Diffusion in copper and copper alloys. Part III. Diffusion in systems involving elements of the groups IA, IIA, IIIB, IVB, VB, VIB, and VIIB

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Diffusion in Copper and Copper Alloys

Part III. Diffusion in Systems Involving Elements of the Groups IA, IIA, IIIB, IVB, VB, VIB, and VIIB

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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 Groups IA, IIA, IIIB, IVB, VB, VIB, and VIIB. 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: Alloy diffusion; beryllium; cerium; cesium; chromium; copper; diffusion; electromigration; europium; grain boundary diffusion; hydