [22] determined interdiffusion coefficients (and solubility limits of copper) in the alpha and gamma phases of the Fe-Cu system from concentration-penetration curves obtained from the electron-probe microanalysis of copper-plated polycrystalline iron diffusion couples. In the other study, Krishtal and coworkers [37] also employed an electron microprobe to analyze their couples, finding concentration-dependent interdiffusion coefficients. The results of Krishtal et al. are not in agreement with the carefully performed tracer experiments of Rothman et al. (Cu in Fe) [21] or Mullen (Fe in Cu) [6], whereas the data obtained by Speich et al. (who only measured the interdiffusion of copper in iron) are in good agreement with the appropriate tracer data.

Speich et al. performed their interdiffusion experiments in the temperature range 700–1020 °C. The concentration-penetration data were analyzed under the assumption of a concentration-independent interdiffusion coefficient (because of the low solubility of copper in the α- and γ-phases of iron [38]. The appropriate solution to the diffusion equations [39–41] (with some iteration) yielded the interdiffusion coefficients (average values) shown in figure 8 and listed in table 10.

TABLE 10. Average copper interdiffusion coefficients in the Fe-Cu system. Data taken from Speich et al. [22].

T (°C)	Phase^a	$\tilde{D}$ (cm^2/s)^b
1020	γ	2.63×10^{-12}
989	γ	1.04×10^{-12}
960	γ	4.82×10^{-13}
929	γ	3.31×10^{-13}
859	α	2.68×10^{-11}
832	α	1.18×10^{-11}
805	α	6.97×10^{-12}
776	α	2.99×10^{-12}
750	α	8.77×10^{-13}
730	α	2.10×10^{-13}
699	α	8.09×10^{-14}

[a] The interdiffusion coefficient in the α-phase (0-2 wt%) and the γ-phase (0-5 wt%) is assumed to be concentration independent.

[b] The mean deviation was no greater than ±20% of the average value.

An anomalous decrease of the interdiffusion coefficient is found to occur below the Curie temperature (~ 759 °C), not unlike that found for other substitutional elements diffusing in iron. Additionally, a large discontinuity in the temperature dependence of the interdiffusion coefficient is observed at the α/γ transformation, similar to the discontinuity in the Arrhenius plot of the copper tracer diffusion coefficient data of Rothman et al. [21].

The interdiffusion coefficients of copper and α-iron (over the composition range 0–2 wt% Cu) in the paramagnetic temperature range (776–859 °C) obey an Arrhenius equation. A least-squares fit to the data gives the following Arrhenius equation:

$$\tilde{D} = 8.6 \exp(-59.7 \text{ kcal} \cdot \text{mol}^{-1}/RT) \text{ cm}^2/\text{s},$$

to describe the interdiffusion coefficient. Similarly, the interdiffusion coefficients of copper and γ-iron (0–5 wt% Cu) can be described by the Arrhenius equation:

$$\tilde{D} = 1.8 \exp(-70.5 \text{ kcal} \cdot \text{mol}^{-1}/RT) \text{ cm}^2/\text{s}.$$

Speich and coworkers experienced a great deal of difficulty in obtaining reproducible concentration-penetration curves in their interdiffusion experiments with γ-iron. The low lattice diffusivity of the copper and the rapid diffusion of copper along austenite grain boundaries combined to mask the true interdiffusion coefficient.

Other interdiffusion investigations have been of a mostly qualitative nature. Arnold [42] and Ponomarenko [43] observed very little interdiffusion of copper in iron at temperatures in the neighborhood of 1000 °C. Guillet and Bernard [44], Arkharov et al. [45], as well as Bokstein and coworkers [46] observed the preferential movement of copper in the grain boundaries of commercially pure iron during interduffusion studies. The results obtained from interdiffusion investigations utilizing copper and mild or plain carbon steels also show that the copper migration is essentially through the grain boundaries [47–49]. Kuczynski and Alexander [50] made a metallographic study of the interdiffusion occurring at interfaces formed during the sintering of copper wires to flat iron blocks (and vice versa).

Sirca and coworkers [51–62] interdiffused copper and iron, where the copper was molten and the iron was in the form of a crucible. The results indicated that volume diffusion was very slow—the intergranular penetration of copper being predominant. Nevertheless, an approximate value of 10^{-11} cm^2/s for the copper interdiffusion coefficient at 1100 °C was estimated. Sirca also added phosphorus, silicon, beryllium, chromium, tin, antimony, and aluminum to the copper and observed the effect of these dilute alloying additions on the interdiffusion process. Only phosphorus, beryllium, and silicon were found to moderate the grain boundary penetration of copper.

Gorbunov, in his book [63], reports experiments with copper diffusion coatings on iron. The iron surface was saturated with copper by being packed in five copper powders at temperatures 1150 to 1250 °C. It was found that the thickness of the copper coatings increased with temperature and duration of the cementation anneal.

The interdiffusion processes occurring between copper and steels has attracted much attention. Melford [47] plated copper onto a mild steel, interdiffused at 875 °C, and then investigated the microsegregation of the copper at grain boundaries with an electron-probe microanalyzer. Bozhko [48] correlated the width of the interdiffusion zone with grain boundary purity in steels. Rolls and Badelek [49] interdiffused copper and plain-carbon steels and found that the copper penetration was essentially intergranular at 1100 °C, and volume at 1200 °C. Pokhmurskii and coworkers [64–70] have investigated the effect of protective coatings of copper on iron and steel during fatigue and corrosion-fatigue.

3.6. Cu-Fe-Ag

Arkharov et al. [71] qualitatively followed the interdiffusion processes occurring between silver and polycrystalline Cu-Fe alloys (0.001–0.04 wt% Fe) at 500 °C. The silver penetration was primarily through the grain boundaries rather than through the lattice. Varying iron concentrations caused no substantial changes in the interdiffusion of the silver. The addition of antimony and beryllium to the Cu-Fe alloys and their effects on the interdiffusion process were also observed.

Arkharov and coworkers [45] also examined the interdiffusion occurring between silver and copper-bearing steels at 900 °C. Metallographic examination revealed little or no preferential diffusion of silver in the grain boundaries of the steels.

3.7. Cu-Fe-Al

When copper, containing aluminum alloy additions of 2.5 and 8 at.%, was interdiffused with iron at 1100 °C, the aluminum was observed to cause an acceleration in the grain boundary diffusion rate of copper [60, 61].

3.8. Cu-Fe-B

The experiments of Lazarev and Golikov [18, 19], described in sections 3.2 and 3.4, revealed that dilute alloying additions of boron (0.003 wt%) to iron have little effect on copper diffusing through the lattice in alpha or gamma-iron. Boron does reduce the amount of copper diffusing in the iron grain boundaries. See figure 12.

3.9. Cu-Fe-Be

Copper, containing beryllium (3.25 at.%), when interdiffused with iron in the temperature range 1000–1100 °C, was found to exhibit a minimum amount of grain boundary penetration [60, 61].

3.10. Cu-Fe-C

The influence of copper on the mobility of carbon in iron and steel has attracted interest because of its obvious technological importance. The results from a number of early papers [72–76] indicate that the effect of the copper alloying additions is minimal, moderating the carbon mobility in α- and γ-iron, if anything. More recently though, Krishtal in his book [77, p. 105] writes of "slight" enhancement of the carbon mobility in austenite due to the presence of copper. Effective diffusion coefficients for carbon in the multiphase ternary alloys were calculated with the data obtained from metallographic investigation and weight losses during decarburization. The results are summarized in table 11.

Rolls and Badelek [49] have reported the results of a preliminary study of the influence of carbon on the interdiffusion of copper in plain carbon-steels at 1100 and 1200 °C. The results revealed that the mode of copper diffusion in austenite was essentially intergranular at 1100 °C and volume diffusion at 1200 °C in the steel specimens of low carbon content (0.2% C

TABLE 11. Effective carbon diffusion coefficients in austenitic Fe-C-Cu alloys. Data taken from Krishtal [77].

Fe-C-Cu Alloy[a] (at.% Cu)	Diffusion Coefficients (10^{-7} cm^2/s)					D_0 (cm^2/s)	Q (kcal/mol)
	920 °C	950 °C	990 °C	1050 °C	1100 °C		
1.02	1.78	2.51	3.64	6.51	10.1	1.0×10^{-1}	31.6
2.04	1.98	2.66	4.07	7.01	11.0	8.7×10^{-2}	31.1
3.10	2.14	2.88	4.59	7.67	11.9	8.1×10^{-2}	30.6
3.95	2.40	3.26	4.85	8.32	12.6	6.92×10^{-2}	30.0

[a] Carbon content approximately 4 at.%.

versus specimens containing 0.85% C). Electron-probe microanalysis, both perpendicular and parallel to the copper/steel interface, revealed copper-enriched zones in the substrate of the high-carbon steel at 1100 °C, whereas there was found to be a linear decrease in copper concentration with distance from the interface displayed by the low-carbon steel. For interdiffusion anneals at 1200 °C, both of the low and high-carbon steels showed the presence of copper-rich bands in the substrate parallel to the interface, although copper concentrations were 1.5 times higher in the high-carbon steel.

Other [53–57] unpublished research notes that carbon hinders the mobility of copper during the interdiffusion of copper and iron.

3.11. Cu-Fe-Cr

The tracer diffusion of ^{59}Fe in Cu-Cr alloys (0.8% Cr) was found by Barreau and coworkers [8] to be essentially the same as the lattice diffusion rate in unalloyed O.F.H.C. copper. These results are discussed in sections 3.1 and 3.21.

When copper containing a dilute alloying addition of chromium (0.92%) was interdiffused with pure iron at 1100 °C, very little copper penetration was observed [60, 61]. The copper was apparently tied up at the interface where several phases were formed during interdiffusion.

A metallographic examination of the diffusion processes encountered during the sintering (at 1300 °C) of Fe-Cr-Cu alloys (containing 2–18% Cr and 4% Cu) has been reported by Ahmed [78], and Ahmed and coworkers [79].

3.12. Cu-Fe-Mo

The experiments of Lazarev and Golikov [17–19], described in sections 3.2 and 3.4, showed that dilute alloying additions of molybdenum (0.7–1.0 wt%) have little effect on copper diffusing through the lattice in α and γ-iron. Molybdenum does reduce the amount of copper diffusing in the iron grain boundaries. See figure 12.

3.13. Cu-Fe-Ni

The effect of copper diffusion on the magnetic properties of permalloy films (Ni-Fe alloys) has resulted in several investigations [80–86].

The data of Crowther [80], and Grishechkin and coworkers [83] are in essential agreement. The interdiffusion process occurring between thin films of copper and Ni-Fe alloys required an activation energy of 34 kcal/mol.

The interdiffusion experiments of von Neida and Hagedorn [81] yielded an activation energy 47.3 kcal/mol. Why their value of the activation energy should be so much higher is not readily apparent. Since all three investigations dealt with thin films, something more than a simple lattice interdiffusion process may have been measured in these experiments.

The interdiffusion processes occurring between Monel (70%Ni–30%Cu) and steel during industrial heat treating operations (temperature range 900–1000 °C) were observed by Golovanenko [87]. The interdiffusion of iron into the Cu-Ni alloy led to the formation of multiphase zones at the interface.

Smiryagin and Kvurt [88] investigated the effect of copper on the rate of iron diffusion in nickel—finding that it causes an increase.

3.14. Cu-Fe-O

Rapp and coworkers [89] interdiffused pure iron and Cu_2O at 1000 °C and then examined the reaction products formed. Copper and iron oxide were found to exist in an aggregate arrangement. The kinetics of this displacement reaction are presented in detail [90].

TABLE 12. Effective carbon diffusion coefficients in austenitic Fe-Si-C-Cu alloys. Data taken from Krishtal [77].

Fe-Si-C-Cu Alloy[a]		Diffusion Coefficients (10^{-7} cm^2/s)						D_0 (cm^2/s)	Q (kcal/mol)
(at.% Si)	(at.% Cu)	890 °C	920 °C	950 °C	990 °C	1050 °C	1100 °C		
1.2	0.09	2.34	3.10	4.03	5.75	9.11	13.0	2.04×10^{-2}	26.4
1.2	0.21	2.57	3.31	4.31	6.03	9.56	13.8	2.14×10^{-2}	26.4
1.2	0.30	2.75	3.55	4.56	6.45	10.2	14.5	2.29×10^{-2}	26.4
1.2	0.39	2.92	3.89	4.80	6.92	10.8	15.9	2.34×10^{-2}	26.3
1.2	0.48	3.02	4.26	5.31	7.41	11.6	16.6	2.52×10^{-2}	26.3

[a] At eutectoid compositions.

3.15. Cu-Fe-P

Sirca [52, 60, 61] interdiffused copper, containing small amounts of phosphorus (up to 1.2%), and iron at temperatures up to 1100 °C. His results indicate that the phosphorus additions minimized the amount of copper diffusion down the iron grain boundaries.

The changes in the microstructure of Fe-Cu alloys induced by the diffusion of phosphorus (from a vapor phase) at 1950 °C were observed by Claussen [91]. The results were much the same as those observed in low carbon-steels. Hauk [92] concludes in her review that phosphorus accelerates copper mobility in steel.

3.16. Cu-Fe-Sb

The addition of antimony (up to 8%) to copper was found to hinder copper interdiffusion when the alloys were interdiffused with pure iron at 1100 °C [60, 61]. The decelerating effect increased with increased antimony content. There appeared to be little or no effect of the antimony on the migration of copper in the iron grain boundaries.

3.17. Cu-Fe-Si

Sirca [60, 61] interdiffused iron and Cu-Si(2%) alloys at 1100 °C. His results indicate that copper diffusion was primarily via the lattice with a minimal grain boundary contribution.

Bozhko [48], while studying the mechanism by which molten copper penetrates into steels, observed that grain boundaries enriched with silicon were probably responsible for the lack of penetration of liquid copper into a 4.5% silicon-steel.

3.18. Cu-Fe-Sn

Dilute alloying additions of tin (1.9%) appear to hinder the interdiffusion of copper at 1100 °C in Cu/Fe couples [60, 61]. The autoradiographic results of these experiments indicate that the copper and tin migrate primarily through the grain boundaries.

3.19. Cu-Fe-Zr

The interdiffusion of copper with Zircaloy-2 (a Zr-alloy whose major alloying constituent is 1.38% Sn) over the temperature range 500–600 °C has been studied [93] at annealing times of up to 500 hours. The width of the interdiffusion zone was measured as a function of time. The existence of several intermetallic compounds in the interfacial area was noted. For a more detailed discussion, see the section dealing with Cu-Zr interdiffusion in Part III of this review series [94].

3.20. Cu-Fe-X

The effect of copper alloying additions to ternary alloys of Fe-Si-C and the consequent influence on the carbon mobility was investigated by Krishtal [77]. Effective diffusion coefficients of carbon in austenite were calculated (for the eutectoid compositions) from decarburization data and are tabulated in table 12. The results indicate a very slight acceleration in the carbon diffusion rate.

Hume and coworkers [95, 96] interdiffused copper and several selected stainless steels over the temperature range 600–1050 °C. The stainless steels chosen had nominal compositions of 17Cr-13Ni-2.5Mo, 25Cr-20Ni, and 25Cr-12Ni-3W. The results revealed that, in the solid state, copper interdiffuses very slowly (maximum penetration at 1050 °C after 10,000 hours was only 3 mm; at 700 °C, less than 30 microns in 10,000 hours). Well defined grain boundary penetration of the copper was observed. Copper penetration was found to be dependent upon nickel content and metallographic structure. A noticeable Kirkendall effect was recorded, leading to considerable porosity in the copper adjacent to the interface. Similar interdiffusion experiments were done with copper in the liquid state (1100–1200 °C). Rapid penetration rates by the liquid copper and lack of a defined interface made the recording of any quantitative data impossible.

Interdiffusion between copper and steel that had been bonded by explosive welding was investigated by Trueb [97]. He found the interdiffusion rate to vary cyclically along the weld interface, probably because of the unique concentration and distribution of lattice defects that characterize explosively-bonded interfaces.

Interdiffusion processes occurring in Cu-Ni plated carbon-steels and Cu-Ni-Cr plated carbon-steels (during anneals at 200 to 600 °C for 50 to 600 hours) were followed by Csokan and coworkers [98] with an electron microprobe and metallographic analysis.

Iron-silicon diffusion coatings on copper were found to be multiphase and somewhat protective of the substrate in some acids [99].

Sirca [60, 61], in addition to his interdiffusion studies with liquid copper and iron, also interdiffused molten copper with a number of austenite and ferritic steels. Interdiffusion was allowed to take place between 1000 and 1100 °C. Grain boundary diffusion of the copper was found to predominate in the austenite steels (18–8 stainless, manganese steels, nonmagnetic steels, and Ni-Cr steels). Preferential diffusion of the copper down grain boundaries was absent in the ferritic steels (Cr-steels, Si-steels, and V-steels) employed in the investigation.

The radiation enhancement of diffusion in Ni-Fe-Cu-Mo alloys has been reported by Ferro and Soardo [82]. Evidence on the contribution to the radiation-enhanced diffusion from mechanisms other than the excess-vacancy one was obtained from experiments on directional ordering in the alloys. The authors suggest that some sort of interstitialcy mechanism gives rise to reordering during irradiation and that the excess vacancy concentration introduced by the irradiation contributes to diffusion only if the ordering takes place after irradiation.

3.21. Grain Boundary Diffusion

A quantitative measurement of the rate of radioactive iron diffusing in the grain boundaries of pure copper has been reported by Barreau et al. [8]. In their experiments, radioactive ^{59}Fe was electrolytically deposited onto polycrystalline (mean grain size $\geqq 250$ μm) copper (O.H.F.C. grade) specimens and diffused at temperatures from 460–1070 °C. Below 700 °C, significent grain boundary contributions to the total diffusion process were revealed in autoradiographs of the specimens. Using Fisher's analysis [100], they found that the following Arrhenius expression approximately characterized the grain boundary diffusion rate of ^{59}Fe in copper:

$$\delta \cdot D_{gb} = 6.04 \times 10^{-3} \exp\left[-(50.5 \pm 10.0)\ \text{kcal} \cdot \text{mol}^{-1}/RT\right]\ \text{cm}^3/\text{s},$$

where δ is the grain boundary width.

The grain boundary diffusion of copper in alpha-iron has been measured. Experiments in the α-phase have been reported by Bergh [101, 102], and Golikov and Lazarev [16–18]. The results of these two independent studies are in disagreement. Bergh [101, 102] used a novel experimental technique based upon chemical interdiffusion and special chemical separation procedures [103] in his investigation. In the experiment, a small piece of pure α-iron was covered with a copper layer and then interdiffused at the desired temperature. By measuring the grain boundary length per unit area of iron surface, establishing the copper concentration gradient in the mouths of grain boundaries, and determining the amount of copper introduced by diffusion (both through the lattice and grain boundaries), a grain boundary diffusion coefficient can be derived.

TABLE 13. Copper grain boundary diffusion coefficients in α-Fe. Data taken from Bergh [102].

T (°C)	D_{gb} (cm^2/s)
772	2.5×10^{-8}
692	1.2×10^{-8}
677	9.0×10^{-9}

The results are tabulated in table 13 and shown in figure 11. When a straight line is fitted to the three data points, an activation energy and pre-exponential factor are found, giving the following Arrhenius expression:

$$D_{gb}^{Cu \to Fe} = 80 \exp(-43.4\ \text{kcal} \cdot \text{mol}^{-1}/RT)\ \text{cm}^2/\text{s}.$$

The error in the grain boundary diffusion coefficient, ±12% (due principally to the x-ray fluorescence and microprobe analysis errors), yields an error of ±7.0 kcal/mol in the activation energy and ±10 cm^2/s in the pre-exponential factor.

Lazarev and Golikov [16–18], in measuring the rate of copper diffusion in the grain boundaries of alpha-iron, used an extension of Gruzin's method of measuring the residual activity to determine grain boundary diffusion coefficients [104, 105].

Radioactive ^{64}Cu was electrodeposited onto the surface of the iron specimens and diffusion annealing was done in the temperature range 707–870 °C. The temperature dependence of the calculated coefficients is displayed in figure 12. Also determined in these experiments was the effect of dilute alloying additions of copper (0.2 and 1.22 wt%), boron (0.003 wt%), and molybdenum (1.0 wt%). As can be seen in the Arrhenius

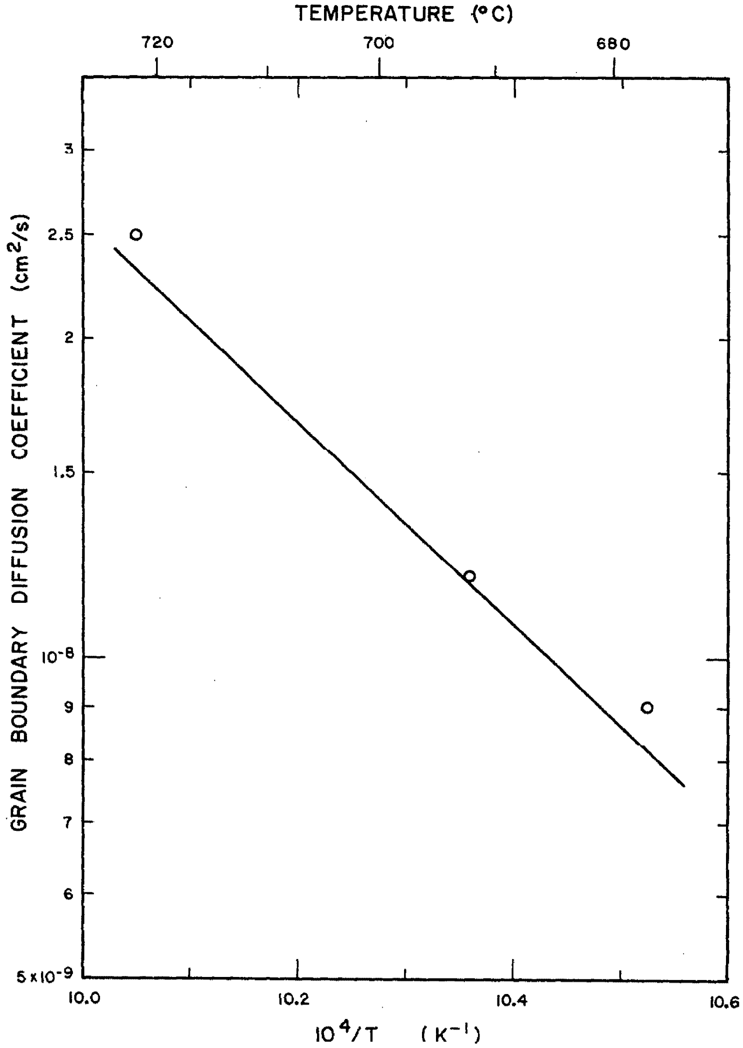

FIGURE 11. The grain boundary diffusion coefficient of copper in α-iron as a function of the reciprocal absolute temperature.

The temperature dependence can be described by the Arrhenius expression: $D_{gb}=80 \exp(-43.4 \text{ kcal} \cdot \text{mol}^{-1}/RT)$ cm^2/s. Data from Bergh [102].

plots, the values of the multiplicative factor, $\delta \cdot D_{gb}$, which characterizes the mobility of copper in the grain boundaries, is less for the alloys than pure iron—the differences increasing at lower temperatures. The Arrhenius expressions found suitable to describe the grain boundary diffusion process were:

for pure iron:

$$\delta \cdot D_{gb}= 2.2 \times 10^{-8} \exp(-28.0 \text{ kcal} \cdot \text{mol}^{-1}/RT) \text{ cm}^3/\text{s},$$

and for the Fe-Cu (0.2 wt%) alloy:

$$\delta \cdot D_{gb}= 6.5 \times 10^{-6} \exp(-38.0 \text{ kcal} \cdot \text{mol}^{-1}/RT) \text{ cm}^3/\text{s}.$$

The authors, from their error analysis, claim that the greatest deviation from the mean of three experiments is 30% for the multiplicative factor, $\delta \cdot D_{gb}$.

Lazarev and Golikov [19] also measured the rate of copper diffusion in the grain boundaries of gamma-iron. The experimental technique in these measurements was that of serial sectioning (although the data and calculations were handled in the same manner as the above investigations with alpha-iron). The results, shown in figure 12, revealed a temperature dependence in the gamma-iron which is best described by the following equation:

$$\delta \cdot D_{gb}=1.6 \times 10^{-6} \exp(-42.5 \text{ kcal} \cdot \text{mol}^{-1}/RT) \text{ cm}^3/\text{s}.$$

As in the alpha-phase, the addition of small quantities of

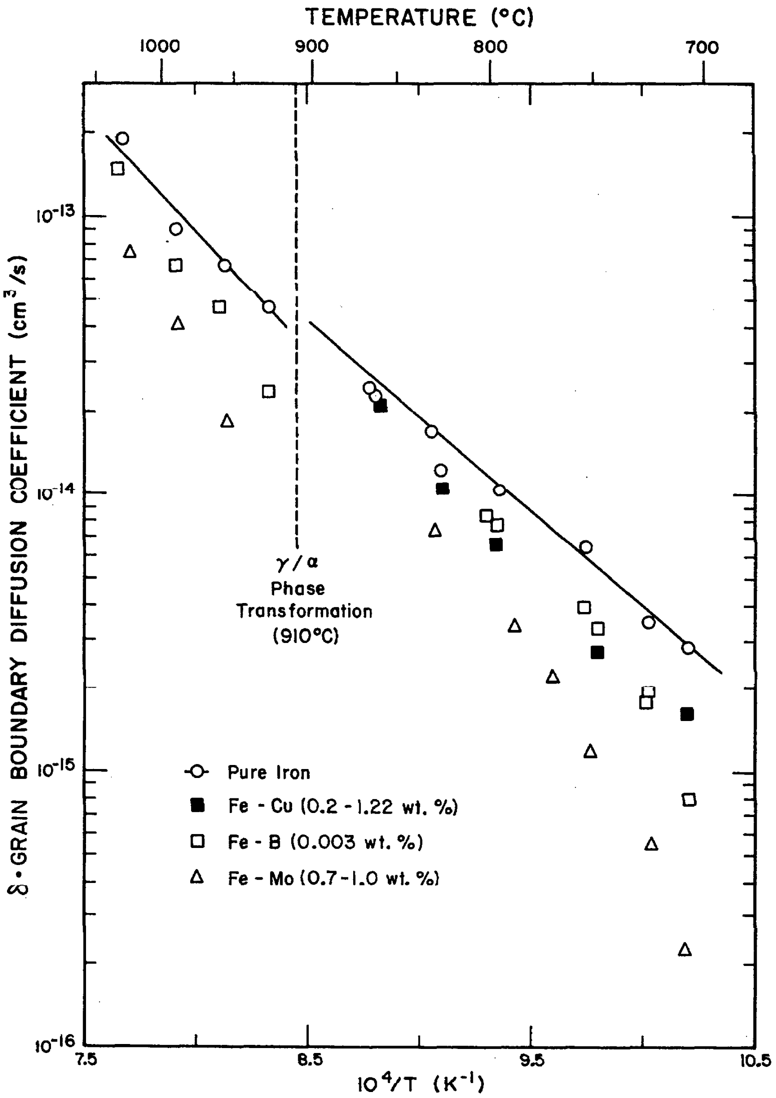

FIGURE 12. Temperature dependence of the factor, $\delta \cdot D_{gb}$ (where δ is the grain boundary half-width, and D_{gb} is the grain boundary diffusion coefficient) of copper in iron and some dilute Fe-alloys as measured by Lazarev and Golikov [16–19].

boron (0.003 wt%) or molybdenum (0.7 wt%) decreases the mobility of copper in the grain boundaries of gamma-iron (see fig. 12).

One wonders at the sensitivity of the experimental technique employed by Lazarev and Golikov [16–19] since the volume diffusion coefficients they obtained for ^{64}Cu diffusing in pure iron failed to reveal an anomaly when passing through the Curie temperature.

There have been a number of other studies dealing with the penetration and microsegregation of copper in iron grain boundaries. Sakharova [106], in her investigation on the diffusion of copper into commercial iron at 1300 °C, noted that copper moved between the grains.

Melford [47] observed the grain boundary diffusion of copper in commercial mild steels, as did Rolls and Badelek [49]. The grain boundary diffusion of molten copper in iron and steels has been studied. Sirca and coworkers [51, 52, 60–62] were interested in the effects of a number of alloying additions on penetration rates. Bozhko [48] found that the activation energy for the grain boundary diffusion of molten copper into iron and steel was dependent on the composition of the material. This composition dependence has been noted by other authors [107–109]. The occurrence of copper grain boundary diffusion during the welding and brazing of copper and its alloys to iron and steels has also attracted much attention [108, 110–112].

Hough and Rolls, in a series of papers [107–109], have reported on liquid copper diffusion in iron during high temperature creep studies, finding that grain boundary penetration of the copper to be a significant factor in the embrittlement of the iron.

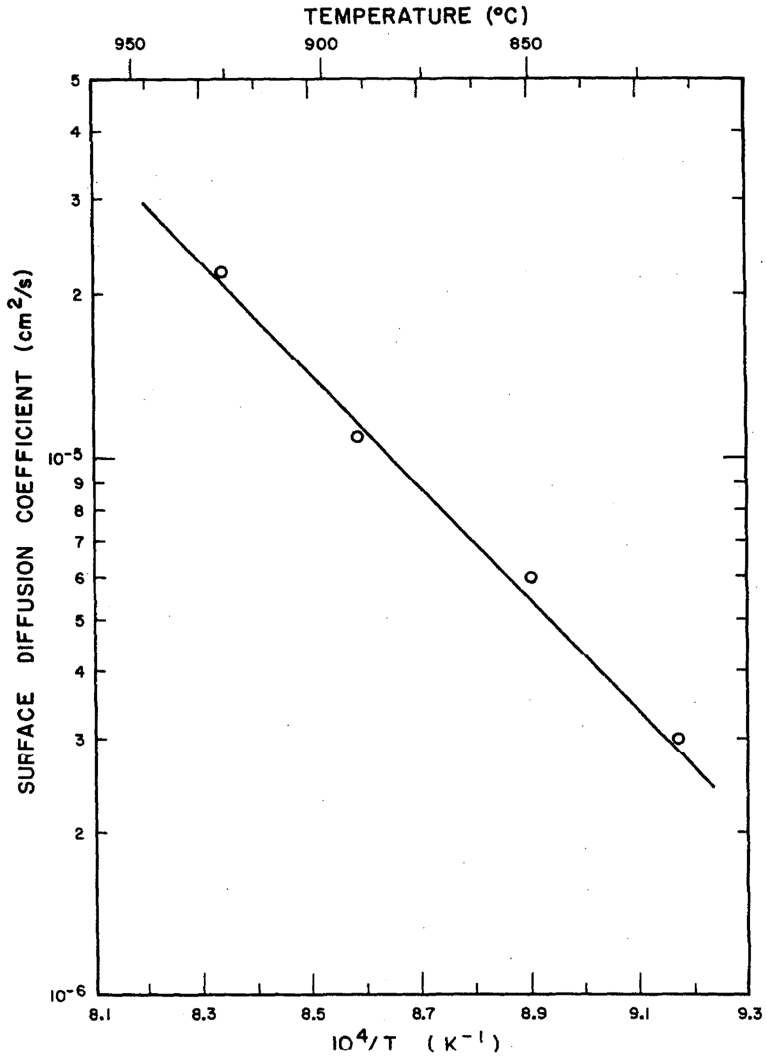

FIGURE 13. The surface diffusion coefficient of iron on copper as a function of reciprocal absolute temperature.

Data taken from Bergh [113].

Pokhmurski and coworkers [64–68], who employed copper as a protective coating on iron and steels during fatigue and corrosion-fatigue studies, observed the grain boundary penetration of copper into the substrate materials.

3.22. Surface Diffusion

A series of papers by Bergh [101, 103, 113, 114] report the results of his surface diffusion studies of copper on alpha and gamma-iron, and of iron on copper. In his experiments, Bergh relied on an unconventional but simple technique, where a very flat regular-shaped ribbon (of known weight) of the diffusing metal was placed on a comparatively large, polished flat specimen of the host metal. Beneath the ribbon, the diffusant will enter the host metal via volume diffusion whereas on the surface, surface diffusion occurs, starting from the ribbon circumference (which is also a phase boundary). The amount of diffusant taking part in the surface diffusion process is determined from the ribbon weight after the diffusion anneal with the appropriate deductions for losses due to volume diffusion and evaporation. The chemical concentration gradient is used as an approximation of the driving force. In table 14 are listed the calculated values of the surface diffusion coefficients for iron on copper. When these values are plotted as a function of reciprocal absolute temperature (see fig. 13), a straight line can be fitted to the few data points obtained and an Arrhenius expression derived to characterize the iron surface diffusion process. The resulting expression (with the author's own estimate of errors) is:

$$D_s = (1.1 \pm 0.1) \times 10^4 \exp[-(47.8 \pm 3.0)\ \text{kcal} \cdot \text{mol}^{-1}/RT]\ \text{cm}^2/\text{s}.$$

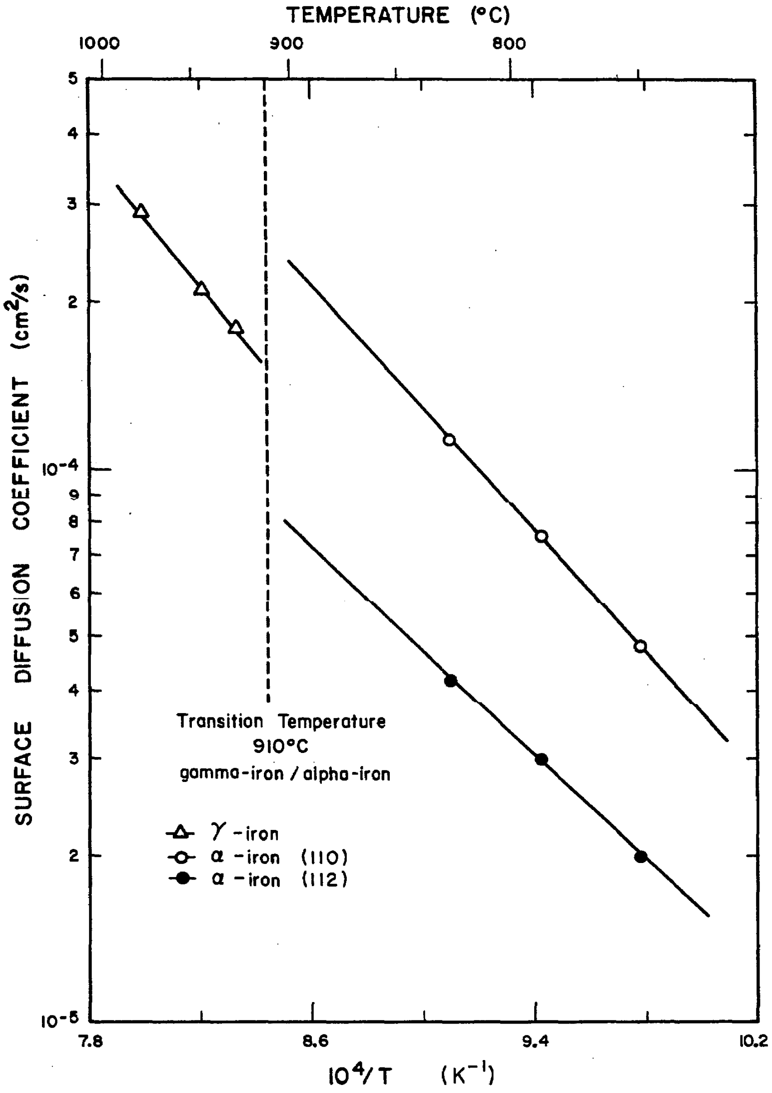

FIGURE 14. The surface diffusion coefficient of copper on alpha and gamma-iron as a function of reciprocal absolute temperature.

The anisotropy of copper diffusion on the (110) and (112) surfaces of ferrite is evident. The lines drawn through the data points in alpha-iron are the result of our least-square analysis of the author's data points. For (110) the Arrhenius equation is $D = 13.1 \exp(-25.4 \text{ kcal} \cdot \text{mol}^{-1}/RT)$ cm²/s, and for the (112), $D = 9.3 \exp(-21.8 \text{ kcal} \cdot \text{mol}^{-1}/RT)$ cm²/s. Data taken from Bergh [113].

Similarly calculated for the surface diffusion of copper on gamma-iron are the values tabulated in table 15. The Arrhenius expression (see fig. 14) used to describe the copper surface diffusion coefficient is:

$$D_S = (21.4 \pm 2.1) \exp[-(27.9 \pm 1.8) \text{ kcal} \cdot \text{mol}^{-1}/RT] \text{ cm}^2/\text{s}.$$

The surface diffusion of copper on ferrite exhibited a fair amount of anisotropy—diffusion on {112}-planes requiring a lower activation energy (see table 16). The resulting coefficients, when plotted as a function of reciprocal absolute temperature (fig. 14), can be fitted to a straight line, and separate pre-exponential factors and activation energies determined for diffusion on the two crystal planes. For copper on {011}-oriented ferrite grains,

$$D_s = (10.5 \pm 1.0) \exp[-(25.5 \pm 1.6) \text{ kcal} \cdot \text{mol}^{-1}/RT] \text{ cm}^2/\text{s}$$

will suffice, whereas diffusion on the {112}-oriented grains, the following expression is adequate:

$$D_s = (1.3 \pm 0.1) \exp[-(21.5 \pm 1.4) \text{ kcal} \cdot \text{mol}^{-1}/RT] \text{ cm/s}.$$

Surprisingly, the α/γ transformation did not appear

TABLE 14. Iron surface diffusion coefficients on copper. Data taken from Bergh [113].

T (°C)	D_s (cm^2/s)
926	2.2×10^{-5}
891	1.1×10^{-5}
850	6.0×10^{-6}
817	3.0×10^{-6}

TABLE 15. Copper surface diffusion coefficients on γ-Fe. Data taken from Bergh [113].

T (°C)	D_s (cm^2/s)
978	2.9×10^{-4}
945	2.1×10^{-4}
928	1.8×10^{-4}

TABLE 16. Copper surface diffusion coefficients on α-Fe. Data taken from Bergh [113].

T (°C)	D_s (cm^2/s) {011}	D_s (cm^2/s) {112}
826	1.14×10^{-4}	4.2×10^{-5}
788	7.6×10^{-5}	3.0×10^{-5}
750	4.8×10^{-5}	2.0×10^{-5}

to exert much influence on the surface diffusion processes.

The results which Bergh published in [103] are less accurate than those he subsequently published in [113] for copper diffusing on the surface of alpha-iron.

Bergh has also observed the Ostwald ripening of particles, precipated on the surface of an Fe-Cu (3 at.%) alloy [111]. From his measurements, he concludes that the process is surface-diffusion controlled, the coarsening rate being dependent on the orientation of individual grains. He describes a method for measuring surface diffusion coefficients (when the lattice diffusion and evaporation losses are minimal).

3.23. Electromigration

The electromigration of radioactive ^{59}Fe impurities in copper has been reported in a number of papers [112, 115, 117]. In all of the investigations, the iron isotope migrated towards the anode.

3.24. Molten Metals

The diffusion of iron in liquid copper has been measured over the temperature range 1100–1300 °C with a modified reservoir technique [118]. The data (within the limits of experimental error) can be fitted to the following Arrhenius equation:

$$D = (3.5_9 \pm 0.5_1) \times 10^{-3} \exp\left[-(12.34 \pm 0.38)\ \text{kcal} \cdot \text{mol}^{-1}/RT\right]\ \text{cm}^2/\text{s}.$$

Diffusion coefficients obtained from dissolution rate experiments [119] are approximately a factor of two greater than the previously-mentioned investigation [118]. Recent studies [120–122] do show that the dissolution rate is dependent on the activity of iron in the bulk liquid and that the presence of oxygen will markedly increase the dissolution rate. Additional experiments [123, 124] reveal the rate of dissolution of solid iron in molten copper increasing with increasing temperature and rotational speed.

The reader is referred to the earlier sections 3.5, 3.17, 3.20, and 3.21 for more data dealing with diffusion in liquid/solid systems.

3.25. Cu-Fe References

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4. Copper-Nickel

4.1. $Ni^* \rightarrow Cu$

A number of investigators have diffused radioactive

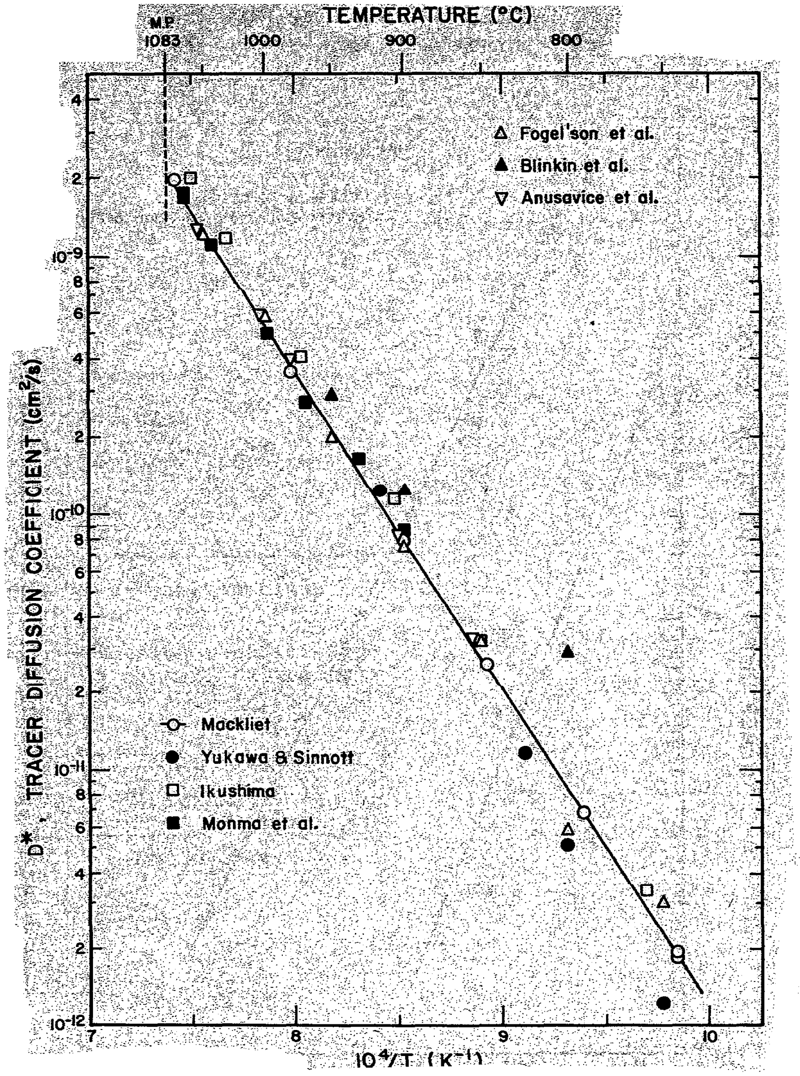

FIGURE 15. The tracer diffusion coefficients of nickel in copper plotted as a function of reciprocal absolute temperature for temperatures > 725 °C.

nickel into copper over a wide range of temperatures [1–16]. The results of the more fruitful of these investigations are plotted in figures 15 and 16 as a function of reciprocal absolute temperature. Mackliet's [3] carefully performed experiments have been used (and rightly so) as a "bench mark" by succeeding investigators (although not always with success). His calculated nickel tracer diffusion coefficients are listed in table 17 and plotted in figure 15. A least-squares calculation of the activation energy and pre-exponential factor yielded the following Arrhenius equation:

$$D^*_{\mathrm{Ni}\to\mathrm{Cu}} = (2.7 \pm 13\%) \exp\left[-(56.5 \pm 0.5\%)\ \mathrm{kcal \cdot mol^{-1}}/RT\right]\ \mathrm{cm^2/s}.$$

Where disagreement exists between the results of Mackliet and other investigators, the differences can be attributed to a number of factors, such as less accurate experimental techniques, grain boundary contributions in polycrystalline specimens, etc.

4.2. Cu*→ Ni

A tracer diffusion coefficient for copper in nickel has been determined by two different groups of investigators [6, 17, 18]. Their results are plotted in figure 17. Although there is fair agreement in the values for the activation energies and pre-exponential factors, the results of Monma and coworkers [6] appear to be most reliable. In their experiments (carried out in the relatively high temperature range of 1054–1359 °C to avoid grain boundary diffusion contributions), they employed large-grained polycrystalline nickel specimens (nominal purity >99.95 at.%, including >0.03 at.%

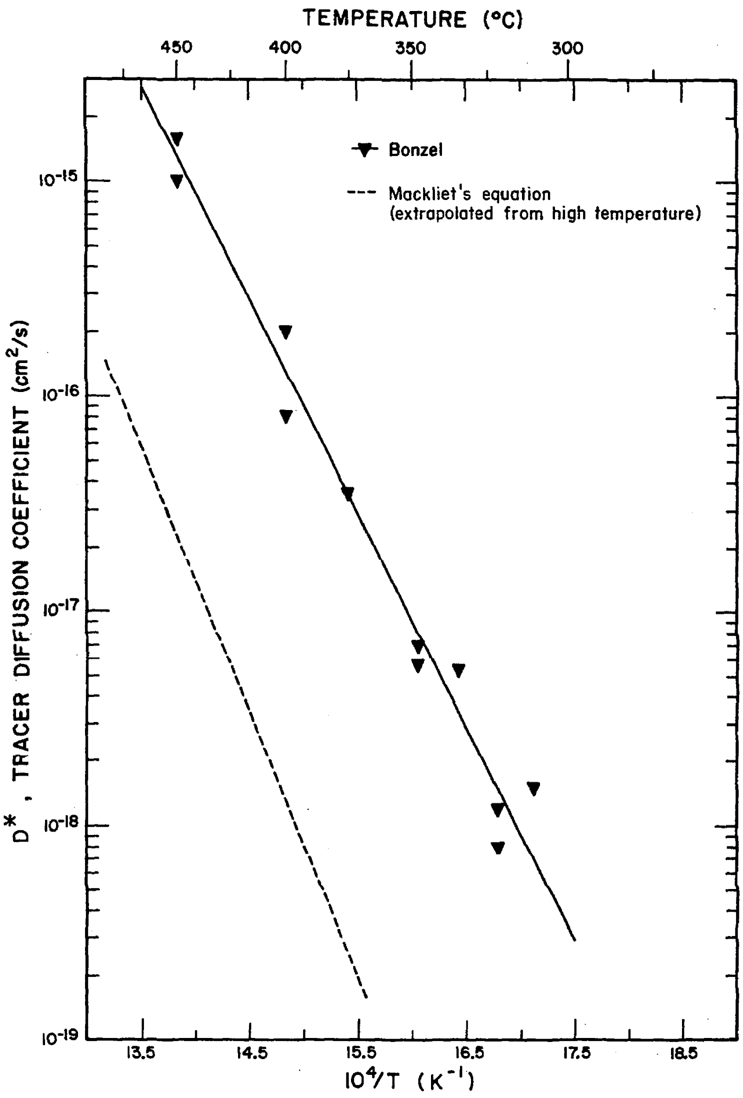

FIGURE 16. The tracer diffusion coefficients of nickel in copper plotted as a function of reciprocal absolute temperature for temperatures < 450 °C.

Mackliet's [3] equation for high temperature is extrapolated for comparison. The data plotted are estimates from Bonzel's work [9] on ^{63}Ni in electropolished fine-grained electrolytic copper (99.995% pure).

cobalt), with diffusion times such that they obtained sufficient ^{64}Cu penetration to allow themselves to do lathe-sectioning over two decades of specific activity.

The calculated copper tracer diffusion coefficients are listed in table 18, and plotted in figure 17 as a function of reciprocal absolute temperature. When a straight line is fitted to this data, the following Arrhenius expression (with the appropriate limits) can be obtained to describe the volume diffusion process:

$$D^*_{Cu \to Ni} = (5.7^{+6.1}_{-2.9}) \times 10^{-1} \exp [-(61.7 \pm 2.2) \text{ kcal} \cdot \text{mol}^{-1}/RT] \text{ cm}^2/\text{s}.$$

Copper self-diffusion measurements made concurrently are in good agreement with the most dependable of those measurements (see section 1.6, reference 1, on self-diffusion in pure copper).

Helfmeier and Feller-Kniepmeier [19–23] performed experiments of the thin-film variety and used an electron-probe microanalyzer to measure the copper concentration profile. Their results are also plotted in figure 17 for comparison. The fact that their measured copper diffusion coefficients are somewhat lower than expected might be attributed to the relatively high copper concentrations occurring close to the nickel surface during the diffusion process. The concentration dependence of

TABLE 17. Tracer diffusion coefficients of ^{63}Ni in copper. After data of Mackliet [3].

T (°C)	D* (cm²/s)
1075.8	1.98×10^{-9}
979.8	3.57×10^{-10}
900.0	7.87×10^{-11}
847.2	2.61×10^{-11}
791.5	6.82×10^{-12}
742.6[a]	1.94×10^{-12}
742.6[a]	1.84×10^{-12}

[a] From opposite faces of same specimen.

TABLE 18. Tracer diffusion coefficients of ^{64}Cu in nickel. After data of Monma et al. [6].

T (°C)	D* (cm²/s)
1359	3.1×10^{-9}
1274	1.32×10^{-9}
1202	3.3×10^{-10}
1149	1.98×10^{-10}
1054	4.1×10^{-11}

the copper diffusion coefficient in this region very likely affected their results.

TABLE 19. Tracer diffusion coefficients of ^{63}Ni in Ni-Cu alloys. After data of Monma et al. [6].

Ni-Cu Alloy (at.% Cu)	T (°C)	D* (cm²/s)
13	1345	2.7×10^{-9}
	1296	1.22×10^{-9}
	1201	3.0×10^{-10}
	1152	1.30×10^{-10}
	1106	4.5×10^{-11}
45.4	1203	1.46×10^{-9}
	1201	1.70×10^{-9}
	1154	7.7×10^{-10}
	1154	7.1×10^{-10}
	1098	2.4×10^{-10}
	1064	1.58×10^{-10}
	1025	6.8×10^{-11}
78.5	1113	9.8×10^{-10}
	1110	9.0×10^{-10}
	1110	8.7×10^{-10}
	1097[a]	7.6×10^{-10}
	1067	5.5×10^{-10}
	1043	4.4×10^{-10}
	1027[a]	2.6×10^{-10}
	1006	2.3×10^{-10}
	968	1.14×10^{-10}
	949	8.7×10^{-11}
	949	8.5×10^{-11}
	930	6.2×10^{-11}
	914[a]	4.4×10^{-11}

[a] Specimens from different ingot.

4.3. Ni* → Ni-Cu

Monma et al. [6] diffused ^{63}Ni into Ni-Cu alloys in addition to the pure metal investigations mentioned in the previous two sections. The alloys (13.0, 45.4 and 78.5 at.% Cu) were large-grained polycrystalline specimens. These specimens were sectioned on a lathe after the tracer was diffused at temperatures ranging from 1050 to 1430 °C and the activity counted to reveal the depth of ^{63}Ni penetration. The calculated tracer diffusion coefficients are listed in table 19 and plotted in figure 18 as a function of reciprocal absolute temperature. The resulting Arrhenius expressions (with probable errors obtained from fitting a straight line to the data) for each of the respective alloys are:

for the Ni-Cu(13 at.% alloy).

$$D^*_{\mathrm{Ni}} = (35^{+17}_{-11}) \exp[-(74.9 \pm 1.7)\ \mathrm{kcal \cdot mol^{-1}}/RT\}\ \mathrm{cm^2/s}:$$

for the Ni-Cu(45.4 at.%) alloy.

$$D^*_{\mathrm{Ni}} = (17^{+11}_{-7}) \exp[-(66.8 \pm 1.5(\ \mathrm{kcal \cdot mol^{-1}}/RT]\ \mathrm{cm^2/s}:$$

and for the Ni-Cu(78.5 at.%) alloy.

$$D^*_{\mathrm{Ni}} = (6.3^{+1.2}_{-1.0}) \times 10^{-2} \exp[-(49.7 \pm 0.5)\ \mathrm{kcal \cdot mol^{-1}}/RT]\ \mathrm{cm^2/s}.$$

Other tracer diffusion measurements (Cu in Ni. and Cu in Cu) made by Monma et al. at the same time as the

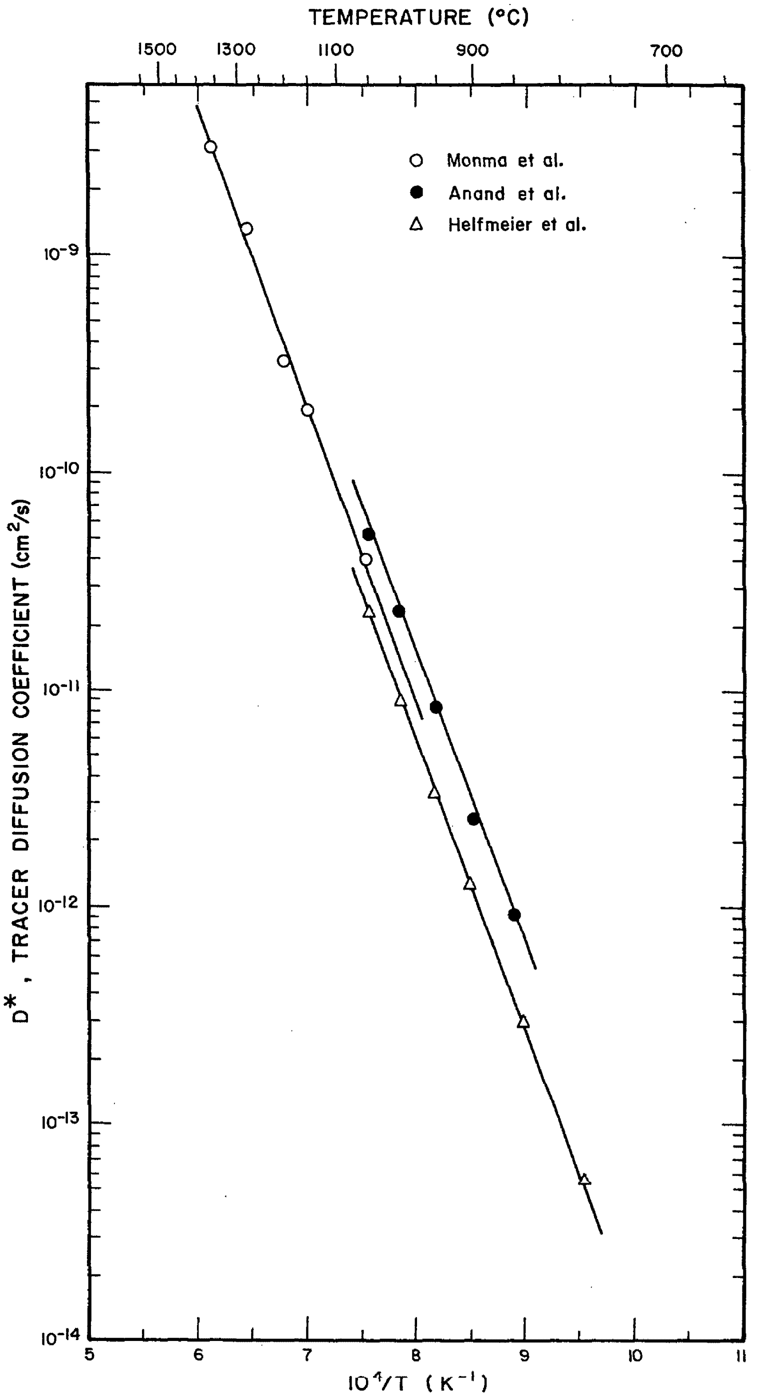

FIGURE 17. The temperature dependence of the tracer diffusion coefficient of ^{64}Cu in pure nickel.

The data of Monma et al. [6] were obtained from lathe sectioning techniques; the data of Anand et al. [17, 18] from residual activity measurements; and the data of Helfmeier et al. [20] were nontracer results using thin films and electron-microprobe measurements.

above alloy measurements are in good agreement with the most reliable measurements of other researchers. This record of experimental consistency may reasonably lead to confidence in these expressions for the alloy tracer diffusion rates.

The activation energy for the diffusion of nickel in

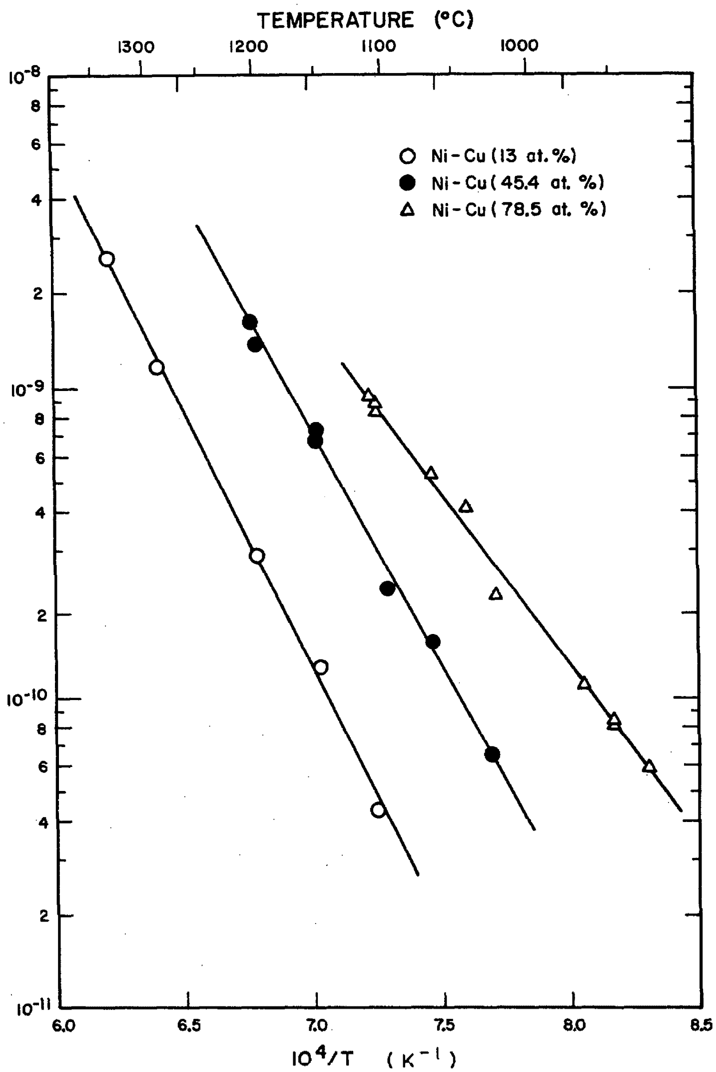

FIGURE 18. The tracer diffusion coefficients of ^{63}Ni into various Ni-Cu alloys plotted as a function of reciprocal absolute temperature.

After the data of Monma et al. [6].

Ni-Cu alloys (containing 0.5 to 10% Cu) was found to be concentration dependent by Bystrov and coworkers [24].

4.4. Cu*→ Ni-Cu

In addition to their nickel tracer studies (discussed in the preceeding section), Monma and coworkers [6] diffused ^{64}Cu tracers into the same Ni-Cu alloys at the same temperatures, and with the same experimental technique. The results, listed in table 20, are plotted in figure 19 as a function of reciprocal absolute temperature. The ^{64}Cu diffusion rates in the three alloys can be represented by the following Arrhenius equations:

for the Ni-Cu (13 at.%) alloy,

$$D^*_{\mathrm{Cu}} = (1.5^{+0.4}_{-0.3}) \exp [-(63.0 \pm 0.07) \text{ kcal} \cdot \text{mol}^{-1}/RT] \text{ cm}^2/\text{s};$$

for the Ni-Cu (45.4 at. %) alloy,

$$D^*_{\mathrm{Cu}} = (2.3 \pm 0.1) \exp [-(60.3 \pm 0.3) \text{ kcal} \cdot \text{mol}^{-1}/RT] \text{ cm}^2/\text{s};$$

for the Ni-Cu (78.5 at.%) alloy,

$$D^*_{\mathrm{Cu}} = (1.9^{+2.0}_{-1.0}) \exp [-(55.3 \pm 1.9) \text{ kcal} \cdot \text{mol}^{-1}/RT] \text{ cm}^2/\text{s}.$$

TABLE 20. Tracer diffusion coefficients of ^{64}Cu in Ni-Cu alloys. After data of Monma et al. [6].

Ni-Cu Alloy (at.% Cu)	T (°C)	D* (cm^2/s)
13	1359	5.8×10^{-9}
	1274	1.93×10^{-9}
	1202	6.4×10^{-10}
	1149	3.0×10^{-10}
	1054	6.8×10^{-11}
45.4	1210	3.0×10^{-9}
	1201	2.7×10^{-9}
	1179	1.86×10^{-9}
	1120	7.6×10^{-10}
	1041	2.1×10^{-10}
	985	7.6×10^{-11}
78.5	1112	3.0×10^{-9}
	1057	2.1×10^{-9}
	1028	9.9×10^{-10}
	985	3.8×10^{-10}
	936	2.3×10^{-10}
	880	5.6×10^{-11}
	863	4.5×10^{-11}

The errors shown are all probable errors. The same comments made previously with regard to diffusion of nickel tracers in these alloys applies here also.

Smirnov and coworkers [25] found that small alloying additions of nickel (1 at.%) to pure copper had little or no effect on the rate of self-diffusion of the ^{64}Cu tracer in the temperature range 760 to 890 °C.

4.5. Cu-Ni Interdiffusion

The copper-nickel binary has been often selected for interdiffusion and Kirkendall-effect measurements. The most recent investigations [12, 26–35], which make use of the electron microprobe as an analytical tool, have yielded the most reliable data.

At 1000 °C, Grundhoff [27], Grundhoff and Heumann [26, 32], and Levasseuer and Philibert [29] obtained interdiffusion coefficients and partial diffusion coefficients over the entire concentration range of this binary system. This concentration dependence is exhibited in figure 20, where the three coefficients are plotted from the most recently published data of Heumann and Grundhoff [32]. The experimental data taken by Heumann and Grundhoff are in very good agreement with the data calculated from Manning's theory [36, 37]. The experimental data of Levasseur and Philibert [29] at this temperature are in agreement with Heumann and Grundhoff. Hehenkamp [30] also performed interdiffusion experiments at 1000 °C but confined his investigation to alloy concentrations of less than 28 wt% copper.

Investigations at temperatures other than 1000 °C were carried out by Brunel and coworkers [12, 31]. Some of these measurements were simply used to obtain diffusion coefficients at infinite dilution with no interdiffusion coefficients being reported [12]. Other measurements were used to calculate (using either the Matano [38] or Hall methods [39]) interdiffusion coefficients as a function of composition at 710, 765, 806, 866, 906, 940, 983, and 1066 °C (see figure 21). Included in these results are some data from the thesis of Masson [28]. Arrhenius plots are made for fixed compositions and these are shown in figure 22. The activation energies obtained for these Arrhenius plots are shown in figure 23 as a function of copper concentration.

Bastow and Kirkwood [40], and Maher [41] obtained similar results in their interdiffusion experiments performed at 890 and 1000 °C. These results are approximately half as large as those obtained by Brunel and coworkers [31]. Bastow and Kirkwood also obtained values of the interdiffusion coefficient close to the solidus in copper-rich alloys (see figure 24 for these results as well as those at lower temperatures). In fact, their values are at temperatures higher than the solidus line shown by Hansen [42]. These studies all utilized electron-microprobe as the means of analysis.

In agreement with these investigations are results obtained by da Silva [43], and da Silva and Mehl [44] at 947 and 1054 °C, and by Thomas and Birchenall [45] at 1022 °C. Both of these groups of investigators sectioned their diffusion couples and chemically analyzed the turnings to determine their concentration-penetration curves. The interdiffusion coefficients calculated from using the Matano analysis are plotted as a function of composition in figure 25. Nyilas and coworkers [46] have since reanalyzed the data of da Silva and Mehl [44].

Mehta and Axon [47] in a single experiment at 950 °C obtained coefficients close to those obtained by da Silva and Mehl (Mehta and Axon also placed thin intermediate layers of gold, tin, zinc, or cadmium at the interface to determine the effect on the concentration-penetration profiles).

The data of Mizuno, Ogawa, and Hirone [48] was re-evaluated by Freise and Sauer [49], bringing it more in line with what one might expect to find at 900 °C.

Tenney and coworkers [50–53] interdiffused copper and nickel at 900 °C and obtained results that are consistent with those found by other researchers.

Pines and coworkers have published papers dealing with interdiffusion in the Cu-Ni system in the temperature range 400 to 1000 °C [54–58]. Krishtal et al. [59] obtained volume diffusion activation energies that are in agreement with those of other researchers [44, 45, 56].

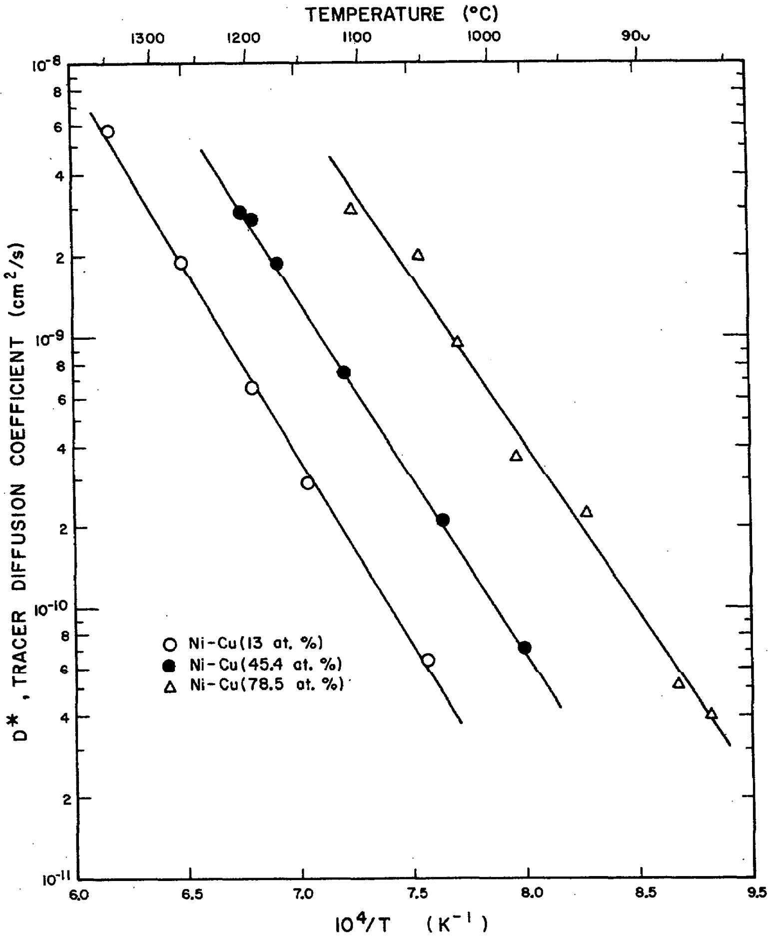

FIGURE 19. The tracer diffusion coefficients of ^{64}Cu into various Ni-Cu alloys plotted as a function of reciprocal absolute temperature.

After the data of Monma et al. [6].

The Pines and Krishtal groups both utilized similar experimental techniques (x-ray diffraction) [54, 60, 61].

Borovskii and Ugaste [62] interdiffused pure copper and nickel at 1000 and 1020 °C and calculated interdiffusion coefficients using Matano's method [38], Hall's method [39], Baroody's method [63], and a "generalized analytic method" that they themselves describe. They conclude that the experimental determination of concentration-penetration curves is the main consideration—the different methods of calculation giving little variation in values of the interdiffusion coefficients.

Austin and Richard [5, 64–67], while studying the grain boundary diffusion of nickel into copper, measured interdiffusion coefficients at 750 °C as a function of composition. Use of the Matano analysis gave values that are consistent with the results described at the beginning of this section.

Interdiffusion coefficients were measured in Cu-Ni alloys using vapor-deposited films between 375 and 500 °C by Paulson [68]. The thin films contained composition modulations between 8 and 60 Å. The interdiffusion coefficients (which varied between 10^{-21} and 10^{-19} cm²/s) were strongly composition dependent, with a minimum occurring between 60 and 70 at.% Ni.

Diffusion couples of pure copper and pure nickel were interdiffused at 1000 °C for 4 hours, and the concentration-penetration profiles were determined with a thermoelectric microprobe as the analytical tool [69]. The instrument yielded reproducible data, which gave results comparable to electron-microprobe analysis.

Reuter and Sichting [70] performed an x-ray flourescence study of the interdiffusion between copper and nickel in the somewhat lower temperature range of 600–800 °C.

Johnson [71], in a relatively early study, interdiffused radioactive nickel isotopes with pure copper and found that the isotopes diffused at rates inversely proportional to the square roots of their masses.

Early studies [38, 72–93] of interdiffusion occurring between copper and nickel, although good experiments in their time, have been superseded by more recent investigations.

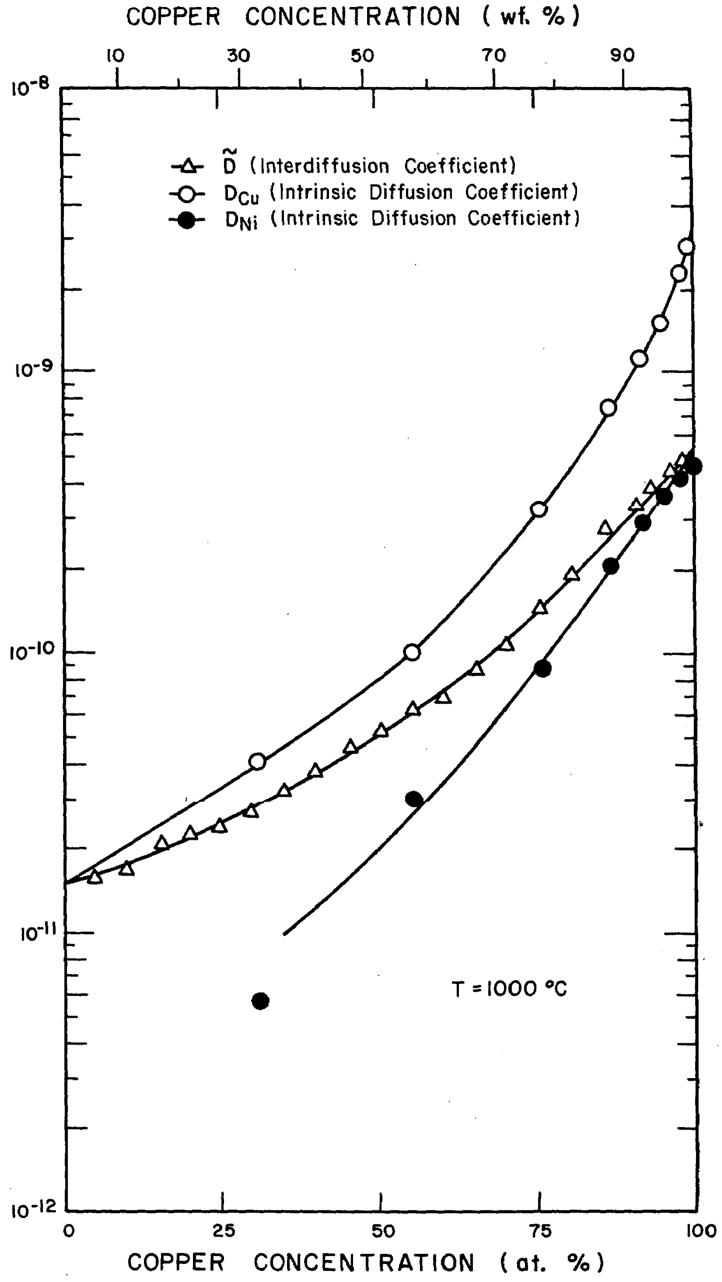

FIGURE 20. The interdiffusion coefficients, $\tilde{D}$, and the copper and nickel intrinsic diffusion coefficients, D_{Cu} and D_{Ni}, in Cu-Ni alloys as a function of copper concentration at 1000 °C.

After the data of Heumann and Grundhoff [32]

The role of discontinuities present in the surfaces of each half of the diffusion couple has been the topic of experiments performed by Walker and Lewis [94, 95], Levasseur and Philibert [96], and Geguzin and coworkers [97].

Bimetal vapor-solid diffusion couples were utilized by Balluffi and Seigle [98, 99] in their experiments, and they were able to calculate the difference in the intrinsic diffusion coefficients from their measurements made at 1060 °C.

The interdiffusion processes occurring during the sintering of copper and nickel have been widely investigated [87–90, 100–138]. The results of such sintering studies, at best, confirm the results obtained from the more conventional interdiffusion experiments performed with massive couples.

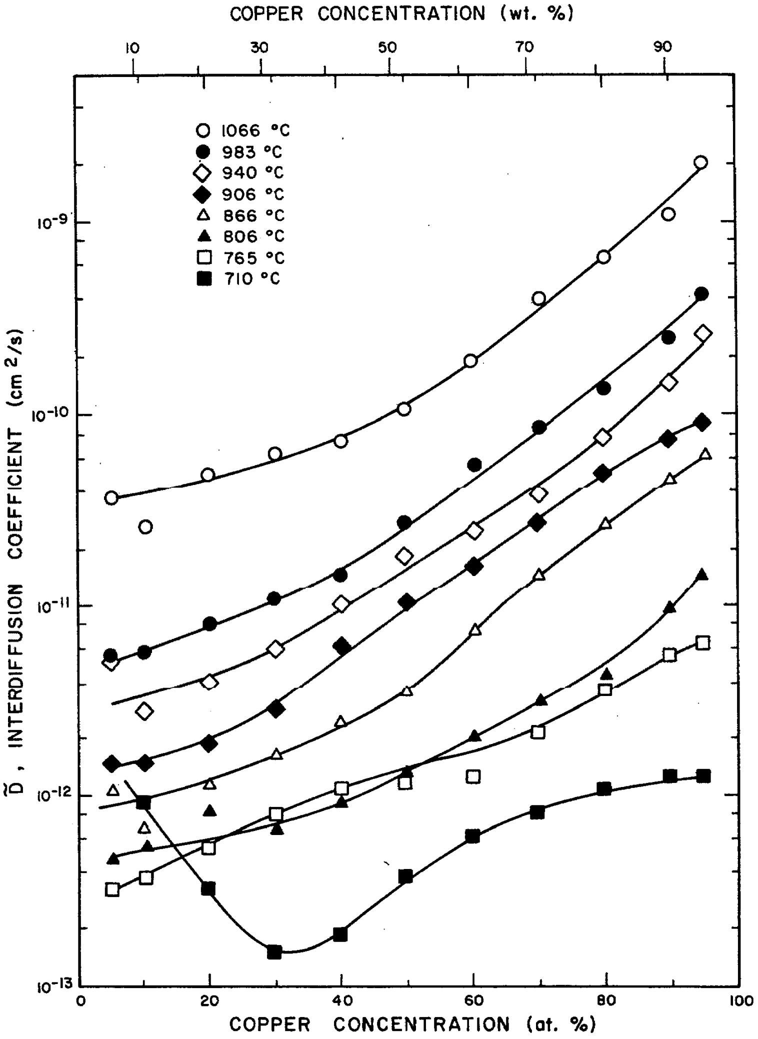

FIGURE 21. The interdiffusion coefficients in Cu-Ni alloys at various temperatures as a function of copper concentration calculated from the Matano method.

After the data of Brunel et al. [31].

Similarly, results have been obtained from experiments with thin films, foils, etc. [14, 17, 18, 132, 139–155] although extraneous effects are often included in what are supposed to be pure lattice diffusion measurements.

Because of the large number of interdiffusion studies utilizing copper and nickel, a fair number of papers have been devoted to the dimensional changes, marker motion and/or Kirkendall effect found in the diffusion couples [91, 99, 112, 119, 134, 153, 156–163]. Where measurements were made, marker motion was in the direction of the copper-rich side of the diffusion couple indicated that copper diffuses faster than nickel.

Porosity in the interdiffusion zone has also attracted the attention of numerous investigators [41, 91, 93, 97–99, 113, 119, 134, 153, 156–173]—the bulk of the research being of a qualitative nature.

Other studies [174–176] have been devoted to the aspect of diffusion coatings, the production of multilayer metal systems [177], bond degradation mechanisms in composites [178], free energy flow during interdiffusion [179], and effect of plastic deformation [180, 181].

4.6. Cu-Ni-As

Helfmeier [19, 23], and Helfmeier and Feller-Kniepmeier [21] studied the influence of small concentrations (2.7 at.%) of arsenic on the diffusion coefficient of copper in nickel at the temperature 843 °C. (The coefficient would be equivalent to the tracer diffusion coefficient since the thin-film solution to the diffusion equation was employed—the penetration plots being obtained with a microprobe.) A significant enhancement (three times as high as in pure nickel) was noted in the single test specimen.

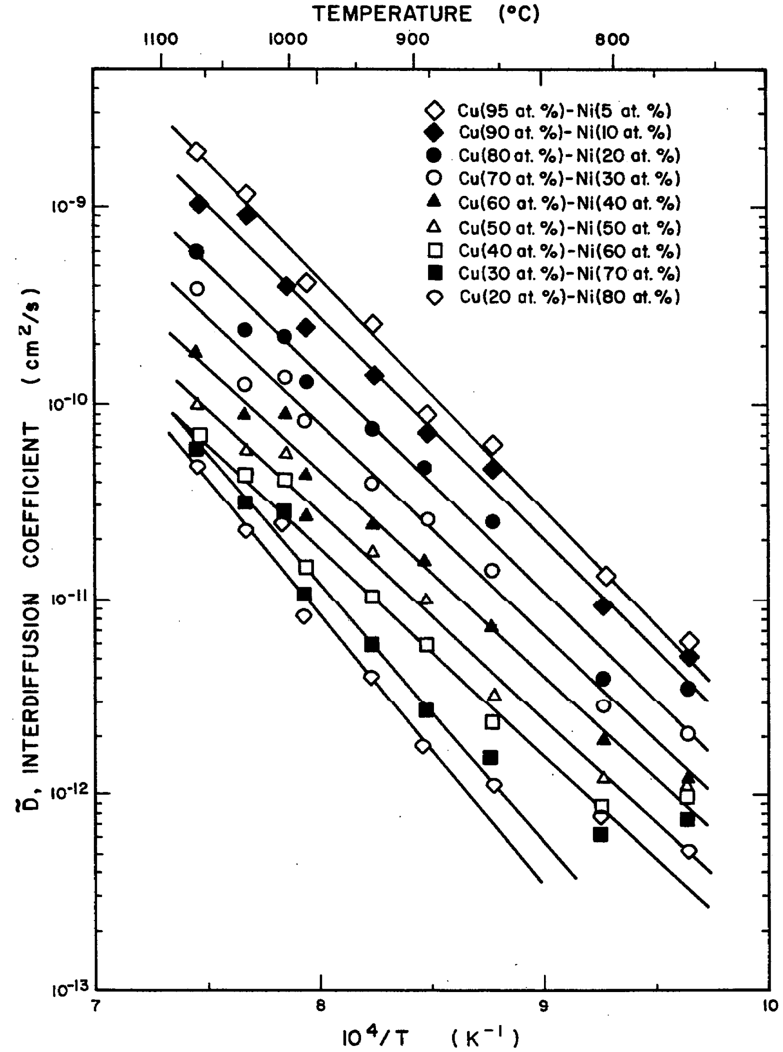

FIGURE 22. The interdiffusion coefficients in various Cu-Ni alloys as a function of reciprocal absolute temperature.

After the data of Brunel et al. [31], and Masson [28].

4.7. Cu-Ni-Au

Helfmeier [19, 23], and Helfmeier and Feller-Kniepmeier [21], studied the influence of small concentrations (0.06 and 0.15 at.%) of gold on the diffusion coefficient of copper in nickel at temperatures ranging from 741 to 1000 °C. Coefficients measured in nickel specimens alloyed with 0.15 at.% gold were the same as those measure in pure nickel at temperatures of 903 and 1000 °C, although at 843 °C there was a positive deviation of 28%. Copper diffusion coefficients obtained from measurements on a nickel alloy containing 0.06 at.% gold at a temperature of 741 °C were 47% greater than those measured in pure nickel specimens.

Mehta and Axon [47] interdiffused pure copper and nickel with a thin foil of gold at the interface. The effect of this gold layer on the interdiffusion processes was minimal, a slight retardation possibly occurring in the composition range 60–80 at.% copper.

4.8. Cu-Ni-C

The reader is referred to section 4.33, Molten Metals, for a discussion of carbon diffusion in liquid Cu-Ni alloys.

4.9. Cu-Ni-Cd

Mehta and Axon [47] interdiffused pure copper and nickel with a thin foil of cadmium at the interface. The effect of this cadmium layer (0.00002 inches) on the interdiffusion process was to accelerate the copper mobility in nickel and retard the nickel mobility in copper.

4.10. Cu-Ni-Cr

The addition of small quantities of chromium (0.8%) to pure copper does not have any measureable effect of the nickel tracer diffusion coefficient [12].

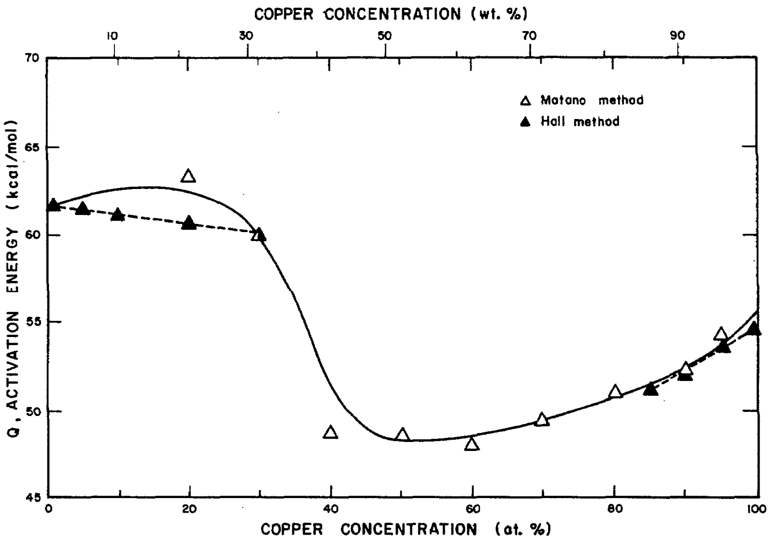

FIGURE 23. The activation energy for interdiffusion in Cu-Ni alloys as a function of copper concentration.

After the data of Brunel et al. [31].

4.11. Cu-Ni-Fe

Diffusion phenomena occurring in this ternary system are reviewed in the section 3.13., Cu-Fe-Ni, dealing with copper-iron alloys.

4.12. Cu-Ni-Ge

There is evidence that copper penetration in germanium is enhanced when the germanium was doped with nickel [182–184].

4.13. Cu-Ni-H

Hydrogen diffusion in bimetallic strips of copper-nickel and the subsequent deflection caused by the diffusion has been of interest to Cermak and Kufudakis [185, 186]. From the measurements of diffusion-induced elastic deformation, diffusivities of hydrogen in nickel and copper are calculated and compared to values obtained from more traditional experimental techniques.

4.14. Cu-Ni-Mn

The rate of diffusion of manganese in Cu-Ni-Mn alloys was measured over a temperature range of 846–1046 °C [187]. The experimental technique [188] employed involved the evaporation of manganese in a vacuum from thin alloy foils and measuring the weight-loss of the foils (the Cu and the Ni were assumed to have a negligible vapor pressure at the annealing temperatures). The evaporation of the manganese from the surface produces a concentration gradient in the alloy, thus requiring additional manganese to be transported to the surface by diffusion. Taking into account the quantity of evaporated (diffused) substances, the authors were able to determine a "diffusion coefficient" of the component (Mn) with the higher vapor pressure. The activation energy for this process was 62.7 kcal/mol. Since the surface composition was maintained at nearly zero manganese concentration, this value is only an average figure over the manganese composition range 0–16 at.%. In addition to the inherent shortcomings in the experimental technique used in the study, the authors make no mention of a prediffusion anneal of their polycrystalline specimens. Recrystallization and grain growth in their cold-rolled foils also may have occurred during the diffusion anneals.

The preliminary results of a more recent study of manganese diffusion have been reported [189]. Alloys of the three binary systems (Cu-Mn, Cu-Ni, Mn-Ni) were diffused at 800 °C for 336 hours. The x-ray intensities obtained from electron microprobe analysis were converted to concentrations by Ziebold and Ogilvie's method [190]. The concentration-penetration curves revealed nonideal thermodynamic behavior and "uphill" diffusion of manganese in which managanese diffuses from a level of 21.5 at.% to a band of 33.9 at.%. An activity plot versus penetration of this same data showed a monotonic decrease, as should be expected.

4.15. Cu-Ni-Mo

The diffusion of radioactive nickel in molybdenum-coated copper specimens has been measured at 700 °C [191]. The rate of diffusion of the ^{63}Ni was accelerated (relative to pure copper) with the increasing percent (by volume) of molybdenum.

4.16. Cu-Ni-O

The oxidation of Cu-Ni alloys and the role diffusion plays in the oxidation mechanism has been attracting attention since 1923 [192–199]. In discussing the experimental results, the influence of diffusion on the oxidation process is often described by Wagner's

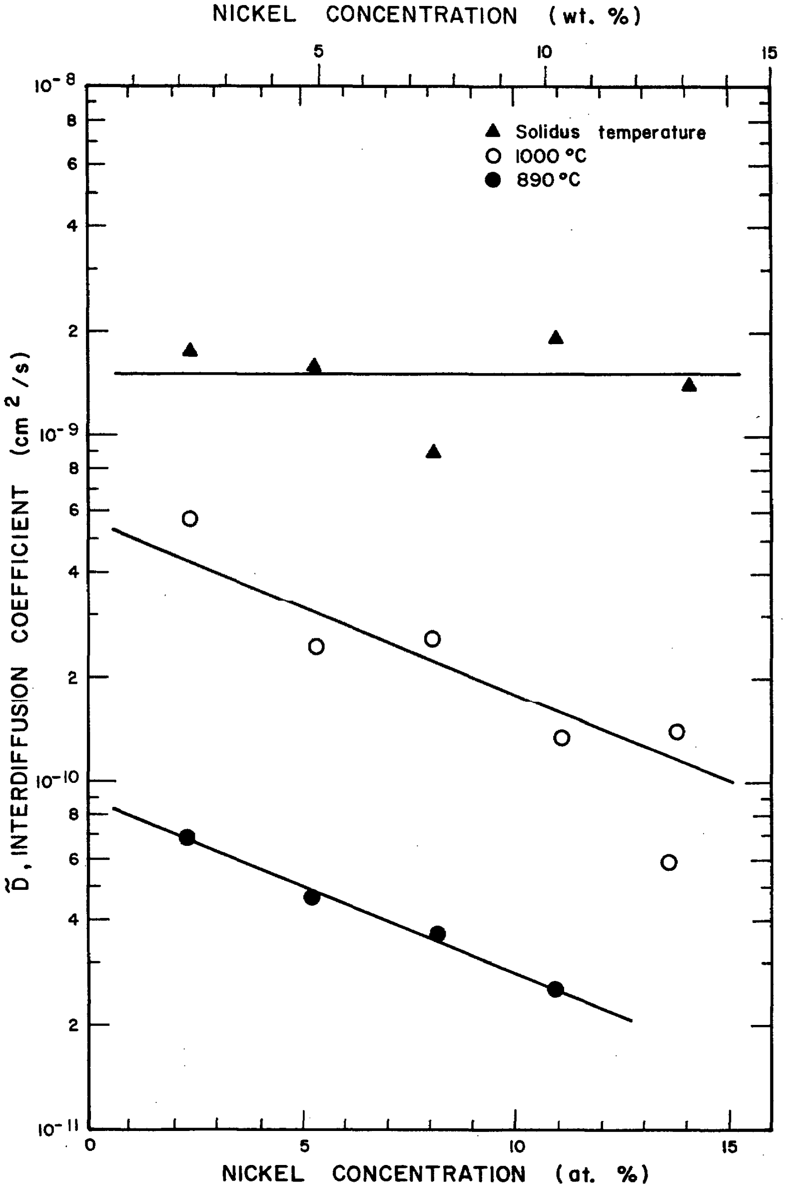

FIGURE 24. The variation of the interdiffusion coefficient with nickel concentration in Cu-rich alloys of the Cu-Ni system.

After the data of Bastow and Kirkwood [40].

nalysis. More recently though, Rapp and coworkers 00] interdiffused nickel with Cu_2O at 1000 °C and xamined the reactions occurring in the diffusion zone. layer of copper and NiO was found after 72 hours of eating. Diffusion, rather than interface control, was etermined to be rate-limiting.

4.17. Cu-Ni-Pd

Helfmeier [19, 23] and Feller-Kniepmeier [21] studied the influence of small concentrations (0.27 at.%) of palladium on the diffusion coefficient of copper in nickel in the temperature range 843–1050 °C. (The coefficient would be equivalent to the tracer diffusion coefficient since the thin-film solution to the diffusion equation was employed; the penetration plots being obtained with a microprobe.) Although no apparent effect was noted on the copper mobility at the upper portion of the temperature range, some enhancement was found at the lower temperatures.

4.18. Cu-Ni-Si

The simultaneous interdiffusion of nickel and silicon in copper was one of the first investigations into the rates of diffusion in ternary systems. In these early investigations, Rhines and Mehl [201, 202] attempted to see whether the two solutes (Ni and Si) in a quasi-binary ternary system (Cu-Ni_2Si) diffused in stoichiometric proportions, despite a radical difference in the separate

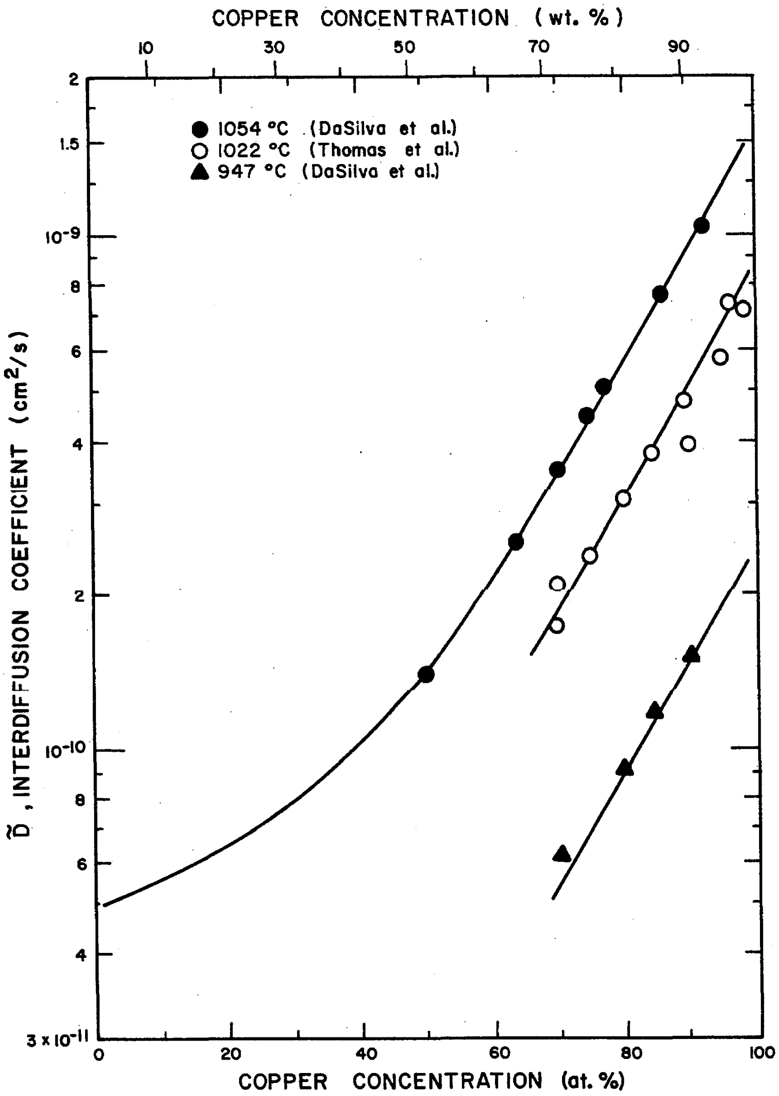

FIGURE 25. The variation of the interdiffusion coefficient with copper concentration in the Cu-Ni system.

After the paper of Vignes and Birchenall [260] of data by Da Silva and Mehl [44], and Thomas and Birchenall [45].

rates of diffusion of each solute (Ni and Si) when diffusing alone in the solvent (copper) lattice.

With the experimental technique, ternary alloy rods (containing approximately 4 wt% Ni_2Si and 8 wt% Ni_2Si) were electroplated with copper (2 mm thickness) and interdiffused for the times and temperatures listed in table 21. Upon completion of interdiffusion, the simultaneous penetration profiles of silicon and nickel were determined by machining successive layers from the specimens in a precision lathe, and then chemically analyzing the turnings. The Matano-analysis [81] was applied to the concentration-penetration data to calculate diffusion coefficients which are plotted in figures 26 and 27. The results of the calculations are also listed in table 22 and are compared with *D* values for nickel [80, 81] and for silicon [203] interdiffusing separately into copper.

It can be seen that the *D* values for nickel are relatively little affected at either of the experimental temperatures by the presence of silicon. The *D* values for silicon, however, are greatly decreased by the presence of the simultaneously diffusing nickel. Also, with increasing dilute solutions, the rate of silicon diffusion becomes increasingly greater than that of nickel (see figure 28). It is interesting to note that the interaction of nickel and silicon (while interdiffusing simultaneously in copper) is such as to approach the ratio of Ni_2Si, with rapidly diffusing silicon retarded by the more slowly diffusing nickel, and the slowly diffusing nickel little, if any, affected by the presence of silicon.

4.19. Cu-Ni-Sn

Mehta and Axon [47] interdiffused pure copper and nickel with a thin foil of tin at the interface. The effect

TABLE 21. Conditions for interdiffusion in the Cu-Si-Ni system studied by Mehl and Rhines [201, 202].

T (°C)	Diffusion Time (s)	Alloy Composition (wt%)		
		Cu	Ni	Si
1000 ± 1	8.38×10^4	91.89	6.54	1.57
850 ± 1	4.45×10^6	95.99	3.20	0.81
850 ± 1	4.64×10^6	96.02	3.18	0.80

TABLE 22. Comparison of interdiffusion coefficients of nickel and silicon in Cu-Ni-Si alloys. Data taken from Mehl and Rhines [201, 202].

T (°C)	Composition (at.%)	D (10^{-10} cm^2/s)			
		Ni (alone)	Ni (with Si)	Si (alone)	Si (with Ni)
1000	1 Si and/or 2 Ni	10	6	71	14
	2 Si and/or 4 Ni	6	6	98	8
	3 Si and/or 6 Ni	5	7	150	8
850	1 Si and/or 2 Ni	2	0.7	13	1
	1.5 Si and/or 3 Ni	1.5	0.7	23	1

of this tin layer (0.00002 inches) on the interdiffusion process was to accelerate the nickel mobility in copper and retard the copper mobility in nickel.

4.20. Cu-Ni-Ti

Helfmeier [19], and Helfmeier and Feller-Kniepmeier [21] studied the influence of titanium impurities (0.18 at.%) on the diffusion coefficient of copper in nickel in the temperature range 843–1050 °C. (The coefficient would be equivalent to the tracer diffusion coefficient since the thin-film solution to the diffusion equation was employed; the penetration plots being obtained with a microprobe.) No apparent effect of the low titanium concentration was noted on the copper mobility over the temperature range investigated.

4.21. Cu-Ni-W

Blinkin and coworkers [11, 191] diffused radioactive ^{63}Ni into copper reinforced with tungsten fibers. In the temperature range investigated, 700–850 °C, the rate of nickel diffusion increased with increased tungsten concentration (volume percent). Near the melting point of copper, the tracer diffusion coefficients were approximately the same, regardless of tungsten fiber content.

4.22. Cu-Ni-Zn

The tracer diffusion of ^{67}Cu, ^{66}Ni, and ^{65}Zn in copper-rich solid solutions of this ternary system have been reported in a series of papers by Anusavice and coworkers [204–207]. In all their experiments, the radioactive tracers were electroplated onto polycrystalline ternary alloys, given a diffusion anneal, and sectioned on a lathe. Activity analysis yielded penetration plots from which the tracer diffusion coefficients were calculated by the method of least-squares.

Arrhenius plots of the three tracer diffusion coefficients in the various compositions (up to 30 at.% nickel and zinc) are shown in figures 29–40. From the slope of these least-squares plots, activation energies for diffusion and pre-exponential factors were determined (along with the probable errors) and these are presented in tables 23, 24 and 25. The activation energies for diffusion of the three tracers vary from 40 to 55 kcal/mol for all compositions studied, being the greatest for the binary high-nickel alloys and decreasing to the lowest

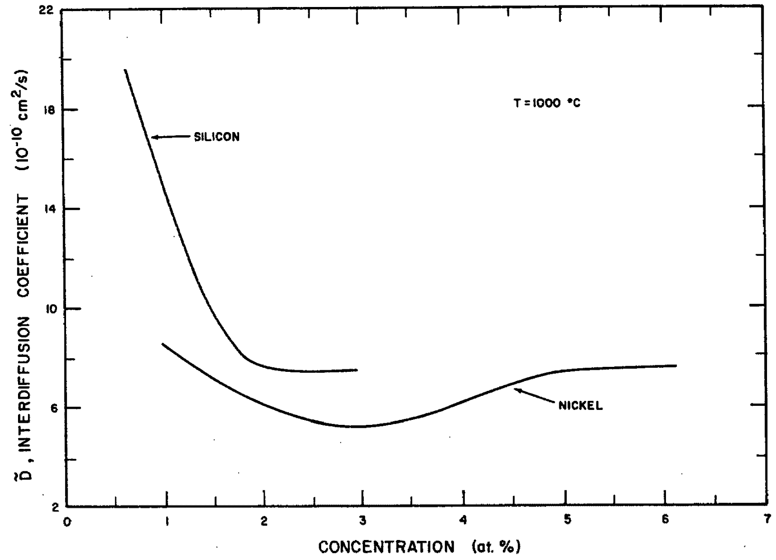

FIGURE 26. The variation of the interdiffusion coefficient with concentration (either Si or Ni) for nickel and silicon diffusing together from a copper solid-solution of Ni_2Si into pure copper at 1000 °C.

After the data of Mehl and Rhines [201].

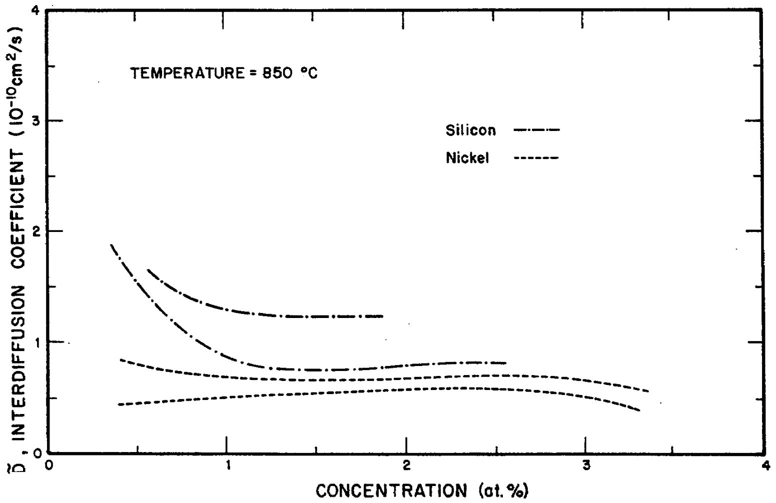

FIGURE 27. The variation of the interdiffusion coefficient with concentration (either Si or Ni) for nickel and silicon diffusing together from a copper solid-solution of Ni_2Si into pure copper at 850 °C.

After the data of Mehl and Rhines [201].

for binary, high-zinc alloys. All three tracer diffusivities decrease as nickel is added, and increase as zinc is added to pure copper.

The diffusivities of the three tracers are consistently of the order:

$$D^*_{Zn} > D^*_{Cu} > D^*_{Ni},$$

and the activation energies are (except for compositions near the Cu-Ni binary) in the order:

$$Q_{Ni} > Q_{Cu} > Q_{Zn}.$$

The composition dependence of the pre-exponential factors tends to parallel that dependence found for the activation energies.

The results for the tracer diffusion of nickel in pure copper obtained by Anusavice and coworkers are compared with those obtained by other researchers in figure 15.

The tracer results reported by Corth [208] on the diffusion of ^{63}Ni in α-brass (Cu-15% Zn) single crystals are inconsistent (activation energies too low) with the experiments of Anusavice et al.

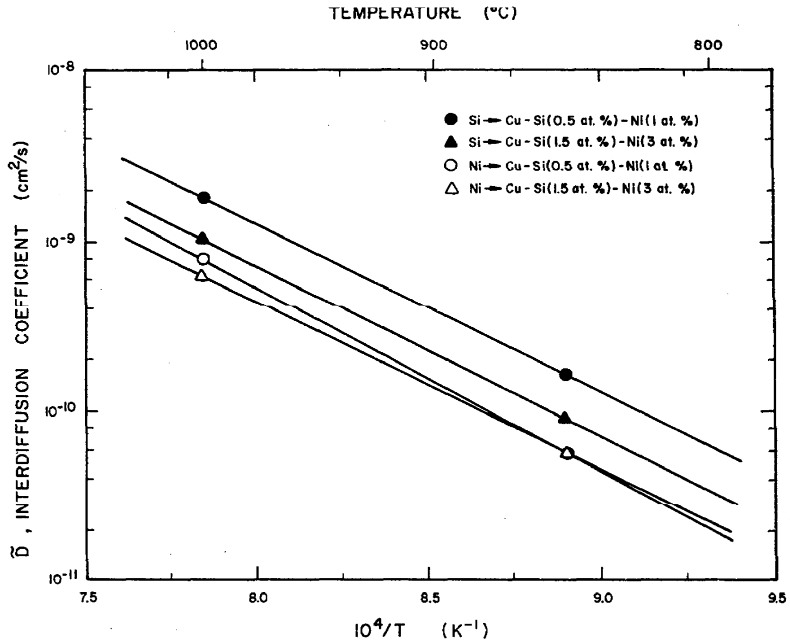

FIGURE 28. The interdiffusion coefficient of silicon and nickel diffusing together for two different Cu-Si-Ni alloys as a function of reciprocal absolute temperature.

After the data of Mehl and Rhines [201].

TABLE 23. Diffusion parameters and conditions for ^{67}Cu tracer diffusion in Cu and Cu-Ni-Zn alloys. Data taken from Anusavice et al. [204].

Composition (at.%)			Temperature (°C)	D_0 (cm^2/s)	Q (kcal/mol)
Cu	Ni	Zn			
99.999	-	-	740-1045	$0.30^{+0.04}_{-0.02}$	48.3 ± 0.2
82.72	12.55	4.73	785-1003	0.36 ± 0.05	49.2 ± 0.3
72.04	11.21	16.75	740-1003	$0.33^{+0.04}_{-0.03}$	46.8 ± 0.2
65.06	10.82	24.12	783-943	$0.21^{+0.04}_{-0.03}$	44.0 ± 0.4
69.68	19.42	10.90	800-1050	$0.18^{+0.05}_{-0.03}$	47.9 ± 0.5
63.95	20.80	15.25	752-1003	0.10 ± 0.01	45.4 ± 0.3
55.17	20.59	24.24	748-949	$0.11^{+0.01}_{-0.02}$	43.9 ± 0.3
60.97	29.49	9.54	904-1050	$0.55^{+0.17}_{-0.13}$	52.2 ± 0.7
47.12	33.08	19.80	866-1065	$0.58^{+0.33}_{-0.21}$	50.8 ± 1.1
40.30	30.70	29.00	807-966	$0.72^{+0.25}_{-0.19}$	50.3 ± 0.7

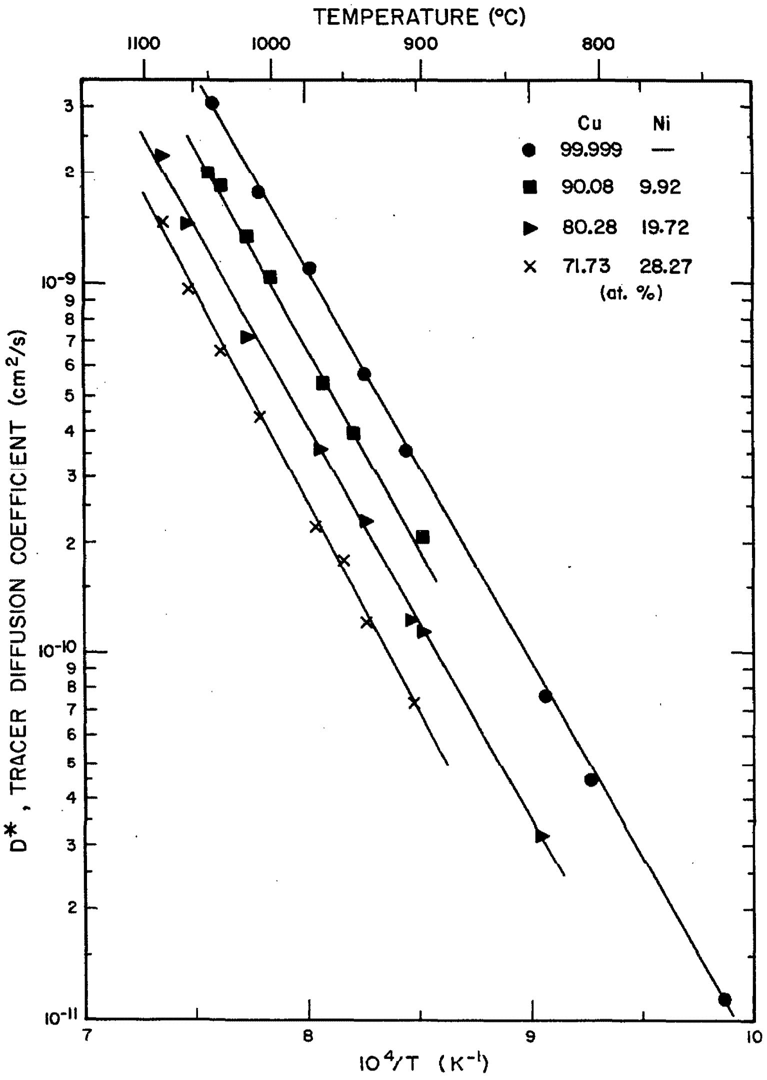

FIGURE 29. The tracer diffusion coefficient of ^{67}Cu in pure copper and several binary Cu-Ni alloys as a function of reciprocal absolute temperature.

Straight lines drawn are the result of a least-squares analysis of the displayed data points. All data taken from Anusavice and DeHoff [204].

The Zener relaxation in alloys in the α-solid solution region of the Cu-Ni-Zn ternary system has been investigated by Coleman and Wert [209].

Multiphase interdiffusion studies in the Cu-Ni-Zn system have been undertaken by several groups of investigators [210–216]. The studies for the most part have utilized procedures which did not allow for the quantitative treatment of the obtained data. Boundary shifts, structures, and morphology of boundary interfaces are usually the data reported in these papers. Coates [215], and Coates and Kirkaldy [216] did report nickel interdiffusion coefficients (at 775 °C) in the α- and β-phases of this ternary system. Solid-solid diffusion couples constructed of ternary alloys were employed to obtain these coefficients (listed in table 26).

Gertsriken and coworkers [217–219] studied the effect of dilute alloying additions on the rate of vacuum evaporation (at constant temperature) of zinc from α-brasses. The initially published results indicated that nickel (up to 2 at.%) alloying additions had no effect on the rate of zinc evaporation from α-brasses (containing approximately 21 at.% Zn) in the temperature range 600–800 °C. Later experiments [219] revealed these results to be in error, with slight enhancement in the vaporization rates being noted.

Mehta and Axon [47] interdiffused pure copper and nickel with a thin foil of zinc at the interface. The effect of this zinc layer on the interdiffussion processes was minimal; a slight retardation possibly occurring in the composition range 60–80 at.% copper.

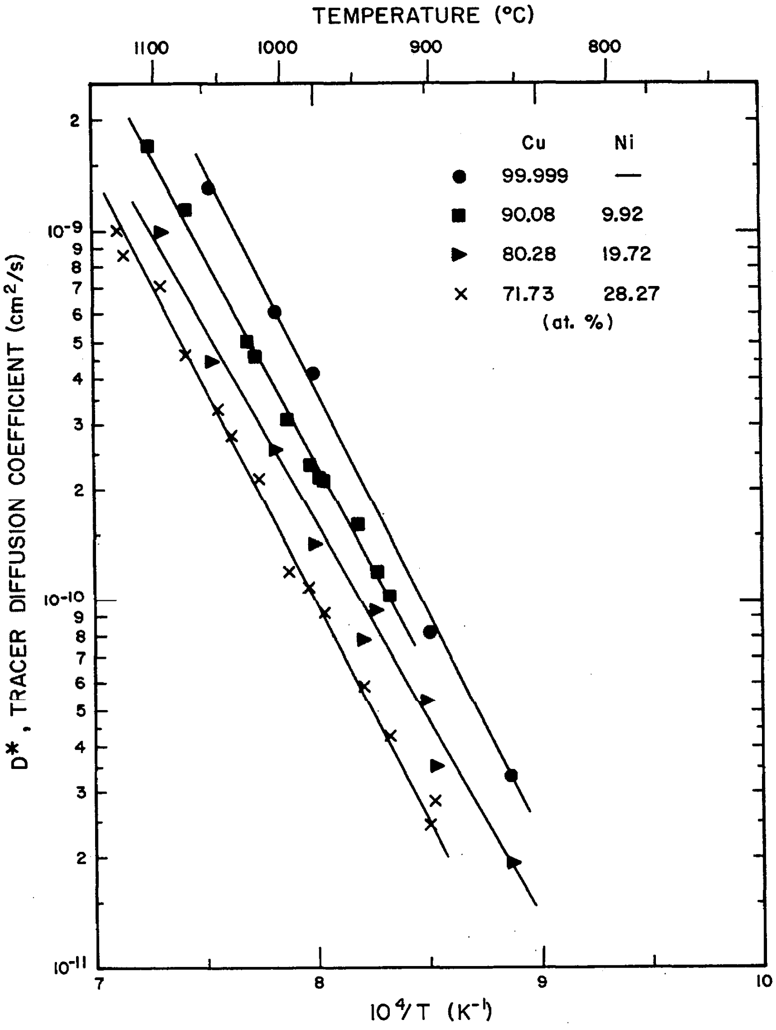

FIGURE 30. The tracer diffusion coefficients of ^{66}Ni in pure copper and binary Cu-Ni alloys as a function of reciprocal absolute temperature.

The straight lines shown are the result of a least-squares analysis. Data taken from Anusavice and DeHoff [204].

4.23. Cu-Ni-X

The research performed by Sirca and coworkers [220, 221] on copper diffusion rates in nickel-bearing steels is reviewed earlier in the Cu-Fe alloys section.

Perrin [222] has interdiffused nickel-bearing steels with copper-tin bronzes, following the diffusion process metallographically.

The interdiffusion processes occurring between electro-deposited layers Cu-Ni-Zn-Pb and Cu-Ni-Zn-Fe at relatively low temperatures (<212 °C) was examined by Creydt and coworkers [223, 224] with an electron-microprobe analyzer.

The joining of several titanium alloys with interlayers of copper, nickel, and cobalt has been studied by Shinyaev and Bondarev [225].

Some increase in the wear and oxidation resistance of copper at high temperatures has been achieved by the diffusion saturation of specimen surfaces with aluminum, nickel, and zirconium [226].

Interdiffusion processes occurring in Cu-Ni and Cu-Ni-Cr-plated carbon-steels (after anneals of 50 to 600 h at temperatures of 200–600 °C) have been examined with the aid of an electron microprobe as well as conventional metallography [227]. The deterioration of mechanical and surface properties of these electroplated metals was in part ascribed to the interdiffusion occurring across the interfaces of these layers.

The diffusion of interstitial elements in several Ni-Cu-Fe base metals was found to be minimized when brazed with a Ni-Mn-Si-Cu filler metal (relative to a number of other filler metals used under similar brazing conditions) [228].

Interdiffusion between slide bearing alloys [Pb-In(10 wt%), Pb-In(13 wt%), Pb-In(20 wt%), Pb-Cu-Sn(12 wt%), Pb-Cu-Sn(16 wt%), Pb-Cu-Sn(20 wt%)] and their backing alloys (Cu-Pb-Sn) was investigated by Semlitsch [229]. Nickel was inserted as a diffusion barrier to

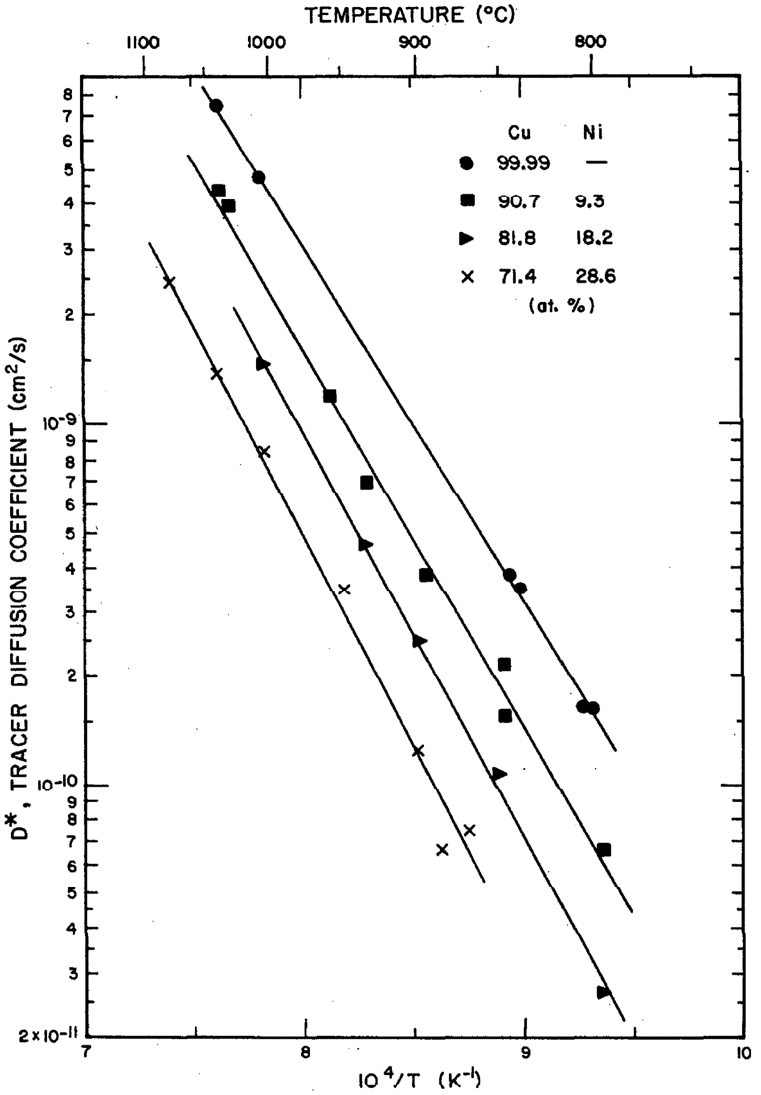

FIGURE 31. The tracer diffusion coefficients of ^{65}Zn in pure copper and binary Cu-Ni alloys as a function of reciprocal absolute temperature.

The straight lines shown are the result of a least-squares analysis. Data taken from Anusavice and DeHoff [204].

prevent the interdiffusion of Sn and In. Experiments were performed at 100, 170, and 220 °C for up to 3000 hours to test the integrity of the nickel barrier. The interdiffusion zone was examined with an electron-beam microprobe analyzer for enrichment in one or more of the elements and formation of one or more intermetallic phases, e.g., Ni_3In, NiIn, $(Ni,Cu)_3Sn$, and/or $(Ni,Cu)_3Sn_4$.

4.24. Dislocation Pipe Diffusion

Bernardini and Cabane [230] diffused radioactive ^{63}Ni into high purity single crystals of copper over the temperature range 465–616 °C. The penetration curves were obtained after counting the residual activity from the sectioned sample. To calculate the pipe-diffusivity, D_{pipe} (defined as equal to the product $D_d^* \cdot A \cdot k$, where D_d^* is the tracer diffusivity in the dislocations, A is the effective cross-sectional area of the dislocation pipe, and k is the ratio of the concentration of the diffusing element along the dislocation, C_d, to its concentration in the lattice, C_v), of ^{63}Ni in single crystals of copper, the mathematical analysis of Pavlov [231] and Brebec [232] (both based on Fisher's arguments [233]) were employed. The results are plotted in figure 41 as a function of reciprocal absolute temperature. The data are fitted with a straight line which can be expressed by the following Arrhenius equation:

$$D_{\text{pipe}} = 6.3 \times 10^{-13} \exp\left(-42 \text{ kcal} \cdot \text{mol}^{-1}/RT\right) \text{ cm}^2/\text{s}.$$

Errors are estimated to be ±40% in the pipe diffusion coefficient and ±3 kcal/mol in the activation energy for diffusion along the dislocations.

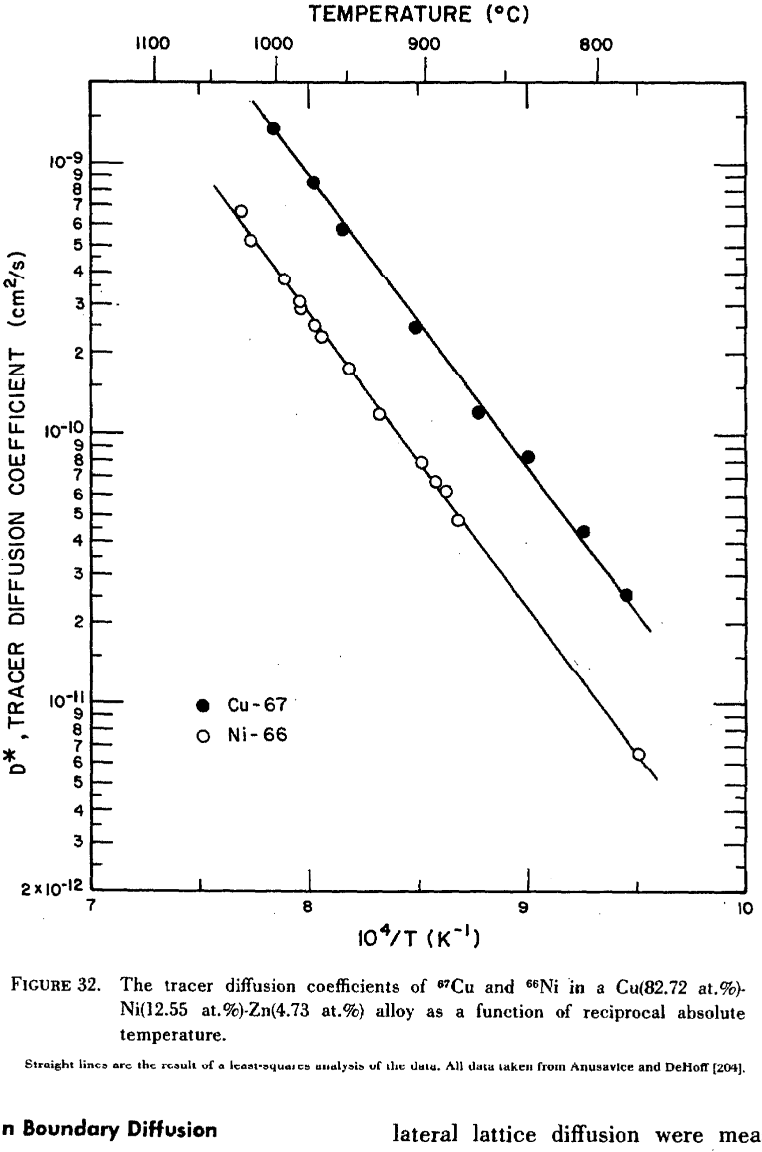

FIGURE 32. The tracer diffusion coefficients of ^{67}Cu and ^{66}Ni in a Cu(82.72 at.%)-Ni(12.55 at.%)-Zn(4.73 at.%) alloy as a function of reciprocal absolute temperature.

Straight lines are the result of a least-squares analysis of the data. All data taken from Anusavice and DeHoff [204].

4.25. Grain Boundary Diffusion

The diffusion of copper along the grain boundaries of nickel has been studied and reported by Barnes [234, 235]. The experiments, performed at 1000 °C, involved the bonding of alternate layers of thin copper and nickel strips which, after interdiffusion, were etched to reveal the contours of concentration in the neighborhood of a grain boundary where preferential diffusion had taken place.

The diffusion of nickel into grain boundaries in pure copper has been investigated by Austin and Richard [5, 64, 66, 67], Krishtal and coworkers [59], Yukawa and Sinnott [1], Unnam and coworkers [15], and Houska [16].

In their experiments, Austin and Richard fabricated copper bicrystals of varying tilt angles, upon which nickel was electrodeposited and diffused at a temperature of 750 °C for varying lengths of time (up to 240 hours). The specimens were then sectioned, and concentration contours from the grain boundary and the lateral lattice diffusion were measured by means of electron-probe microanalysis. From this data, the product of the grain boundary width (δ) and grain boundary diffusion coefficient (D_{gb}) were calculated from both Fisher's [233] and Whipple's [236] solutions. The results of the calculations reveal the nickel grain boundary diffusion coefficient to be concentration dependent. At the lower concentration (<3 at.% nickel), the coefficient is essentially constant for the high angle, 45° boundaries. For lower tilt angles (30 and 22°), the grain boundary diffusion coefficient decreases for concentrations greater than 0.5 at.% nickel. The amount of grain boundary diffusion was found to decrease rapidly at nickel concentrations above 5 at.% nickel.

Krishtal et al. [59] performed their experiments at 500, 700, and 800 °C and determined "effective diffusion coefficients." Analyzing their specimens by x-ray diffraction [54, 61], and utilizing Hassner's relation [237], the product of the grain boundary diffusion coefficient times

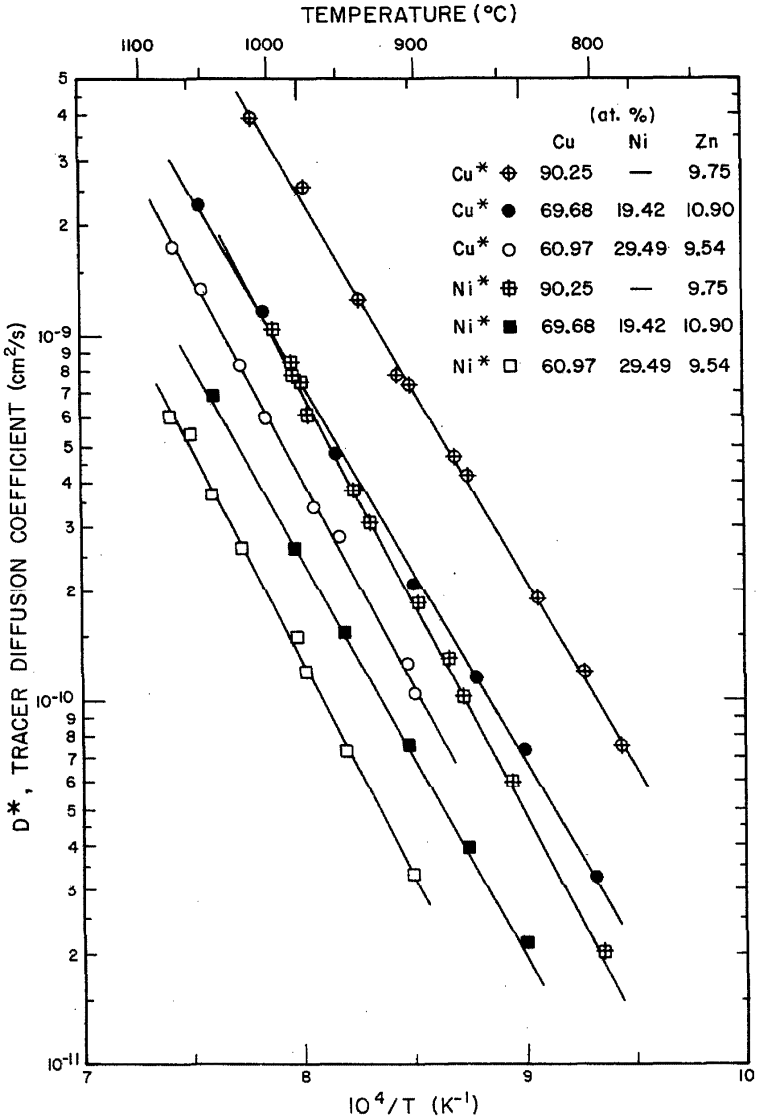

FIGURE 33. The tracer diffusion coefficients of ^{67}Cu and ^{66}Ni in binary Cu-Zn alloys and ternary Cu-Ni-Zn alloys as a function of reciprocal absolute temperature.

The straight lines drawn are the result of a least-squares analysis of the data. All data taken from Anusavice and DeHoff [204].

the grain width could be calculated. Between 700 and 800 °C, the activation energy for nickel grain boundary diffusion was 23.0 kcal/mol. More recently, Krishtal et al. [238] analyzed the contributions of dislocations.

The autoradiographic study of Yukawa and Sinnott [1] revealed the dependence of ^{63}Ni penetration on the degree of crystallographic misfit between the grains forming the boundary (maximum penetration occurring at maximum misfit). Their experiments were performed in the temperature range 650–925 °C.

Unnam and coworkers [15] diffused thin films of nickel on a (111)-oriented copper crystal at 600and 900 °C and calculated activation energies and pre-exponential factors for grain boundary (as well as volume) diffusion which are in agreement with earlier published values.

4.26. Surface Diffusion

Gal and Gruzin [239] diffused radioactive ^{63}Ni over the (100) and (111) surfaces of pure copper at temperatures ranging from 900 to 1050 °C. The activation energy for diffusion on the (100) crystal face was 33 kcal/mol, and over the (111) face, 48.5 kcal/mol. Similar experiments performed on polycrystalline specimens yielded an activation energy of 37.4 kcal/mol.

Pines and coworkers [240] have studied surface diffusion in thin films (~10^{-6} cm) using electron-diffraction techniques. Measurements of "effective diffusion coefficients" were made in the temperature

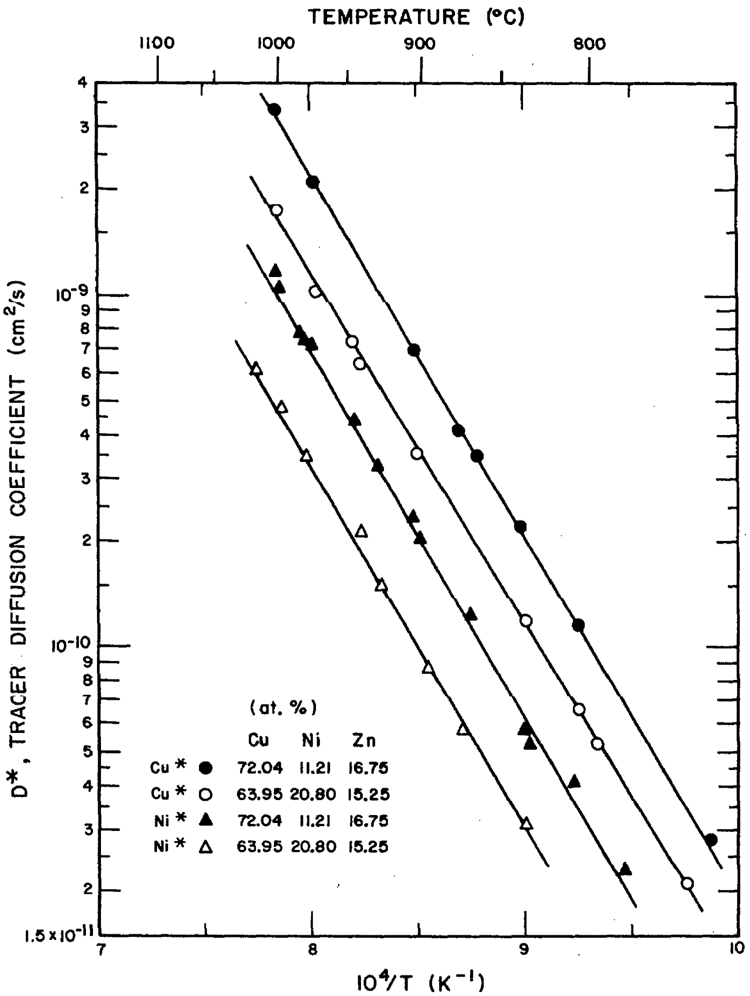

FIGURE 34. The tracer diffusion coefficients of ^{67}Cu and ^{66}Ni in ternary alloys of Cu-Ni-Zn as a function of reciprocal absolute temperature.

The straight lines shown are the result of a least-squares analysis. Data taken from Anusavice and DeHoff [204].

range 630–790 °C. The results of the calculations are plotted in figure 42 as a function of reciprocal absolute temperature. The pure surface diffusion coefficient is estimated to be five to 10 times the value of the effective diffusion coefficient.

Geguzin and coworkers [239, 241] determined a surface diffusion coefficient at 1000 °C which had a concentration dependence. Their results indicate that surface diffusion takes place in a surface layer whose depth is greater than an interatomic spacing.

Torkar and Neuhold [116] sintered unpressed nickel and copper powders. From magnetic measurements they attempted to sort out the activation energies for the surface and volume diffusion processes.

4.27. Electromigration

Stepper [242], and Stepper and Wever [243, 244] passed direct currents through a Cu-Ni(1.0 at.%) alloy and found that the nickel was transported towards the anode portion of the specimen. The values obtained for the effective valence are unrealistically high, as are calculated nickel diffusion coefficients.

4.28. Thermomigration

Meechan [245, 246] interdiffused copper and nickel in large temperature gradients in the range 2000–3000 °C/cm. The width of the zone was established with a microhardness, coloration, or an etching technique, and it was found that interdiffusion was appreciably altered by the temperature gradients.

Schroerschwarz and Heitkamp [247] used the method of stationary redistribution of radioactive ^{63}Ni impurities in a linear temperature gradient in pure copper. The nickel impurities were found to be enriched on the hot side, corresponding to a negative heat of transport.

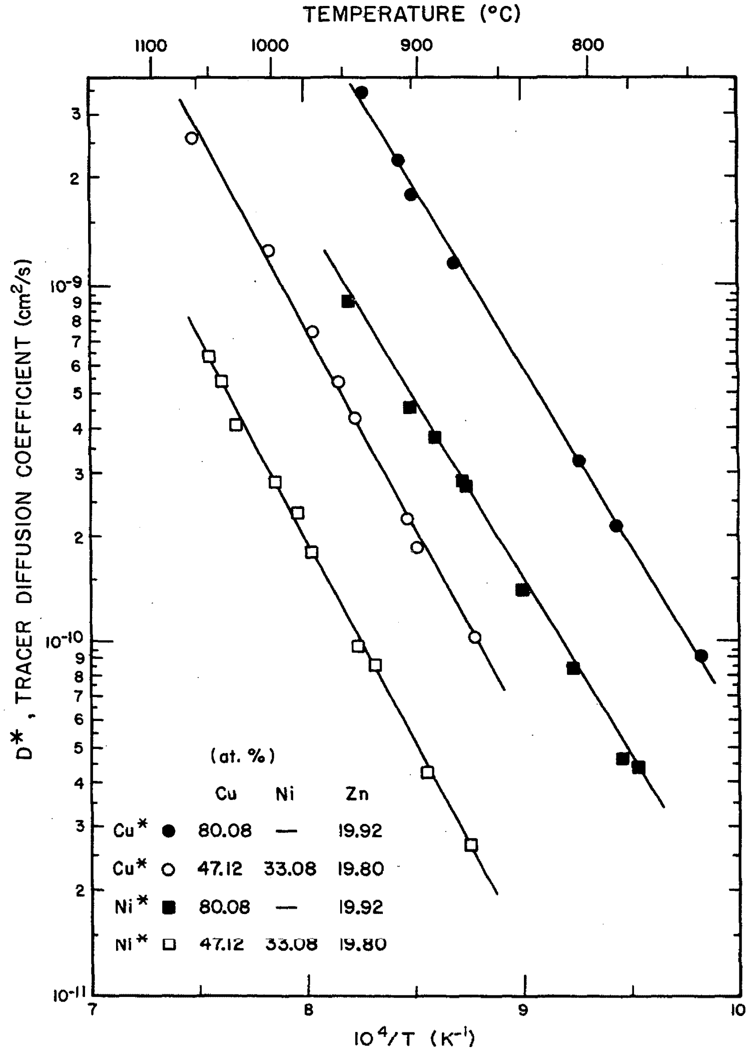

FIGURE 35. The tracer diffusion coefficients of ^{67}Cu and ^{66}Ni in a binary Cu-Zn alloy and a ternary alloy of Cu-Ni-Zn as a function of reciprocal absolute temperature.

The straight lines shown are the result of a least-squares analysis of the data taken from Anusavice and DeHoff [204].

4.29. Pressure Effects

Clay and Greenwood [173] interdiffused copper and nickel at 850 °C over a range of pressures from 0.7–60 MN/m^2 in argon gas. Five tungsten wires were embedded at the interface to act as inert markers, and after each diffusion anneal, marker displacement measured. The size, number, and distribution of voids forming on the copper-rich side of the couple were examined in optical and scanning electron microscopes. It was found that in the early stages of interdiffusion voids nucleate and increase in size and number, reaching a maximum size, whereupon they shrink and finally disappear. Hydrostatic pressure exerted during interdiffusion reduces total porosity, maximum size of the pores, as well as the time of growth. A hydrostatic pressure of approximately 20 MN/m^2 at 850 °C suppresses pore formation completely, although the authors detected no pressure effect on the rate of interdiffusion. The same authors conclude from their results that void formation neither enhances nor retards the interdiffusion process they observed in their couples.

Barnes and Mazey [165] applied hydrostatic pressures of ~ 15 MN/m^2 and reduced (or eliminated) void formation in their diffusion couples of Cu and Ni.

Geguzin and coworkers [163, 171] noted that the application of increasing hydrostatic pressure in their interdiffusion experiments would increase marker velocity and decrease pore formation. The surface relief of specimens during the interdiffusion of copper and nickel resulting from the application of low hydrostatic pressure has been of some concern, especially the role of pores, dislocations, and free surfaces [97].

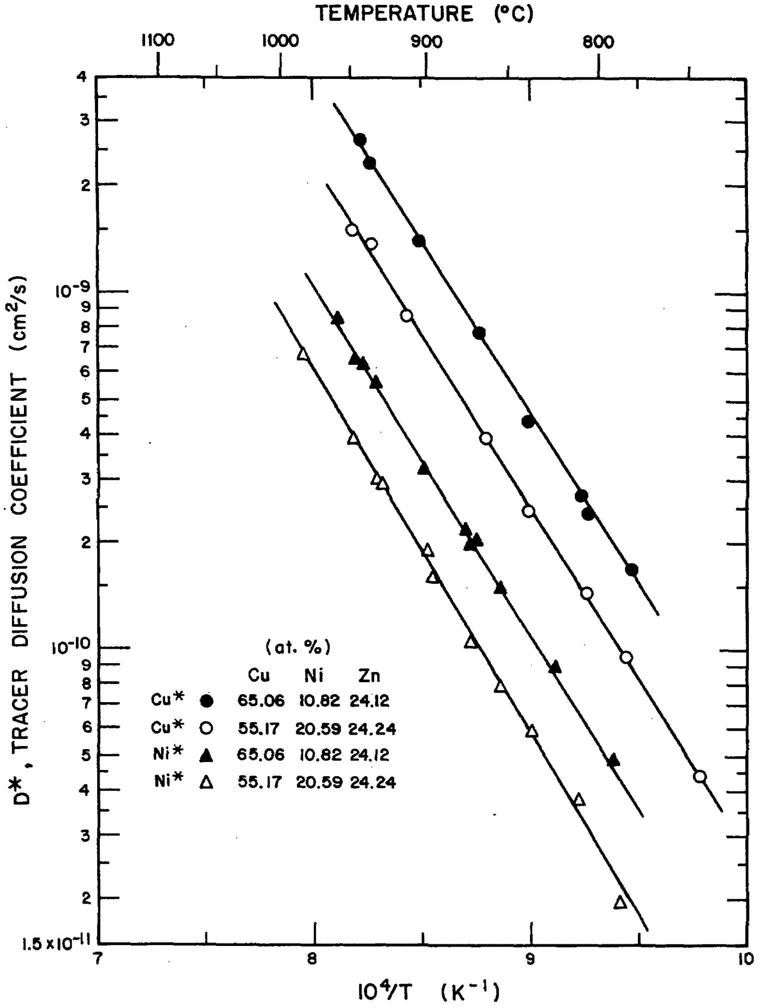

FIGURE 36. The tracer diffusion coefficients of ^{67}Cu and ^{66}Ni in ternary alloys of Cu-Ni-Zn as a function of reciprocal absolute temperature.

The straight lines shown are the result of a least-squares analysis. Data taken from Anusavice and DeHoff [204].

4.30. Ultrasonic Vibration

The influence of ultrasonic vibrations on the interdiffusion of copper and nickel has been reported [248]. The amount of diffusion was determined from metallographic examination and microhardness readings of the interdiffusion zone. In the temperature range 950–1050 °C, a measureable acceleration was noted.

4.31. Creep

High-temperature tensile creep studies [249, 250] using Cu-Ni(0–100% Cu alloys) revealed that the activation energy for steady-state creep is close to that for the lattice self-diffusion of the tracer component in the alloys. More recent low-stress creep experiments [251] in single phase alloys of Cu-Ni yield diffusion coefficients which are near values reported for interdiffusion coefficients.

4.32. Irradiation-Enhanced Diffusion

Bonzel [7] has studied the influence of alpha-irradiation (3 MeV α-particles) on the diffusion of radioactive ^{63}Ni in polycrystalline copper. In the temperature range 210–285 °C, the diffusion caused by irradiation was found to be independent of temperature (see figure 43); the tracer diffusion coefficient being of the order of 10^{-18} cm²/s. Brimhall [252] has also observed void formation in Cu-Ni alloys.

4.33. Molten Metals

The diffusion of nickel in liquid copper has been investigated by Ejima and Kameda [253]. Their measurements were made over the temperature range of 1100–1300 °C using a modified capillary-reservoir method.

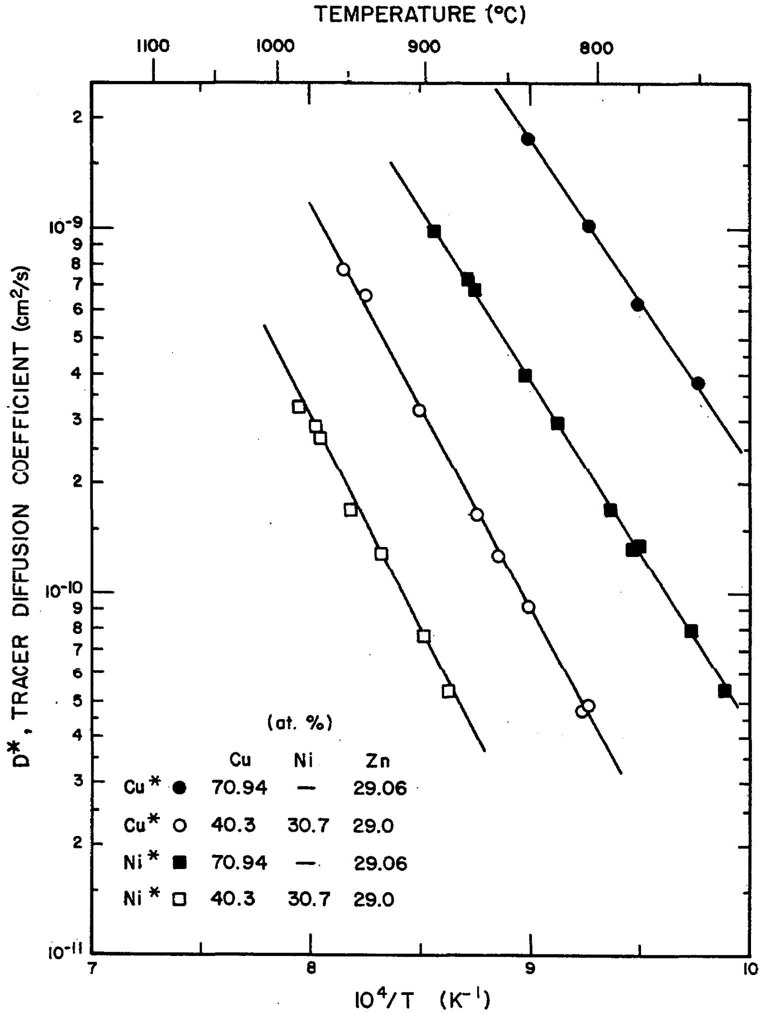

FIGURE 37. The tracer diffusion coefficients of ^{67}Cu and ^{66}Ni in a binary alloy of Cu-Zn and a ternary alloy of Cu-Ni-Zn as a function of reciprocal absolute temperature.

The straight lines shown are the result of a least-squares analysis of the data taken from Anusavice and DeHoff [204].

The data fit the following Arrhenius-type equation:

$$D = (1.7_1 \pm 0.3_0) \times 10^{-3} \exp [-(10.5 \pm 0.31)\ \mathrm{kcal \cdot mol^{-1}}/RT]\ \mathrm{cm^2/s}.$$

Gerlach and Leidel [254], also relying on the capillary-reservoir technique, measured the diffusion coefficients of nickel in copper-base alloys (containing 0.025, 0.25, 2.5, and 3.25 at.% Ni) over the temperature range 1150–1400 °C. Their data can be described by the parameters in table 27.

The dissolution kinetics of nickel in molten copper over the temperature range 1100–1400 °C was examined by Shurygin and Shantarin [255]. Using similar techniques, Ereminko and Churakov studied the dissolution kinetics of graphite [256] and chromium carbide [257] in Cu-Ni(20 wt%) and Cu-Ni(40 wt%) alloy melts.

The diffusivity of oxygen in molten copper (at 1200 °C) was found to be increased by the addition of 5 at.% nickel [258].

Rinaldi and coworkers [259] measured diffusion coefficients of the order of 10^{-5} cm²/s in ternary alloys from the aluminum-rich corner of the Al-Cu-Ni system while studying the growth of ternary composites from the melt.

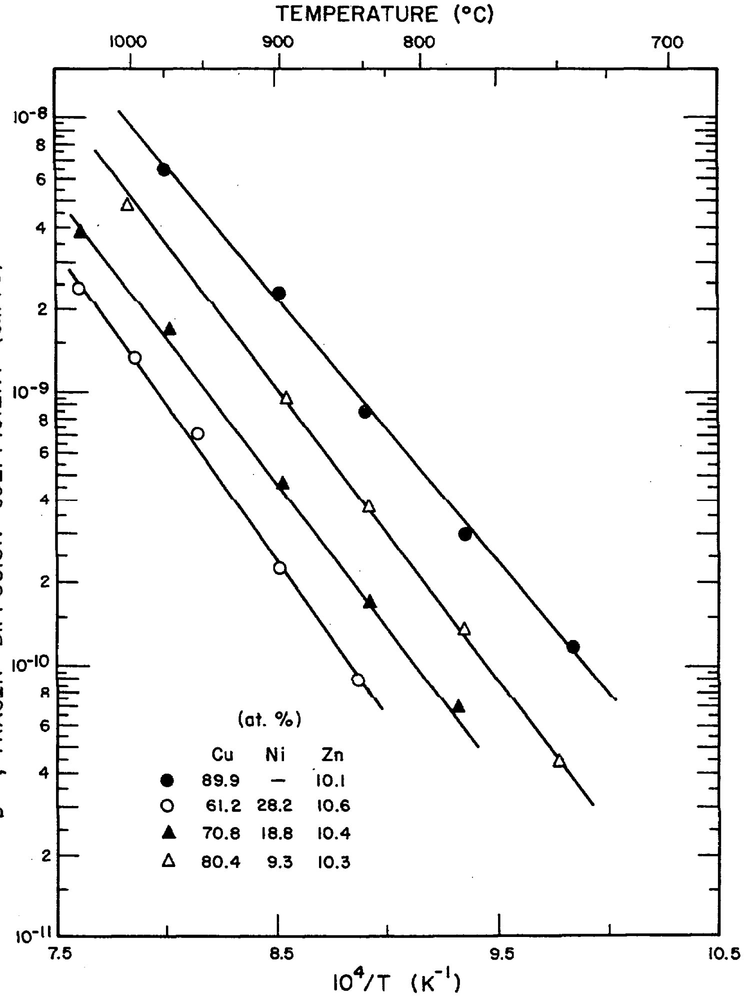

FIGURE 38. The tracer diffusion coefficients of ^{65}Zn in Cu-Zn and Cu-Ni-Zn alloys as a function of reciprocal absolute temperature.

The straight lines are obtained from a least-squares analysis of the appropriate data points. Data taken from Anusavice and DeHoff [204].

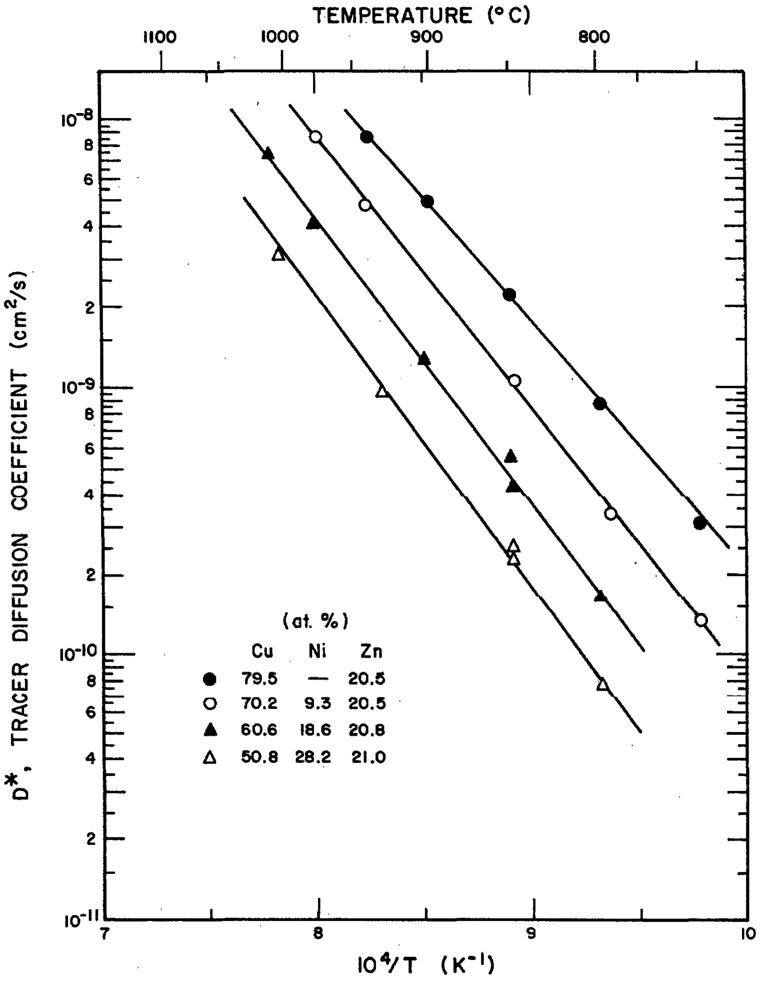

FIGURE 39. The tracer diffusion coefficients of ^{65}Zn in copper alloys containing zinc, or zinc and nickel, as a function of reciprocal absolute temperature.

The straight lines are obtained from a least-squares analysis of the data points shown. Data taken from Anusavice and DeHoff [204].

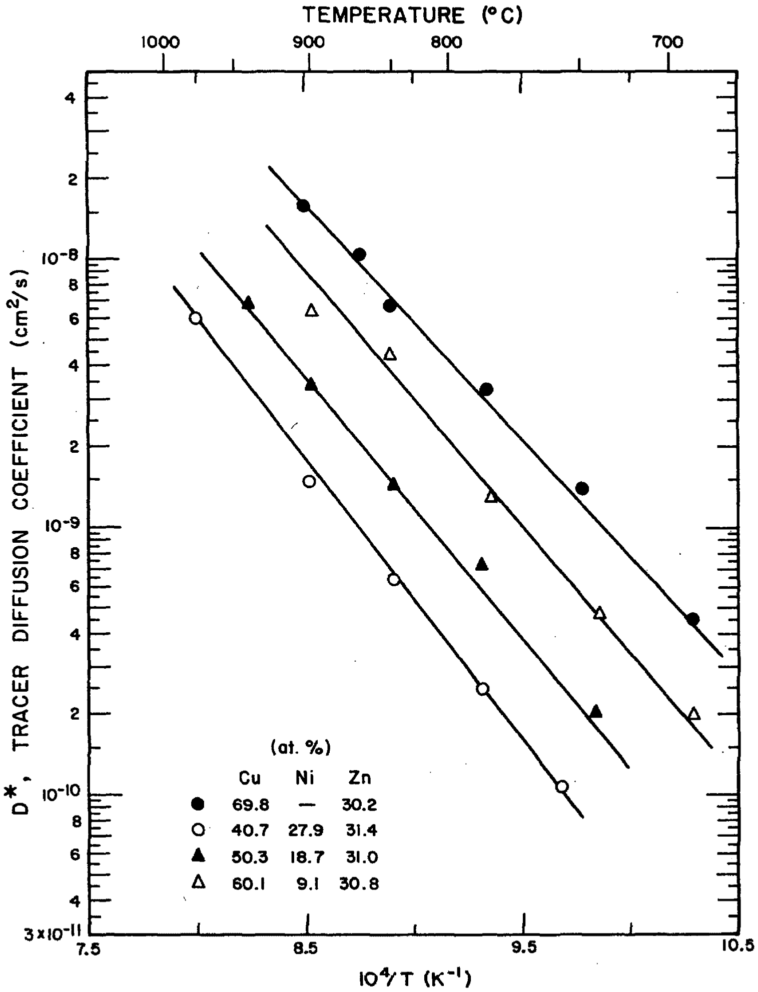

FIGURE 40. The tracer diffusion coefficients of ^{65}Zn in Cu-Zn and Cu-Zn-Ni alloys as a function of reciprocal absolute temperature.

The straight lines are obtained from a least-squares analysis of the displayed data points. Data taken from Anusavice and DeHoff [204].

TABLE 24. Diffusion parameters for ^{66}Ni tracer diffusion in Cu, Cu-Zn, and Cu-Ni-Zn alloys. Data taken from Anusavice et al. [204].

Composition (at.%)			Temperature (°C)	D_0 (cm^2/s)	Q (kcal/mol)
Cu	Ni	Zn			
99.999	-	-	855-1055	$1.94^{+0.73}_{-0.50}$	55.6 ± 0.8
90.25	-	9.75	791-995	$1.06^{+0.25}_{-0.16}$	52.3 ± 0.4
80.08	-	19.92	777-946	$0.22^{+0.05}_{-0.04}$	46.6 ± 0.5
70.94	-	29.06	739-895	0.12 ± 0.02	43.2 ± 0.4
82.72	12.55	4.73	779-1027	$0.13^{+0.03}_{-0.02}$	49.6 ± 0.5
72.04	11.21	16.75	784-999	$0.16^{+0.14}_{-0.13}$	47.8 ± 0.5
69.68	19.42	10.90	837-1041	0.12 ± 0.02	49.7 ± 0.4
65.06	10.82	24.12	794-959	$0.0844^{+0.0180}_{-0.0149}$	45.2 ± 0.5
63.95	20.80	15.25	837-1013	$0.0917^{+0.0332}_{-0.0243}$	48.2 ± 0.7
60.97	29.49	9.54	904-1074	$0.42^{+0.11}_{-0.09}$	54.4 ± 0.6
55.17	20.59	24.24	791-983	$0.0990^{+0.0320}_{-0.0245}$	46.9 ± 0.7
47.12	33.08	19.80	870-1050	$0.33^{+0.09}_{-0.07}$	52.8 ± 0.6
40.30	30.70	29.00	885-995	$0.31^{+0.10}_{-0.09}$	51.6 ± 0.7

TABLE 25. Diffusion parameters for ^{65}Zn tracer diffusion in Cu, Cu-Ni, and Cu-Ni-Zn alloys. Data taken from Anusavice et al. [204].

Composition (at.%)			Temperature (°C)	D_0 (cm^2/s)	Q (kcal/mol)
Cu	Ni	Zn			
99.999	-	-	800-1040	0.24 0.05	45.1 ± 0.5
90.7	9.3	-	759-1040	$0.36^{+0.22}_{-0.14}$	47.8 ± 1.1
81.8	18.2	-	795-1005	$0.89^{+0.36}_{-0.26}$	51.3 ± 0.8
71.4	28.6	-	870-1080	$1.37^{+1.18}_{-0.63}$	54.1 ± 1.5
80.4	9.3	10.3	750-1005	0.49 ± 0.05	46.8 ± 0.2
70.2	9.3	20.5	750-976	$1.14^{+0.24}_{-0.23}$	46.9 ± 0.4
60.1	9.1	30.8	700-901	$0.39^{+0.62}_{-0.24}$	41.4 ± 3.2
70.8	18.8	10.4	800-1040	$0.36^{+0.17}_{-0.11}$	47.7 ± 0.9
60.6	18.6	20.8	800-1011	$1.09^{+0.60}_{-0.39}$	48.1 ± 1.0
50.3	18.7	31.0	748-940	$0.73^{+0.19}_{-0.15}$	44.7 ± 0.5
61.2	28.2	10.6	855-1041	$1.44^{+0.58}_{-0.41}$	52.6 ± 0.8
50.8	28.2	21.0	800-1005	$1.17^{+0.69}_{-0.40}$	49.9 ± 1.1
40.7	27.9	31.4	760-976	$1.15^{+0.39}_{-0.26}$	47.4 ± 0.7

TABLE 26. Nickel interdiffusion coefficients in Cu-Zn-Ni ternary alloys at 775 °C. Data taken from Coates and Kirkaldy [215-216].

Couple Configuration and Composition (wt%)	$\tilde{D}_{Ni}$ (cm^2/s)
Cu-Zn(35.0) - Ni(5.0) / Cu-Zn(35.2) - Ni(2.5)	$1.35 \pm 0.15 \times 10^{-10}$
Cu-Zn(44.1) - Ni(2.5) / Cu-Zn(44.0) - Ni(5.0)	$6.4 \pm 0.9 \times 10^{-8}$
Cu-Zn(45.9) - Ni(7.5) / Cu-Zn(46.0) - Ni(10.0)	$3.5 \pm 0.7 \times 10^{-8}$

TABLE 27. Parameters for the diffusion of nickel in liquid Cu-Ni alloys in the temperature range 1150-1400 °C. From the experiments of Gerlach and Leidel [254].

Cu-Ni Alloy (at.% Ni)	D_0 (10^{-3} cm^2/s)	Q (kcal/mol)
0.025	5.90 ± 0.8	12.96 ± 1.10
0.25	2.31 ± 0.35	7.69 ± 0.90
2.5	17.9 ± 1.5	9.90 ± 0.83
3.25	58.1 ± 4.5	12.56 ± 1.00

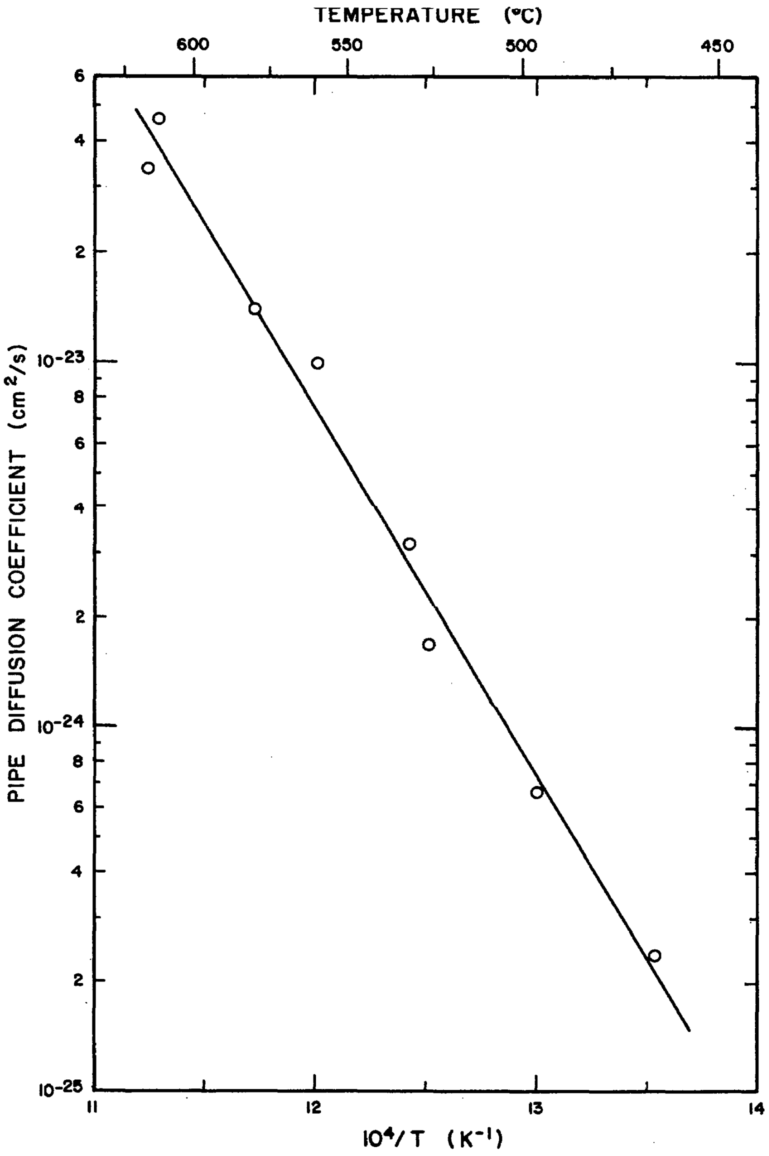

FIGURE 41. The pipe diffusion coefficients of ^{63}Ni in single crystals of pure copper as a function of reciprocal absolute temperature.

From the data of Bernardini and Cabane [230]. The line shown is a result of our least-squares analysis of the authors' data. The Arrhenius equation is: $D=7.30\times10^{-12}\exp(-45.7\ \mathrm{kcal\cdot mol^{-1}}/RT)\ \mathrm{cm^2/s}$.

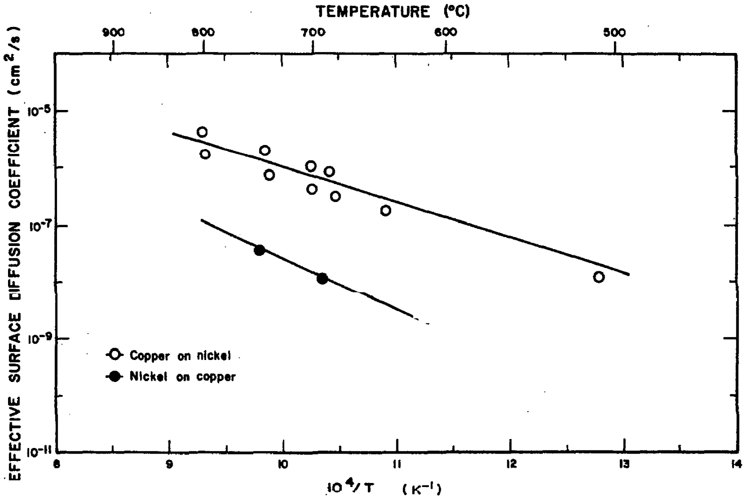

FIGURE 42. The "effective" surface diffusion coefficients of copper on nickel and of nickel on copper as a function of reciprocal absolute temperature.

From a thin-film study of Pines et al. [240].

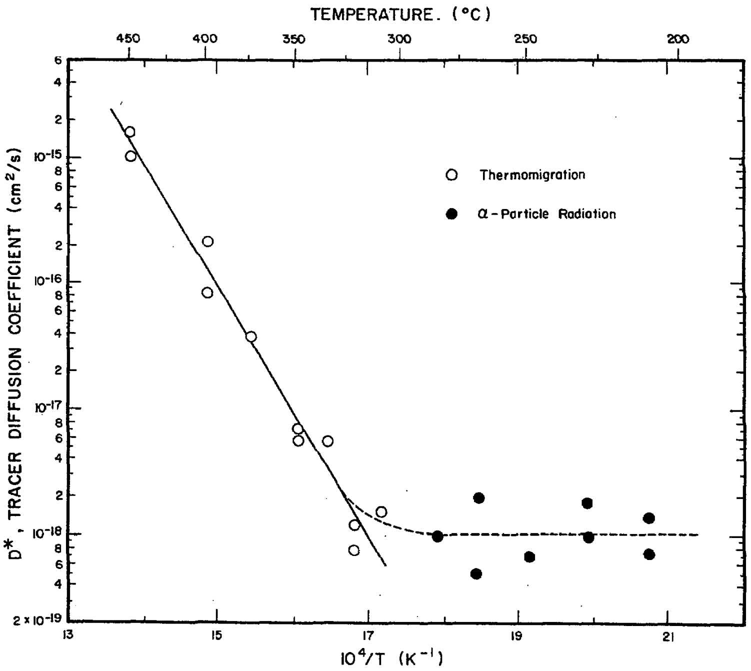

FIGURE 43. The tracer diffusion coefficients of ^{63}Ni in polycrystalline copper under the influence of alpha-irradiation as a function of reciprocal absolute temperature.

From the data of Bonzel [7].

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5. Copper-Palladium

5.1. Pd* → Cu

The diffusion of radioactive tracers in single crystals of pure copper has been measured in the temperature range 807–1055 °C by conventional tracer-sectioning methods [1]. The ^{103}Pd was electrodeposited onto the electropolished copper surfaces, diffused, sectioned on a precision lathe, and the chips counted to determine the amount of activity contained. The palladium tracer diffusion coefficients were calculated by the method of least-squares from the linearized Gaussian penetration-plots and are listed in table 28. A plot of the diffusion coefficients as a function of temperature is shown in figure 44. A least-squares fit of the data gives the straight line shown, and the diffusion parameters can be expressed by the Arrhenius expression:

$$D^* = (1.71\,^{+0.23}_{-0.21})\exp[-(54.37 \pm 0.30)\mathrm{kcal}\cdot\mathrm{mol}^{-1}/RT]\quad \mathrm{cm}^2/\mathrm{s}.$$

The quoted errors are the standard-errors obtained from a least-squares treatment of the data.

Although no other tracer experiments have been reported, the above results appear to have been arrived at after careful experimental technique and are probably quite reliable.

5.2. Cu-Pd Interdiffusion

Analysis of interdiffusion phenomena in the Cu-Pd system began with Matano [2] and continued with the studies of Birchenall and coworkers [3, 4], two Soviet investigations [5, 6], and most recently, Badia and Vignes [7, 8], and Neukam [9]. All of the results (except those of Matano, who assumed a concentration-independence shown to be untrue by later studies) are plotted in figure 45. In this figure, the interdiffusion coefficients are displayed as a function of composition for various temperatures. Also shown are the limiting values for palladium diffusion in copper as determined by radio-

TABLE 28. Tracer diffusion coefficients of ^{103}Pd in pure single crystals of copper as determined by Peterson [1].

Temperature (°C)	D* (cm^2/s)
1055.6	2.00×10^{-9} 1.99×10^{-9}
1015.2	1.01×10^{-9} 1.01×10^{-9}
987.6	6.11×10^{-10} 6.23×10^{-10}
953.0	3.48×10^{-10} 3.42×10^{-10}
902.0	1.30×10^{-10} 1.33×10^{-10}
872.9	7.90×10^{-11} 7.64×10^{-11}
843.5	3.92×10^{-11} 3.77×10^{-11}
807.0	1.68×10^{-11} 1.66×10^{-11}

active tracers [1]. The concentration-dependence of the interdiffusion coefficient is apparent at all temperatures.

The data reported by Badia and Vignes [7, 8, 29] temperature range 931–1061 °C appear to be quite reliable. The interdiffusion coefficients were calculated by the Matano analysis [10] and the Hall analysis [11] from data obtained with an electron-microprobe analyzer on incremental couples. In agreement with the data of Badia and Vignes is that of Neukam, taken in the temperature range 775–1040 °C.

The two sets of data [5, 6] reported at 859, 950, and 1019 °C appear to originate from the same experiments, although the separate publications show small differences in the concentration dependencies. The experimental technique again involved electron-microprobe analysis for determining the concentration gradients and the Matano and Hall analyses for calculation of interdiffusion coefficients, but the diffusion couples were constructed of the pure metals. The authors estimate the accuracy of the interdiffusion coefficients to be of the order of 15 to 20%, with the temperatures being in error as much as 5 to 7 °C. In view of the possible errors, these results should be used with caution. Also, the concentration-dependence reported for the dilute solid solutions are probably not correct. More reliable values of the interdiffusion coefficients in the copper-rich alloys can probably be obtained by extrapolating the data from the more concentrated solid solutions through the dilute region to the palladium tracer diffusion coefficients (see dashed lines in figure 45).

The results [3, 4] reported at 878, 972, and 1038 °C are too few and scattered to establish definite trends and should only be considered as providing a correct order-of-magnitude.

The interdiffusion of 8 μm-thick deposits of palladium and single crystals of copper at 900 °C was followed with x-ray diffraction by Tenney and Talty [12]. Their data are displayed in figure 45 for comparison.

The effect of coherency strains on interdiffusion in thin films of Cu-Pd alloys (containing 70–90 at.% Pd) has been measured [13, 14]. In these experiments, composition-modulated Cu-Pd thin films (total thickness of the films ranged from 0.3 to 0.8 μm) were interdiffused at temperatures between 355 to 440 °C (±0.05 °C), and the decay rate of the composition modulations and the state of coherency were determined from x-ray diffraction measurements. Effective interdiffusion coefficients (which were dependent on the wavelength of the composition modulations) were calculated and found to progressively decrease with the loss of coherency (coherency strains acting as a driving force). Extrapolation of the observed (effective) interdiffusivities to infinite wavelength should yield the true bulk interdiffusivities, and these values are shown in figure 46 for the composition Cu-Pd (89.8 at.%). An extrapolation of these low-temperature bulk interdiffusivities to higher temperatures is also shown in the same figure.

The interdiffusion of bulk copper specimens and thin foils of palladium has been observed in the temperature range 330–530 °C [15]. With the aid of an electron microscope, the formation and growth of the intermetallic phase, β-CuPd, was observed continuously during the heating of the specimens. Concentration profiles in the interdiffusion zone were determined with an electron-microprobe analyzer—discontinuities being present at the phase boundaries.

5.3. Cu-Pd-H

The effect of ordering on hydrogen movement in the alloy Cu$_3$Pd has been studied [16]. The temperature dependence of the rate of permeation, P(cm^3 · mm/cm^2 · s · atm$^{1/2}$), and the diffusion coefficients, D(cm^2/s), were measured in the temperature range 300–700 °C. The experimental procedures and apparatus employed (see references 17–19) yielded errors of ±3% in the measurement of permeation rates, and ±5% in the diffusion coefficients, according to the authors. The results of the experiments are plotted in figures 47 and 48 as a function of reciprocal absolute temperature. The influence of ordering on the permeation rates and diffusion coefficients is evident in the figure. Measurements made with alloy specimens that had been heated-and-cooled from 300 to 730 °C indicated the effects of short-range order. Specimens that had been given long (20, 45, and 70 h) isothermal anneals at 400 °C exhibited the ef-

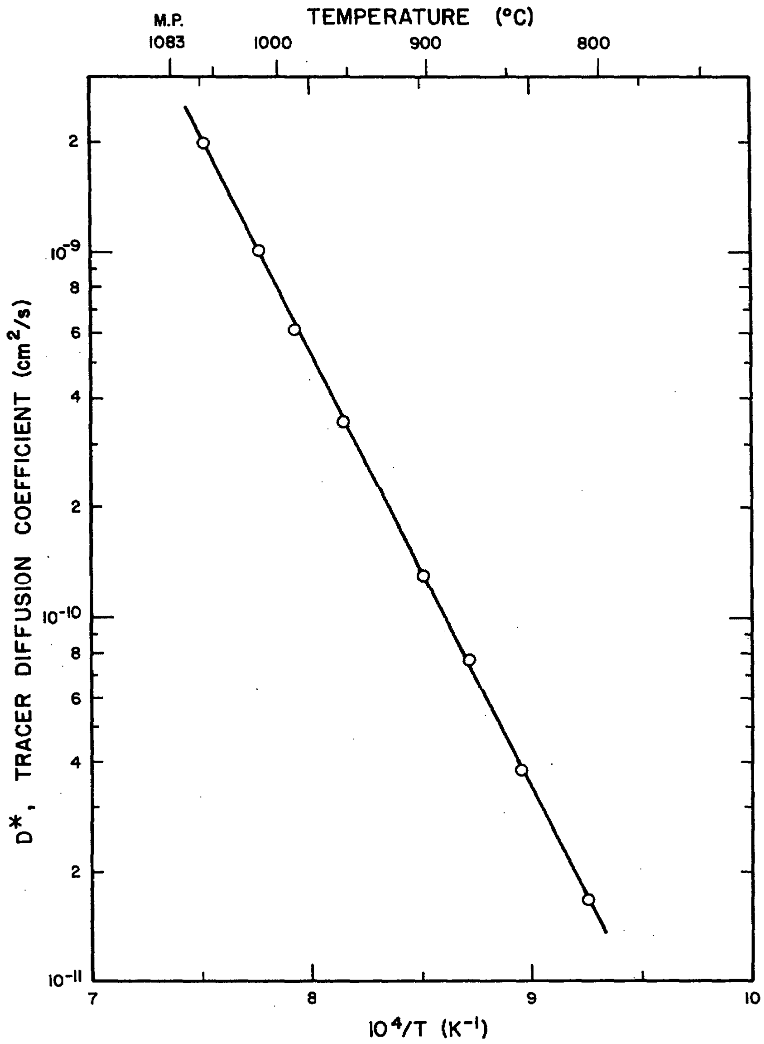

FIGURE 44. The tracer diffusion coefficients of ^{103}Pd in pure single crystals of copper as a function of reciprocal absolute temperature.

Data taken from Peterson [1].

fects of long-range order. The reversibility of the transformation is demonstrated by the measurements made on alloy specimens that were heated to above the transition temperature (~460 °C) and cooled. In the region of linear temperature dependence, the results can be expressed by Arrhenius equations, with the parameters listed in tables 29 and 30.

The diffusion of hydrogen (and deuterium) in Cu-Pd alloys at relatively low temperatures (25–130 °C) has been investigated [20]. The alloys ranged in copper content from 0 to 58 at.%. Although the hydrogen diffusion coefficients were relatively insensitive to alloy composition, marked changes occurred at the α-β phase change.

At elevated temperature, Cu-Pd alloys form a continuous α-phase(fcc) across the phase diagram [21], but at lower temperatures, 400–600 °C, ordering takes place at compositions above approximately 50 at.% copper. At 350 °C and in the absence of hydrogen, there exists a stable α-phase(fcc), an ordered β-phase(bcc), and an intermediate two-phase region. The author noted that dissolved hydrogen shifts the phase boundaries to higher palladium concentrations.

The hydrogen diffusion coefficients were calculated from measurements made of the time-dependence of the electrical resistivity in given sections of alloy foil specimens, with the resistivity being related to the hydrogen concentration. The room temperature (25 °C) diffusion coefficients are listed in table 31, along with alloy compositions, prediffusion heat-treatments (which usually took place at 350 °C), and the phases present before diffusion (determined by x-ray diffraction). Measurements near 130 °C are listed in table 32 for a Cu-Pd(47.5 at.%) alloy. The large increase in the hydrogen diffusion coefficient at the α-β transition is

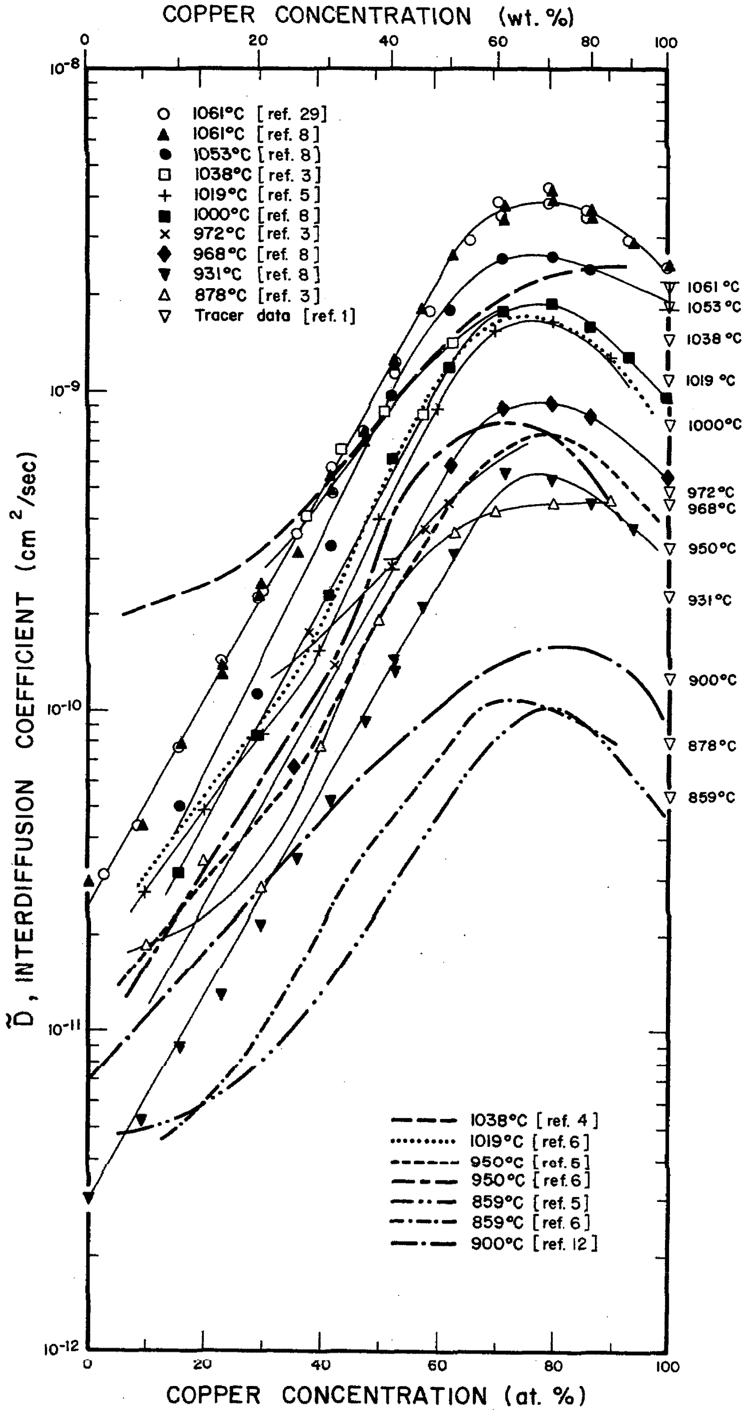

FIGURE 45. The interdiffusion coefficients in Cu-Pd as a function of copper concentration.

Data at 1061 °C taken from reference [8, 29], at 1053 °C from reference [8], at 1038 °C from reference [3, 4], at 1000 °C from reference [8], at 972 °C from reference [3], at 968 °C from reference [8], at 931 °C from reference [8], at 900 °C from reference [12], and at 878 °C from reference [3]. The differing data shown at temperatures 1019, 950, and 859 °C appears to have been obtained from the same experiments [5, 6]. The diffusion of palladium tracer in pure copper is shown for comparison (tracer data excerpted from reference [1]).

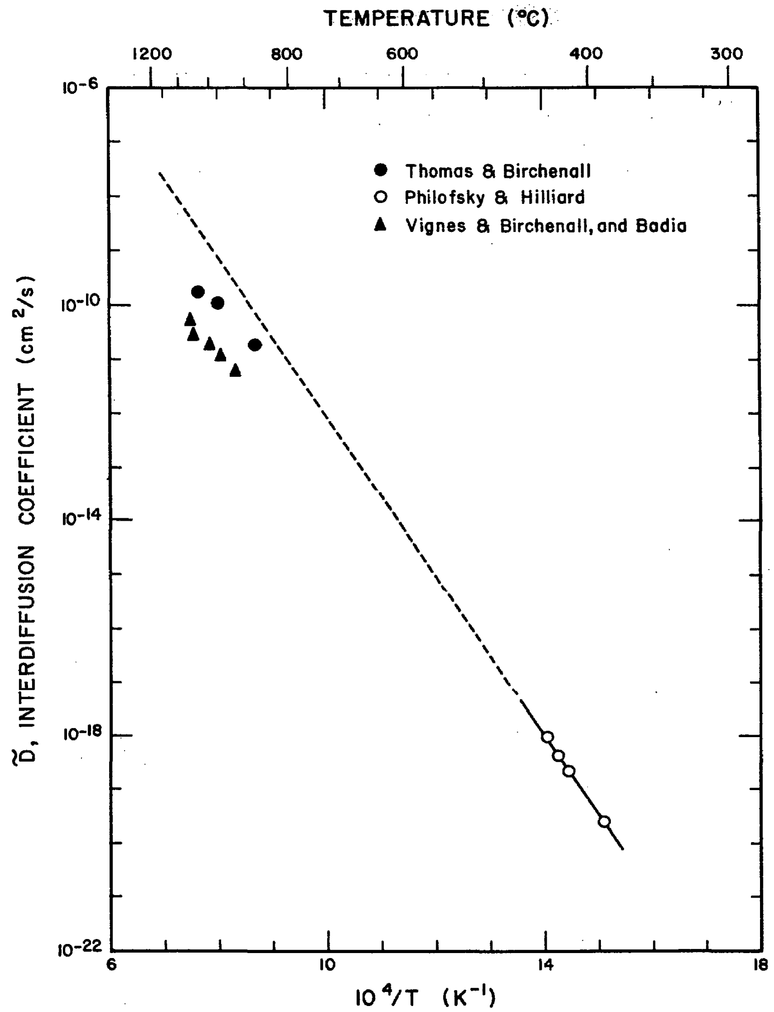

FIGURE 46. The interdiffusion coefficients as a function of the reciprocal absolute temperature for the composition Cu-Pd(89.8 at%).

The low temperature results obtained with incoherent thin films [14] of the metals are extrapolated to the high temperature regime and compared with data taken from the experiments of Thomas and Birchenall [3], Vignes and Birchenall [29], and Badia [8].

TABLE 29. Parameters for the rates of permeation and diffusion of hydrogen in a disordered alloy of Cu_3Pd. Data taken from Vykhodets et al. [16].

Temperature (°C)	Permeation Parameters		Diffusion Parameters	
	P_0 $\left(\frac{cm^3 \cdot mm}{cm^2 \cdot s \cdot atm^{\frac{1}{2}}}\right)$	Q_p (kcal/mol)	D_0 (cm²/s)	Q_d (kcal/mol)
>480	2.5×10^{-2}	8.30	2.80×10^{-3}	9.65
<410	1.06×10^{-2}	7.77	1.80×10^{-3}	8.50

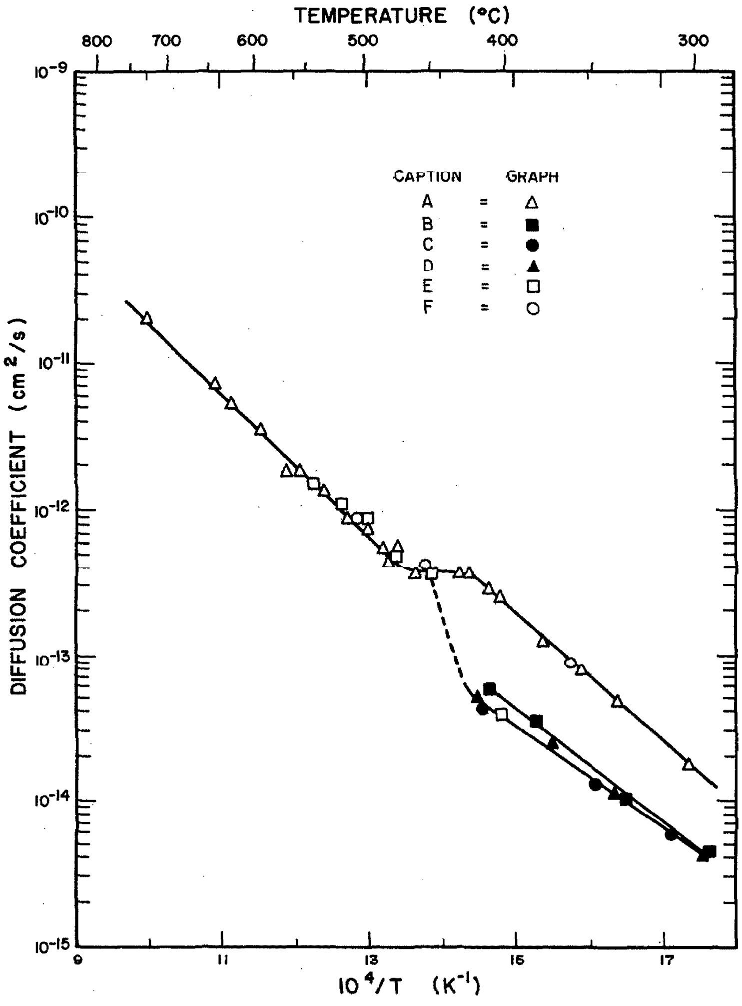

FIGURE 47. The temperature dependence of the diffusion coefficient, D(cm^2/s), of hydrogen in a Cu_3Pd alloy.

The *data points* "A" *correspond* to heating-and-cooling from 300 to 730 °C; the discontinuities in the linear behavior occurring near the critical temperature are caused by the creation (or destruction) of short-range order. The data points "B", "C", and "D", are measurements made on specimens that had undergone an isothermal anneal at 400 °C, for 20, 45, and 70 hours, respectively, to allow ordering to take place. The data points "E" and "F" were taken from measurements on alloy specimens that had been heated to above the order-disorder transition temperature and then cooled (to demonstrate the reversibility of the transformation reliability of their measurements). Data taken from Vykhodets et al. [16].

attributed to the decrease in the activation energy for diffusion.

Measurements of the deuterium diffusion coefficient in a Cu-Pd(47.5 at.%) alloy (β-phase) at a temperature of 25 °C were also made in these experiments. The value $(3.2 \pm 0.2) \times 10^{-5}$ cm^2/s was calculated (compared to 4.9×10^{-5} cm^2/s for hydrogen).

5.4. Cu-Pd-Ni

The addition of 0.27 at.% palladium to pure nickel *single crystals was found to increase the rate of copper* diffusion at 843.3 °C [22, 23]. The impurity diffusion coefficient of copper in nickel was found to be 17% higher than measurements made in pure nickel specimens. Similar measurements between 903.3 and 1050 °C showed that palladium additions had no effect on the copper diffusion rates at these temperatures.

5.5 Cu-Pd-O

The high temperature (850–1000 °C) oxidation of Cu-Pd(5.19–95.14 at.%) alloys has been investigated [24]. The relationship between the oxidation-rate constants and various diffusion coefficients in the *reaction zones are derived. The results and conclusions* reached in these experiments were subsequently re-analyzed by Wagner [25].

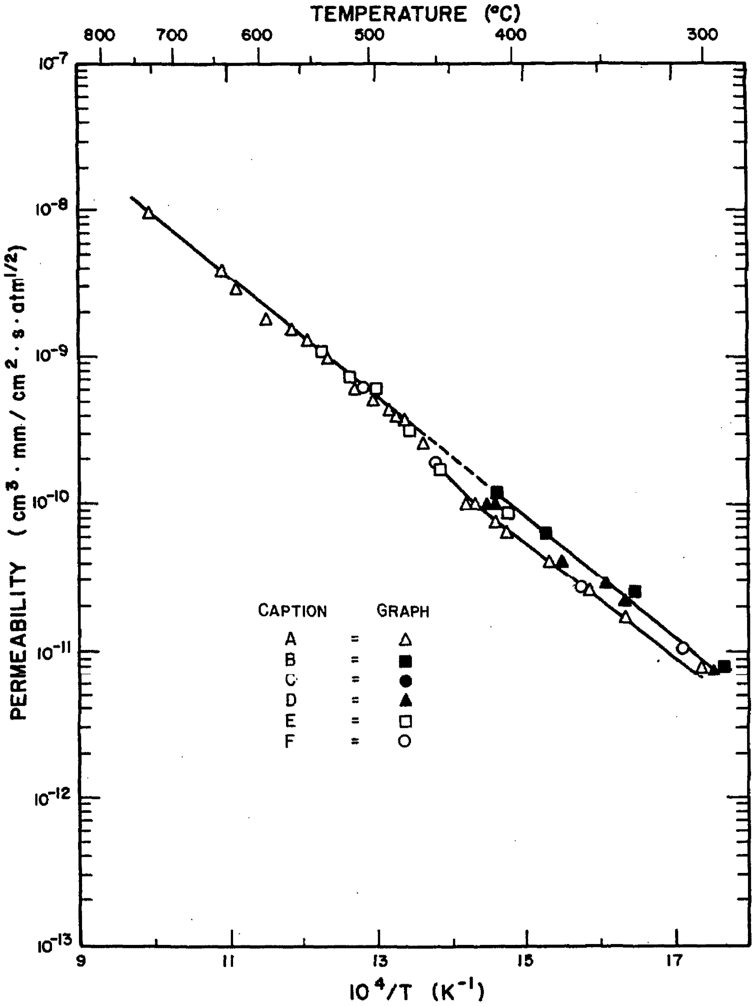

FIGURE 48. The temperature dependence of the permeability (or rate of permeation), $P(\mathrm{cm^3 \cdot mm/cm^2 \cdot s \cdot atm^{1/2}})$, of hydrogen in a Cu_3Pd alloy.

The data points "A" correspond to heating and colling from 300 to 730 °C; the discontinuities in the linear behavior occurring near the critical temperature are caused by the creation (or destruction) of short-range order. The data points "B", "C", and "D", are measurements made on specimens that had undergone an isothermal anneal at 400 °C, for 20, 45, and 70 hours, respectively, to allow ordering to take place. The data points "E" and "F" were taken from measurements on alloy specimens that had been heated to above the order-disorder transition temperature, and then cooled (to demonstrate the reversibility of the transformation reliability of their measurements). Data taken from Vykhodets et al. [16].

5.6. Surface Diffusion

Diffusion on thin (~ 10^{-6} cm) films of copper and palladium has been reported [26]. In these experiments, copper and palladium were evaporated onto each other to form the specimen couples. The degree of spreading was followed with electron diffraction (the technique described in an earlier paper [27]), with the lattice constants determined from diffraction patterns yielding the corresponding concentrations. The diffusion constants that were calculated were termed "effective surface diffusion coefficients." The calculation leading to such constants [28] includes not only surface diffusion, but volume diffusion contributions as well and is based upon half-plane source geometry. Most likely, though, other accompanying processes are included in this diffusion constant. The rates of migration were found to be dependent on film thickness. The data are plotted in figure 49 for copper on palladium, and in figure 50 for palladium on copper.

TABLE 30. Parameters for the rates of permeation and diffusion of hydrogen in an ordered alloy of Cu_3Pd. Alloys were annealed at 400 °C for 20, 45, and 70 hours to create long-range order. Data taken from Vykhodets [6].

Annealing Time (hrs)	Permeation Parameters P_0 $\left(\frac{cm^3\cdot mm}{cm^2\cdot s\cdot atm^{1/2}}\right)$	 Q_p (kcal/mol)	Diffusion Parameters D_0 (cm^2/s)	 Q_d (kcal/mol)
20	2.5×10^{-2}	8.30	5.30×10^{-4}	7.75
45	1.60×10^{-2}	8.00	3.35×10^{-4}	7.30
70	1.60×10^{-2}	8.00	3.35×10^{-4}	7.30

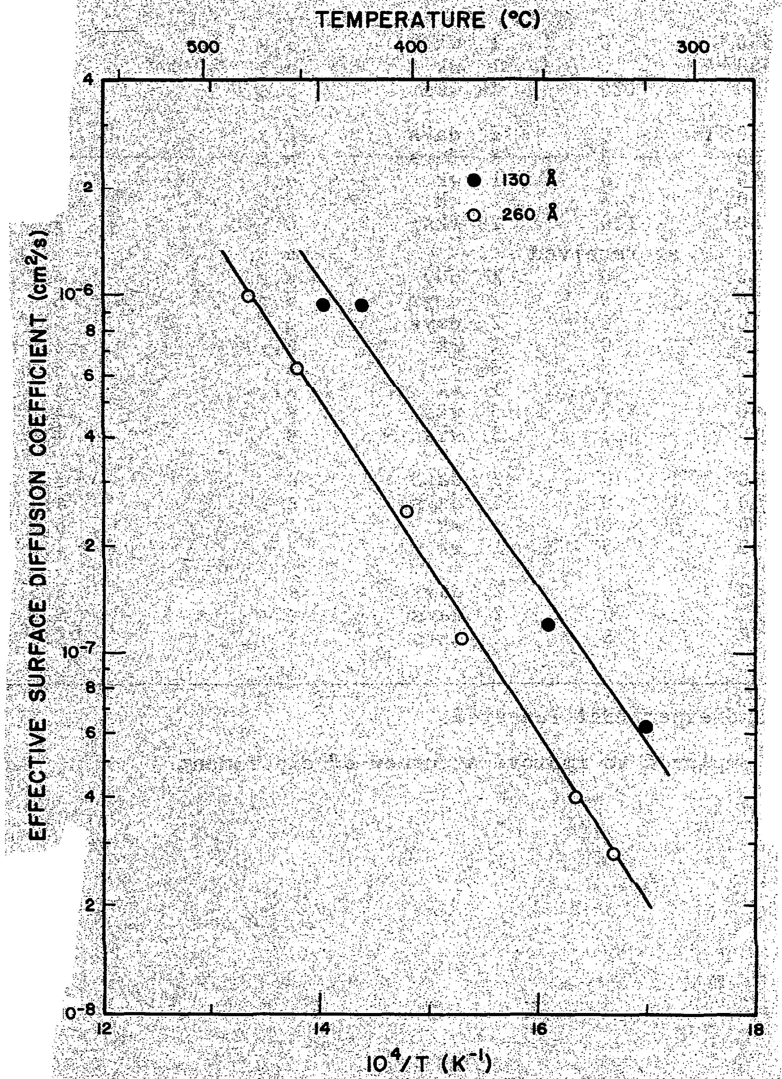

FIGURE 49. The effective surface diffusion coefficients of copper on thin films of palladium as a function of reciprocal absolute temperature.

The copper spreads on the palladium foil and contains bulk diffusion contributions. The constants are dependent on the palladium foil thickness (130 Å and 260 Å). From the data of Grebennik and Zyman [26].

TABLE 31. Room-temperature [25 °C) diffusion coefficients of H_2 in Cu-Pd alloys. Specimen compositions, pre-diffusion heat treatments (and the resulting phases) are also listed. Hydrogen will shift the phase boundaries to higher palladium concentration. Data taken from Piper [20].

Cu-Pd Alloy (at.% Cu)	Pre-Diffusion Heat Treatment			Phases Present in Specimen	Hydrogen Diffusion Coefficient (cm^2/s)
	T (°C)	H_2 Pressure (atm.)	Time		
0	25	1	2 wks	β-Pd-H	2×10^{-7}
15.3		as received		α	4×10^{-7}
41.5	350	0	2 days	α, β	1×10^{-6}
44.7	350	0	1 wk	α, β	1.4×10^{-6}
	350	5	1 wk	α, β	9.4×10^{-6}
	350	120	2½ wks	α, β	2.4×10^{-5} [a] 2.5×10^{-5}
47.8	350	0	1 wk	α, β	9.0×10^{-6}
	350	5	1 wk	α, β	2.3×10^{-5}
	350	120	2½ wks	α, β	5.3×10^{-5}
50.1	350	0	2 days	α, β	4.7×10^{-6}
	350	0	2 days	α, β	1.7×10^{-5}
	350	0	1 wk	α, β	2.1×10^{-5}
	350	5	1 wk	α, β	4.3×10^{-5}
	350	120	2½ wks	β	5.6×10^{-5}
52.5		as received		α	2×10^{-6}
	350	0	1 day	α, β	4.6×10^{-5}
	350	0	2 days	α, β	3.2×10^{-5}
	350	0	2 days	α, β	3.6×10^{-5}
	350	0	1 wk	β, (α)	4.9×10^{-5}
	350	5	3½ h	β	5.8×10^{-5}
	350	5	1 wk	β	5.0×10^{-5}
	350	6.7	3 wks	β	4.9×10^{-5}
	350	6.7	3 wks	β	4.9×10^{-5}
55.4	350	0	2 days	β	3.0×10^{-5}
	350	0	2 days	β	4.1×10^{-5}
	350	0	1 wk	β	6.0×10^{-5}
	350	5	1 wk	β	4.6×10^{-5}
57.1	350	0	2 days	β	3.5×10^{-5}
	350	0	2 days	β	5.2×10^{-5}
	350	5	2 days	β	[b] 5.2×10^{-5}

[a] Specimen rebuilt and experiment repeated.

[b] Extra long sample employed to improve accuracy of experiment.

TABLE 32. Diffusion coefficients of hydrogen at elevated temperatures (~130 °C) in an alloy of Cu-Pd (47.5 at.%) compared to room temperature (25 °C) values. Pre-diffusion heat treatments are listed in addition. From the data of Piper [20].

Pre-Diffusion Heat Treatment			Diffusion Measurement	
T (°C)	Hydrogen Pressure (atm.)	Time of Anneal	Diffusion Temperature (°C)	Diffusion Coefficient (cm^2/s)
350	0	2 days	25	3.6×10^{-5}
350	0	2 days	132	10.3×10^{-5}
350	0	2 days	27	3.2×10^{-5}
350	0	2 days	137	8.9×10^{-5}
350	6.7	3 wks	25	4.9×10^{-5}
350	6.7	3 wks	121	13.2×10^{-5}
350	6.7	3 wks	133	15.2×10^{-5}

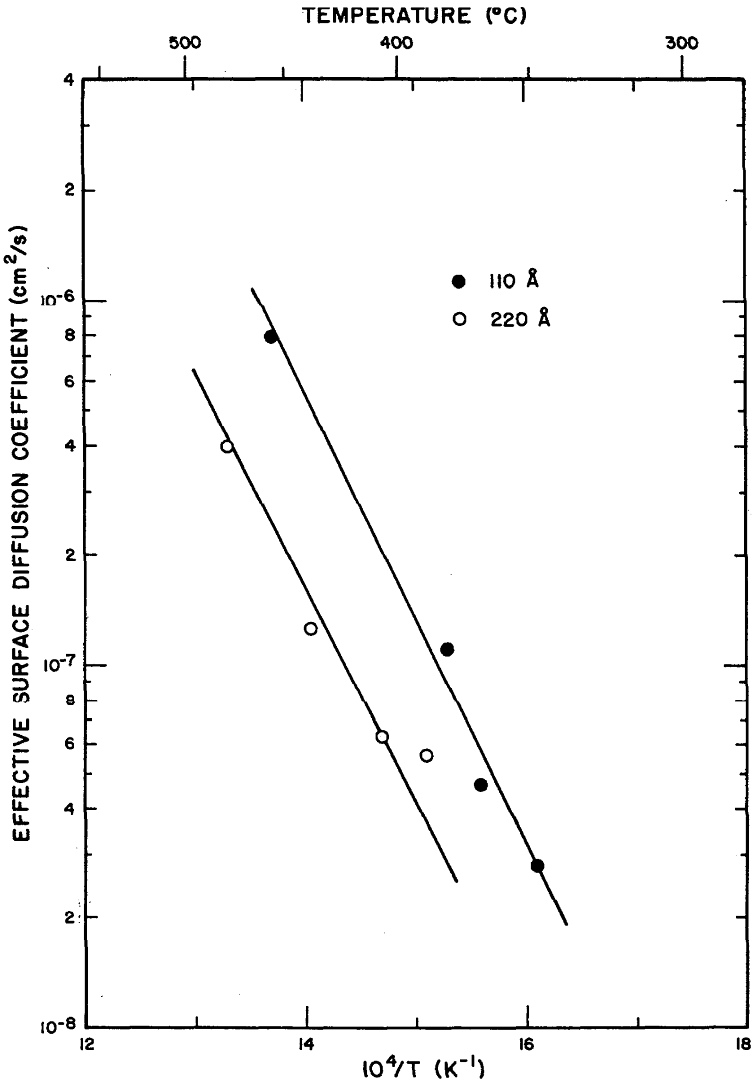

FIGURE 50. The effective surface diffusion of palladium on thin films of copper as a function of reciprocal absolute temperature.

The palladium spreads on the copper foil and contains bulk diffusion contributions. The constants are dependent on the copper foil thickness (110 Å and 220 Å). From the data of Grebennik and Zyman [26].

5.7. Cu-Pd References

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6. Copper-Platinum

6.1. $Pt^* \rightarrow Cu$

There has been only one study reported where the radioactive tracers of platinum were diffused into pure polycrystalline copper—that of Johnson and Faulkenberry [1]. In their experiments, a thin layer of radioactive ^{195m}Pt was electroplated onto the surface of coarse-grained specimens of copper which were subsequently diffusion-annealed in the temperature range 843–997 °C (±2°). The concentration-penetration plots were obtained from conventional lathe-sectioning procedures, and the measured diffusion coefficients are presented in figure 51 and summarized in table 33. The calculated diffusion coefficients were fitted to the Arrhenius plot in figure 51 by a least-squares method. The straight line can be described by the following equation (with probable errors):

$$D_{Pt^* \rightarrow Cu} = (4.8^{+11.2}_{-3.3}) \times 10^{-4} \exp[-(37.5 \pm 2.8) \text{ kcal} \cdot \text{mol}^{-1}/RT] \text{ cm}^2/\text{s}.$$

The pre-exponential factor and activation energy appear to be somewhat low, possibly because of significant grain boundary diffusion contributions.

Fogel'son and coworkers [2] also investigated the diffusion of platinum (from a thin electrodeposited layer) in polycrystalline copper and measured a diffusion coefficient which should be comparable (though less accurate) to that obtained using radioactive tracers and conventional lathe-sectioning techniques. Their x-ray diffraction techniques follows the shift of the diffraction line edge to find the surface concentration of the diffusing platinum. The relationships between the surface concentration and the diffusion coefficient are ob-

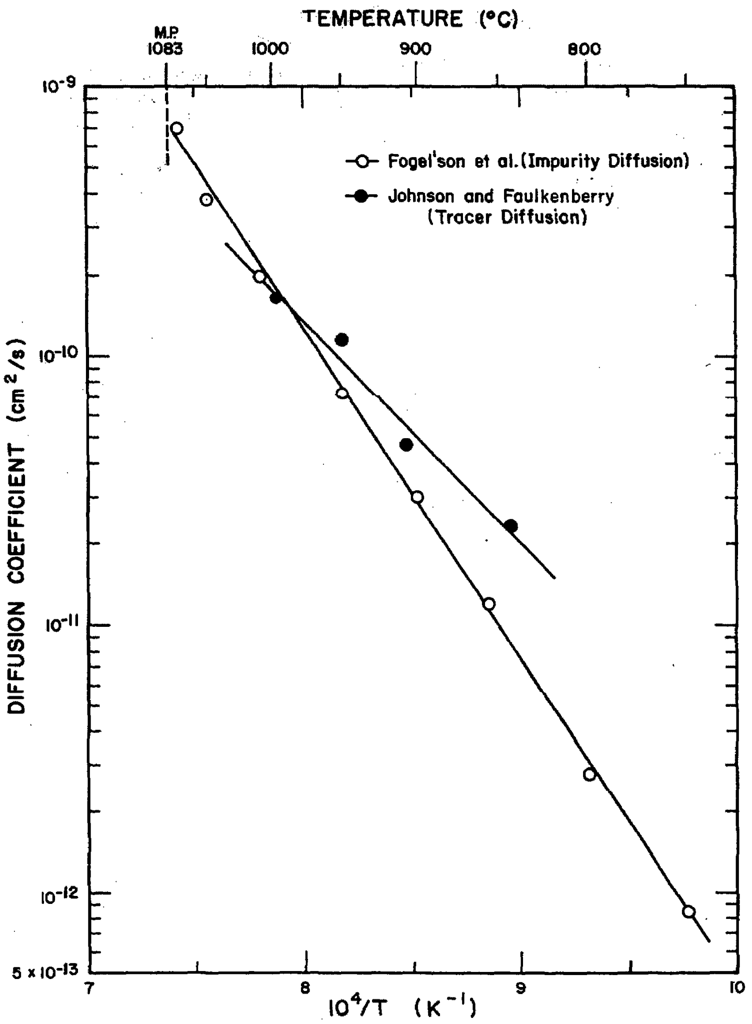

FIGURE 51. Diffusion coefficients of platinum in polycrystalline copper as a function of reciprocal absolute temperature.

Johnson and Faulkenberry [1] used ^{195m}Pt as a tracer, whereas Fogel'son et al. [2] employed a thin film of platinum.

TABLE 33. Tracer diffusion coefficients of ^{195m}Pt in pure polycrystalline copper. Data from Johnson and Faulkenberry [1].

T (±2°C)	D* (cm^2/s)
997	1.64×10^{-10}
950	1.14×10^{-10}
906	4.69×10^{-11}
843	2.36×10^{-11}

tained from the solution to the diffusion equation for the case of diffusion from a very thin layer into a semi-infinite body [3–6]. The temperature dependence of the platinum diffusion coefficients (see table 34) measured in the temperature range 750–1075 °C (±2°) is illustrated in figure 51. The Arrhenius equation (with probable errors) arrived at after a least-squares analysis is:

$$D_{\mathrm{Pt}\rightarrow\mathrm{Cu}} = (0.67 {}^{+0.26}_{-0.19}) \exp[-(55.7 \pm 0.78) \text{ kcal}\cdot\text{mol}^{-1}/RT] \text{ cm}^2/s.$$

These values of the pre-exponential factor and activation energy are more in agreement with those values found for other metals in this periodic group (Ni and Pd).

TABLE 34. Diffusion coefficient of platinum from an electrodeposited thin layer into polycrystalline copper. From data of Fogel'son et al. [2].

T (±2°C)	D (cm^2/s)
1075	7.0×10^{-10}
1050	3.8×10^{-10}
1009	2.0×10^{-10}
950	7.3×10^{-11}
900	3.0×10^{-11}
856	1.2×10^{-11}
800	2.8×10^{-12}
750	8.5×10^{-13}

6.2. Cu*→ Pt

Concurrent with their previously described experiments, Johnson and Faulkenberry [1] also measured the diffusion rates of radioactive ^{64}Cu in chemically pure polycrystalline platinum over the temperature range 1098–1375 °C (±2°). The experimental procedures employed were similar to those employed and described for their platinum tracer diffusion studies in pure copper. The results of their experiments are summarized in table 35 and figure 52. A least-squares method was utilized to fit the measured tracer diffusion coefficients to the straight line shown in figure 52. The resulting Arrhenius expression (with probable errors) used to describe the diffusion process is:

TABLE 35. Tracer diffusion coefficients of ^{64}Cu in pure polycrystalline platinum. Data from Johnson and Faulkenberry [1].

T (±2°C)	D* (cm^2/s)
1375	7.93×10^{-10}
1290	4.06×10^{-10}
1199	1.02×10^{-10}
1098	2.32×10^{-11}

$$D_{\mathrm{Cu}^*\rightarrow\mathrm{Pt}} = (0.074^{+0.090}_{-0.041}) \exp[-(59.5\pm2.4)\ \mathrm{kcal\cdot mol^{-1}}/RT]\ \mathrm{cm^2/s}.$$

No other investigations have been reported to confirm these data.

6.3. Pt*→ Cu-Pt

In addition to their investigations with pure copper, Johnson and Faulkenberry [1] also diffused platinum tracers into a series of Cu-Pt alloys. Of the four compositions studied [Cu-Pt(9.8, 24.6, 49.4, and 74.5 at.%)], two had the nominal composition for the intermetallic compounds (Cu_3Pt and CuPt), and the remaining two were located on the copper-rich and platinum-rich side of the phase diagram. As in their experiments with pure copper, the relative concentration of the diffusion platinum in the annealed specimens were determined by measuring the relative activities of radioactive platinum in each sample section. The calculated platinum diffusion coefficients are listed in table 36 and plotted as a function of reciprocal absolute temperature in figure 53. The straight lines were fitted using a least-squares fit of the tracer diffusion coefficients to the Arrhenius equation. The diffusion constants (and their probable errors) defining these lines are listed in table 36 along with the other experimental data.

The large amount of scatter evident in the specimen containing 9.8 at.% platinum was attributed to a "flake" forming on the plated portion of the specimen and which subsequently broke off during the first lathe-sectioning cut.

6.4. Cu*→ Cu-Pt

Johnson and Faulkenberry [1] measured the ^{64}Cu diffusion coefficients in the same alloys employed in the platinum tracer diffusion studies described in the previous section. Again, the experimental technique was the same as described in the previous section—electrodeposition of the copper tracer followed by diffusion anneals and subsequent lathe-sectioning, counting, etc. The calculated copper tracer diffusion coefficients are summarized in table 37 and plotted as a function of reciprocal absolute temperature in figure 54. A least-squares fit of the diffusion coefficients to the Arrhenius equation yields the straight line shown in the figure. The values of the pre-exponential and activation energy (and their probable errors) are listed in table 37.

It should be noted here that in these experiments of Johnson and Faulkenberry (as well as the previously discussed work of theirs), they experienced a deviation from linearity in their concentration-penetration relationship when the concentrations were plotted on semilog paper against the square of the penetration distance,

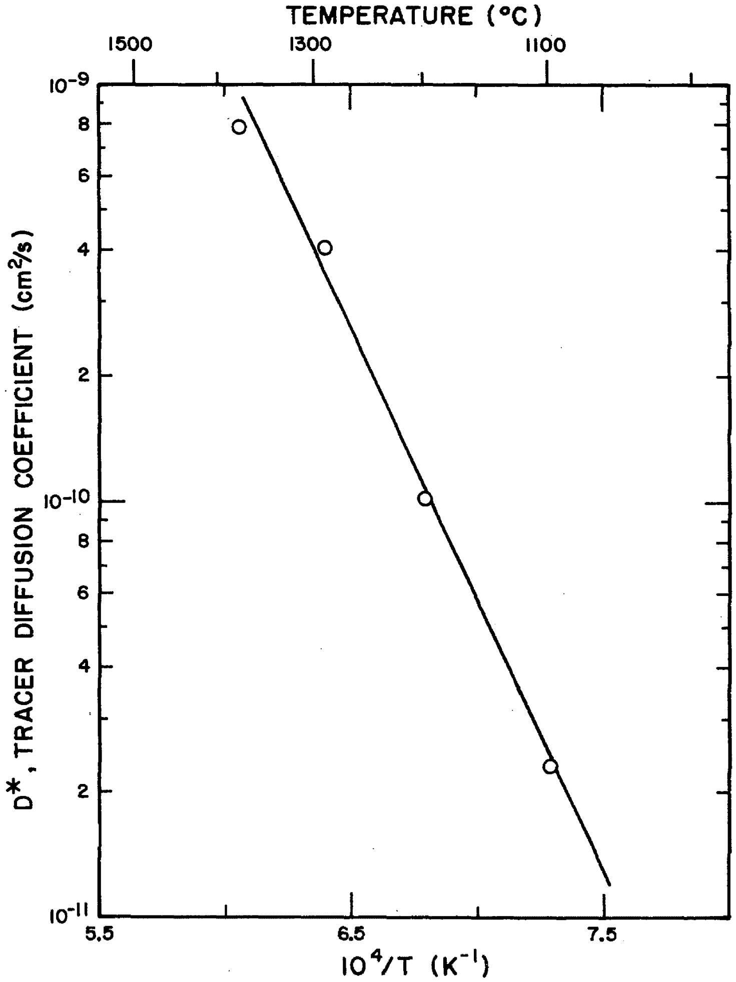

FIGURE 52. Tracer diffusion coefficients of ^{64}Cu in polycrystalline platinum as a function of reciprocal absolute temperature.

Data taken from the experiments of Johnson and Faulkenberry [1].

thus causing some uncertainty in their measurements. Additionally, the preparation of their alloys, particularly near the compositions CuPt and Cu_3Pt, proved to be difficult, with the very brittle alloys often cracking. The possibility of a new phase forming in some of the couples was mentioned by the authors.

In view of the experimental problems which plagued Johnson and Faulkenberry, their results should be treated with a great deal of caution. Their numbers are shown here in sections 6.1 to 6.4 only because of the paucity of data available for this alloy system.

6.5. Cu-Pt Interdiffusion

Matano [7], and Kubaschewski and Ebert [8] in early publications reported widely varying activation energies for interdiffusion between copper and platinum. The more recent studies have employed the electron-microprobe analyzer, and include the investigations of Hartley and Steedly [9], and Ogilvie et al. [10] The former never published the results of their experiments in the temperature range 794–1021 °C, whereas the latter noted the considerable difficulty incurred in bonding the sandwich couples (both pure metal couples and incremental couples) of this alloy system, as well as the development of a considerable amount of non-Kirkendall porosity at the interfaces of the couples. Although concentration versus distance data (at temperatures from 794 to 1021 °C) were determined, no diffusion coefficients were calculated for the 24 couples studied. The concentration gradients obtained from experiments at 794 °C exhibited two discontinuities in concentration, probably caused by long-range ordering in the alloy. Also found was that the marker-interface concentration was nearly pure copper in the diffusion zones of couples constructed of pure copper and platinum, and those couples of pure copper bonded to a Cu-Pt alloy.

TABLE 36. Tracer diffusion coefficients and diffusion parameters of ^{195m}Pt in polycrystalline Cu-Pt alloys. After data of Johnson and Faulkenberry [1].

Cu-Pt Alloy (at.%/wt% Pt)	T (±2°C)	D* (cm^2/s)	Diffusion Parameters	
			D$_0$ (cm^2/s)	Q (kcal/mol)
9.8/25	1058	2.86×10^{-10}	$0.093^{+0.42}_{-0.076}$	52.6 ± 4.3
	1057	1.84×10^{-10}		
	1000	9.52×10^{-11}		
	952	2.70×10^{-11}		
	906	2.08×10^{-11}		
24.6/50	1094	1.18×10^{-10}	$0.019^{+0.041}_{-0.013}$	51.4 ± 3.0
	1055	5.46×10^{-11}		
	1001	2.84×10^{-11}		
	946	1.07×10^{-11}		
49.4/75	1287	4.12×10^{-10}	$0.066^{+0.126}_{-0.044}$	59.5 ± 3.0
	1171	6.47×10^{-11}		
	1140	3.69×10^{-11}		
	1034	7.57×10^{-12}		
74.5/90	1382	2.81×10^{-10}	$0.022^{+0.081}_{-0.017}$	60.3 ± 4.7
	1288	5.70×10^{-11}		
	1171	1.93×10^{-11}		
	1140	9.30×10^{-12}		

TABLE 37. Tracer diffusion coefficients and diffusion parameters of ^{64}Cu in polycrystalline Cu-Pt alloys. Data from Johnson and Faulkenberry [1].

Cu-Pt Alloy (at.%/wt% Pt)	T (±2°C)	D* (cm^2/s)	Diffusion Parameters	
			D$_0$ (cm^2/s)	Q (kcal/mol)
9.8/25	1046	2.09×10^{-9}	$1.1^{+1.8}_{-0.7}$	52.8 ± 2.5
	990	6.75×10^{-10}		
	939	3.26×10^{-10}		
	899	1.63×10^{-10}		
24.6/50	1096	1.13×10^{-9}	$0.53^{+1.01}_{-0.42}$	54.7 ± 3.9
	1054	4.09×10^{-10}		
	1002	2.27×10^{-10}		
	947	8.63×10^{-11}		
49.4/75	1293	2.38×10^{-9}	$0.027^{+0.022}_{-0.012}$	51.0 ± 1.7
	1203	7.00×10^{-10}		
	1104	2.66×10^{-10}		
	1000	4.90×10^{-11}		
74.5/90	1385	2.08×10^{-9}	$0.67^{+0.83}_{-0.37}$	64.4 ± 1.2
	1290	7.40×10^{-10}		
	1199	1.52×10^{-10}		
	1098	3.94×10^{-11}		

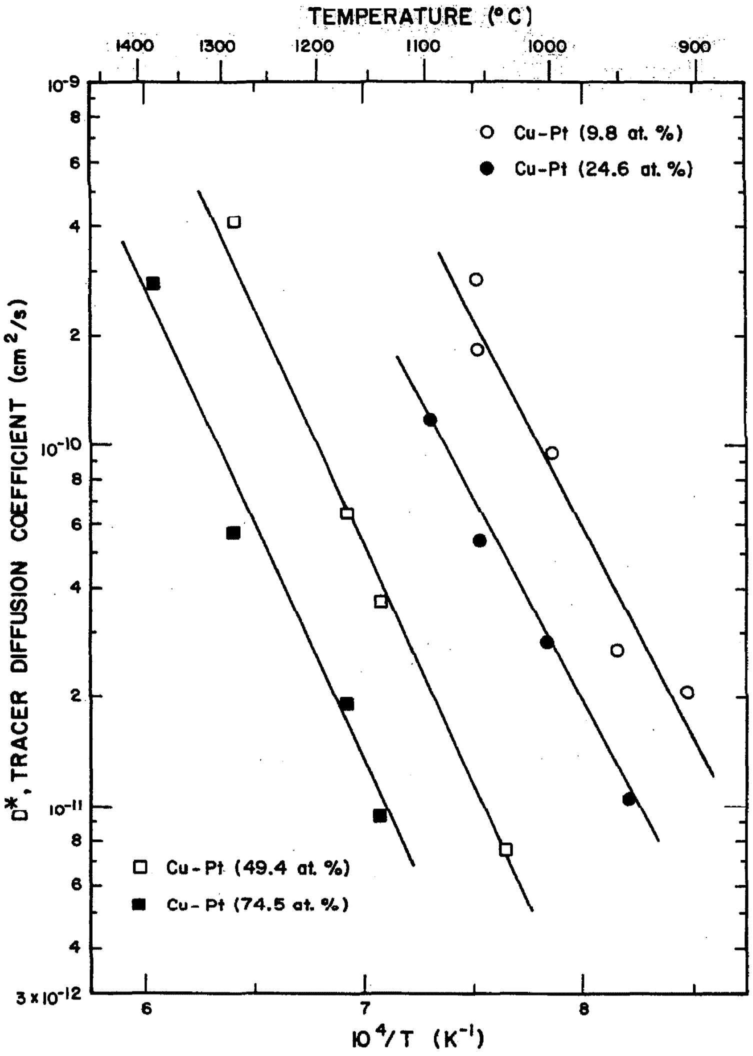

FIGURE 53. Tracer diffusion coefficients of ^{195m}Pt in polycrystalline Cu-Pt alloys as a function of reciprocal absolute temperature.

Data taken from the experiments of Johnson and Faulkenberry [1].

6.6. Cu-Pt-O

Wagner [11] has made a theoretical analysis of the concurrent diffusion processes occurring during the internal oxidation of Cu-Pt alloys where Cu_2O is formed as an external scale (as well as deeper in the Cu-Pt alloy due to inward diffusion of oxygen).

6.7. Cu-Pt References

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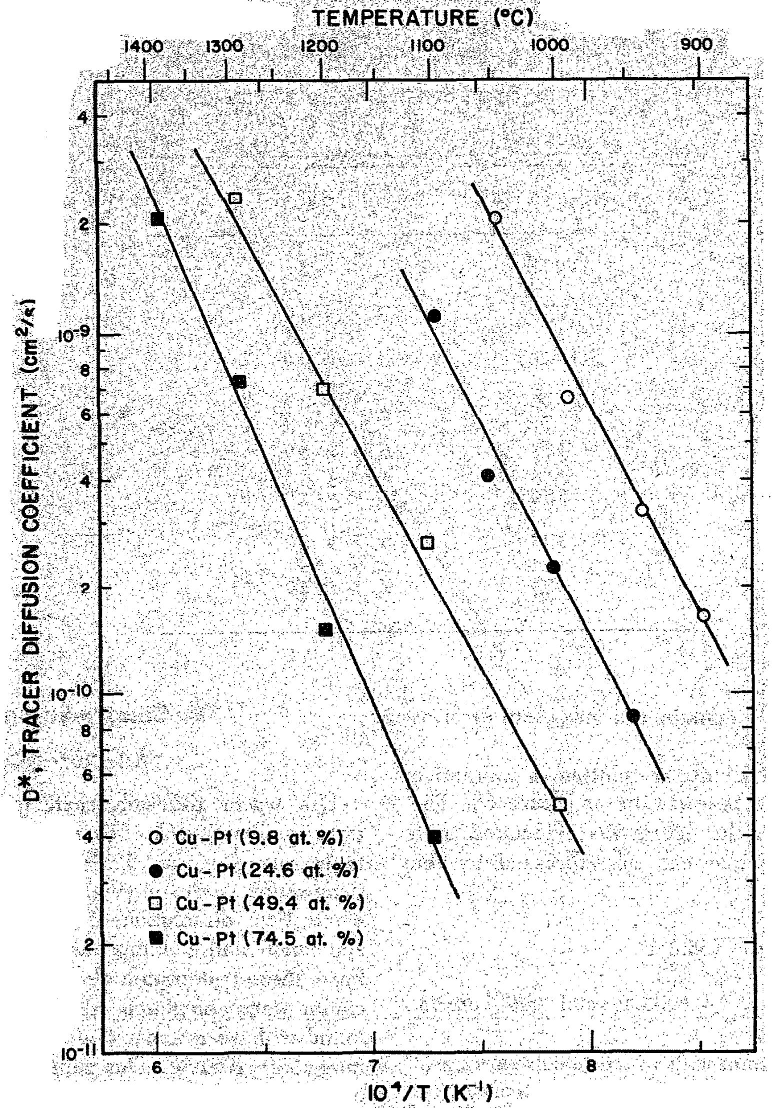

FIGURE 54. Tracer diffusion coefficient of ^{64}Cu in polycrystalline Cu-Pt alloys as a function of reciprocal absolute temperature.

Data taken from the experiments of Johnson and Faulkenberry [1].

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7. Copper-Rhodium

7.1. Rh→ Cu

The impurity diffusion of rhodium in copper foils has been measured in the temperature range 750–1075 °C by Fogel'son and coworkers [1]. The experiments utilized an x-ray diffraction technique [2–4] to follow the impurity diffusing in the thin (3 to 15 μm) polycrystalline copper foils. A thin layer (0.06 to 0.4 μm) of rhodium was initially deposited on the copper foil. The lattice parameter changes occurring during the diffusion anneals were followed by diffraction-line profile shifts. From the knowledge of the changes in surface concentration of the rhodium and the application of the diffusion equation for the above-mentioned boundary conditions, the diffusion coefficients (mean values) listed in table 38 were arrived at. Although no errors in the values of the coefficients were mentioned in the authors' paper, earlier published work [2] using this

TABLE 38. Impurity diffusion coefficients of rhodium in thin polycrystalline copper foils. Data excerpted from Fogel'son et a. [1].

T (°C)	D (cm^2/s)
1075	1.3×10^{-9}
1050	8.1×10^{-10}
1000	3.5×10^{-10}
950	1.4×10^{-10}
907	6.6×10^{-11}
856	2.0×10^{-11}
800	4.7×10^{-12}
750	1.4×10^{-12}

experimental technique contained a maximum error of 25%.

These diffusion coefficients are plotted as a function of reciprocal absolute temperature in figure 55. The straight line shown in the figure was calculated by a least-squares analysis and can be expressed by the Arrhenius equation:

$$D_{\text{impurity}} = (3.3^{+0.9}_{-0.7}) \exp[-(58.0 \pm 0.6) \text{ kcal} \cdot \text{mol}^{-1}/RT] \text{ cm}^2/\text{s}.$$

There are no other data with which to compare these results. It may be noted that although the experimental method employed by the authors is not as accurate as some of the traditional radioactive-tracer sectioning techniques, the above results are not unusual when compared to other transition metals, and particularly those of the same group (Pd, Ni).

7.2. Cu-Rh References

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8. Copper-Ruthenium

8.1. Ru*→ Cu

The tracer diffusion coefficient of ^{103}Ru in high-purity single crystals of copper has been measured in the temperature range 725–1062 °C [1–4]. Ruthenium penetration curves in copper were obtained through the electrolytic dissolution of thin layers of the diffused specimens and counting the activity contained therein. From these penetration plots, the tracer diffusion coefficients were calculated (see fig. 56 and table 39) and found to have a linear temperature dependence in the range 950–1062 °C. This dependence can be expressed by the Arrhenius equation:

$$D^*_{\text{Ru} \rightarrow \text{Cu}} = 8.5 \exp(-61.50 \text{ kcal} \cdot \text{mol}^{-1}/RT) \text{ cm}^2/\text{s}.$$

The authors estimate that an error of 5–10% to be present in the value of the tracer diffusion coefficient and ±1 kcal in the activation energy.

The large positive deviations from linearity below approximately 950 °C are attributed to the dislocation network (5×10^6 dislocations per square centimeter present in the single crystals used) and the segregation of the solute along these line defects.

8.2. Dislocation Pipe Diffusion

Taking the data discussed above, Bernardini and Cabane [2–4] separated out the enhancement ΔD (the difference, ΔD, is defined as the experimentally-measured tracer diffusion coefficient, $D^*_{\text{meas.}}$, minus the true tracer diffusion coefficient, D^*) due to the presence

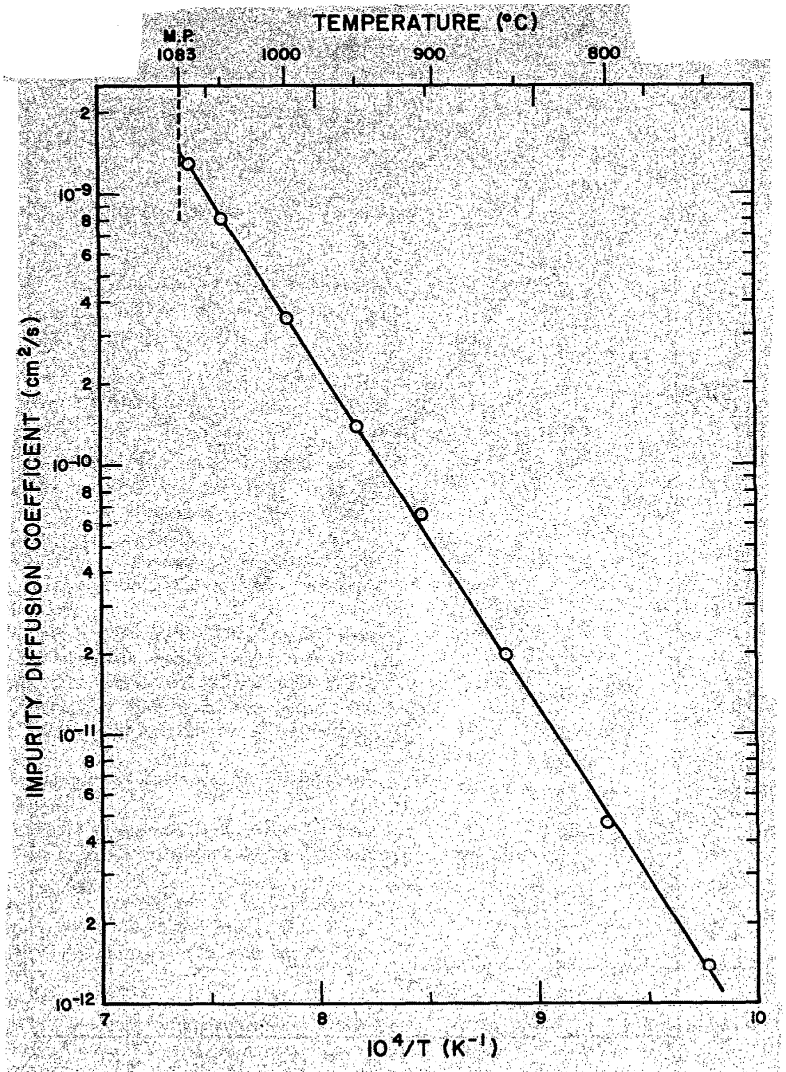

FIGURE 55. The impurity diffusion coefficients of rhodium in copper foils as a function of reciprocal absolute temperature.

From the data of Fogel'son et al. [1].

of dislocations. Calculation of enhancement was accomplished through the application of Hart's model [5] (influence of dislocation density) and Mortlock's analysis [6] (influence of solute segregation along the dislocations). The results of the calculations are shown in table 40, and are plotted in figure 57 as log $\Delta D/D^*$ versus reciprocal absolute temperature. A straight line was fitted to the data allowing for the evaluation of the appropriate diffusion parameters. The resulting Arrhenius expression for the diffusion occurring along the dislocation network was calculated as:

$$D_d(C_d/C_v) = 10^3 \exp(-36.0\ \text{kcal}\cdot\text{mol}^{-1}/RT)\ \text{cm}^2/\text{s},$$

where D_d is the diffusion coefficient of ^{103}Ru along the dislocations; C_u is equilibrium concentration of ^{103}Ru along the dislocations; and C_v is the concentration of ^{103}Ru in the lattice.

Bernardini and Cabane supplemented the above-mentioned measurements with experiments [4] to obtain the pipe-diffusivity, D_{pipe} (D_{pipe} is defined as equal to the product $D^*_d \times A \times k$, where D^*_d is the tracer diffusivity in the dislocation, A is the effective cross-sectional area of the dislocation pipe, and k is the ratio of the concentration of the diffusing element along the dislocation, C_d, to its concentration in the lattice, C_v) of ^{103}Ru in single crystals of copper. The authors take the effective cross-sectional area of a dislocation to be 10^{-14} cm². These measurements relied on measuring the residual activity contained in specimens diffused at temperatures between 672 and 840 °C. To calculate the pipe diffusivity, the mathematical analysis of Pavlov

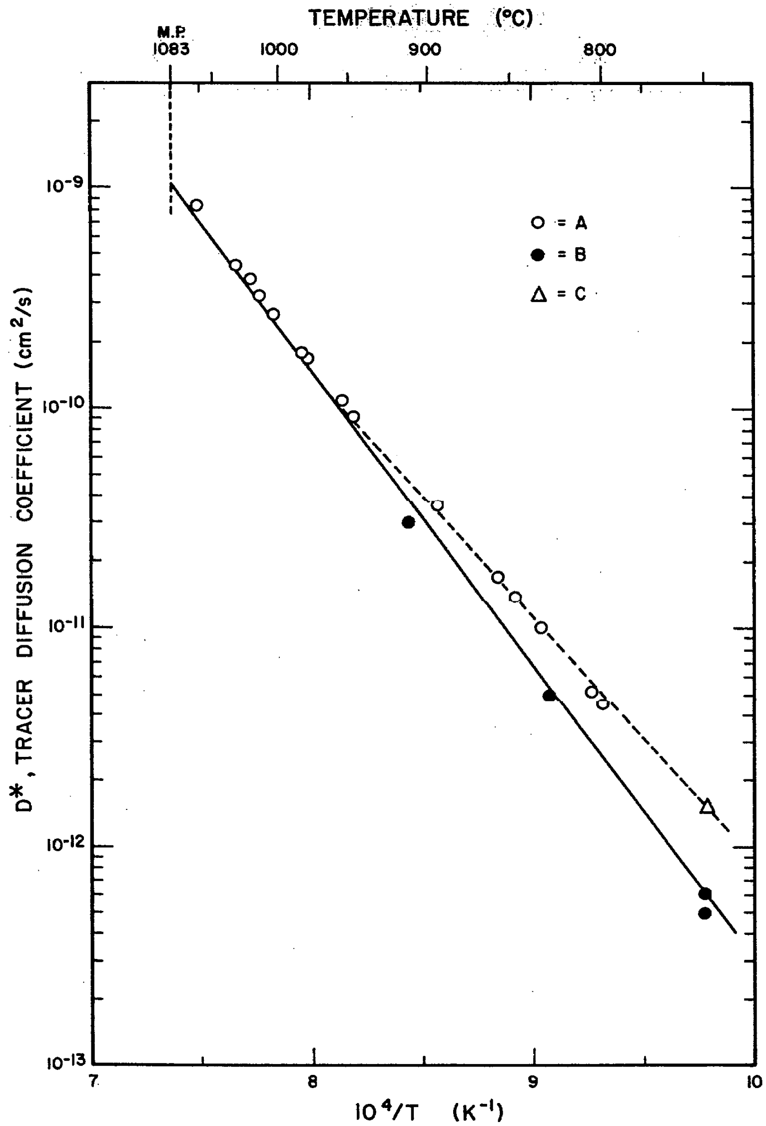

FIGURE 56. The tracer diffusion coefficients of ^{103}Ru in pure single crystals of copper as a function of reciprocal absolute temperature.

The "A" data points represent D values determined from long-time diffusion. The "B" data points were determined from the initial part of penetration curves where the treatment time was such that $(D_v \cdot t)^{1/2} < 5 \times 10^{-4}$ cm. The "C" datum point was calculated from the residual activity of the sample; the penetration curve typical of the volume kinetics obtained from a treatment time such that $(D_v \cdot t)^{1/2} > 5 \times 10^{-4}$ cm.

The data exhibit a linear temperature dependence in the range 950–1062 °C. Below 950 °C an enhanced penetration rate is attributed to dislocations. Data taken from Bernardini and Cabane [3, 4].

[7] and Brebec [8] (both based on Fisher's arguments [9]) were employed. The results are shown in table 41 and plotted in figure 58 as a function of reciprocal absolute temperature. The data are fitted with a straight line which can be expressed by the Arrhenius equation:

$$D_{\mathrm{pipe}} = 2.6 \times 10^{-13} \exp(-33\ \mathrm{kcal} \cdot \mathrm{mol}^{-1}/RT)\ \mathrm{cm}^2/\mathrm{s}.$$

Errors are estimated to be ±40% in the pipe diffusion coefficient, and ±3 kcal/mol in the activation energy for diffusion along the dislocations.

8.3. Cu-Ru References

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TABLE 39. Tracer diffusion coefficients of ^{103}Ru in pure single crystal copper. Data from Bernardini [2].

T (°C)	D* (cm²/s)
1062	8.4×10^{-10}
1033	4.5×10^{-10}
1020	3.9×10^{-10}
1015	3.3×10^{-10}
1003	2.7×10^{-10}
984	1.8×10^{-10}
980	1.7×10^{-10}
955	1.1×10^{-10}
948	9.2×10^{-11}
912	[a] 3×10^{-12}
894	3.6×10^{-11}
857	1.7×10^{-11}
857	1.4×10^{-11}
848	1.4×10^{-11}
833	1×10^{-11}
830	[a] 5×10^{-12}
807	5.2×10^{-12}
800	4.5×10^{-12}
750	[b] 1.5×10^{-12}
750	[a] 6×10^{-13}
750	[a] 5×10^{-13}

[a] Determined from the initial part of the penetration curve where the treatment time was such that $(D_V \cdot t)^{1/2} < 5 \times 10^{-4}$ cm.

[b] Determined from the initial part of the penetration curve where the treatment time was such that $(D_V \cdot t)^{1/2} > 5 \times 10^{-4}$ cm.

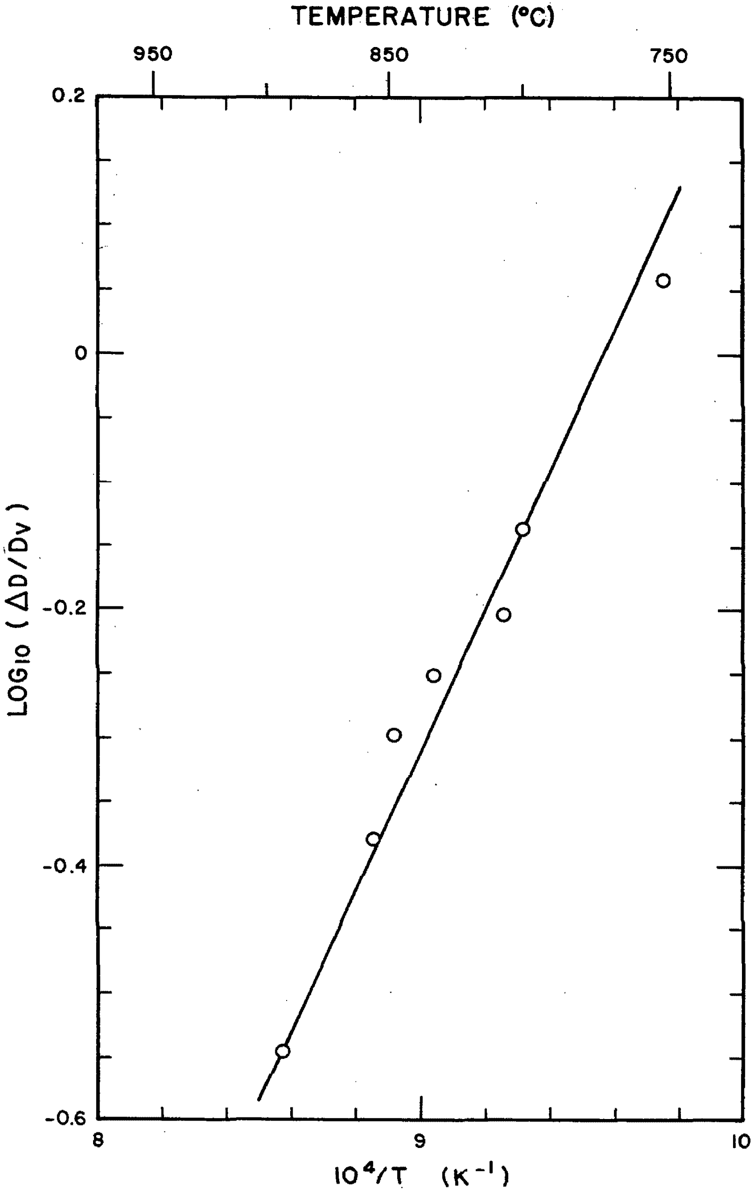

FIGURE 57. The logarithm of the ratio of enhancement of the tracer diffusion coefficient of ^{103}Ru in pure copper (due to the presence of dislocations) as a function of reciprocal absolute temperature.

Data taken from Bernardini and Cabane [3].

TABLE 40. Logarithm of the ratio of the increase in the diffusion coefficient of ^{103}Ru in copper due to dislocations, to the lattice diffusion coefficient. Data from Bernardini [2].

T (°C)	Diffusion Coefficient (cm^2/s) D^*_{meas}	 D^*_{vol}	Log_{10} $(\Delta D/D^*_{vol})$
894	3.6×10^{-11}	2.8×10^{-11}	-0.54
857	1.7×10^{-11}	1.2×10^{-11}	-0.38
848	1.4×10^{-11}	9.3×10^{-12}	-0.30
833	1×10^{-11}	6.4×10^{-12}	-0.25
807	5.2×10^{-12}	3.2×10^{-12}	-0.20
800	4.5×10^{-12}	2.6×10^{-12}	-0.13
752	1.5×10^{-12}	7.0×10^{-13}	-0.06

TABLE 41. Pipe diffusion coefficients of ruthenium in copper along dislocations. Data from Bernardini [2].

T (°C)	D_{pipe} (cm^2/s)
840	6.5×10^{-20}
809	1×10^{-19}
780	3.6×10^{-20}
750	2.4×10^{-20}
750	1.8×10^{-20}
720	2.1×10^{-20}
700	1×10^{-20}
689	9.5×10^{-21}
672	7×10^{-21}

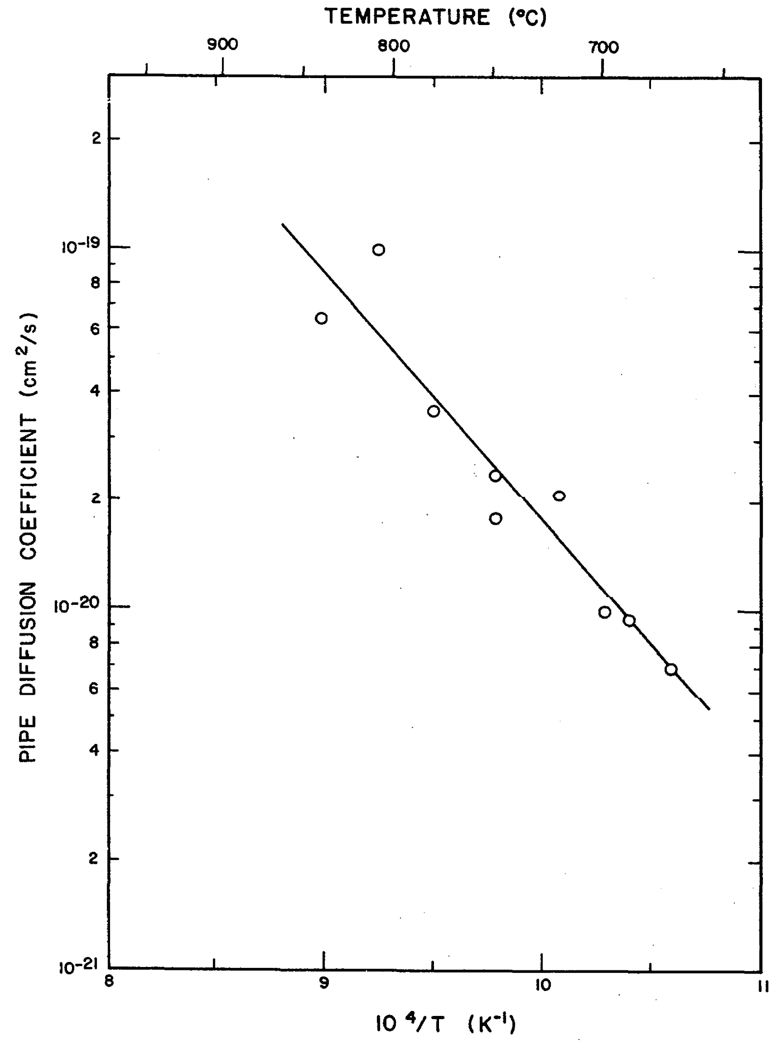

FIGURE 58. The logarithm of the pipe diffusivity of ^{103}Ru along dislocations in pure copper as a function of reciprocal absolute temperature.

Data taken from Bernardini and Cabane [4].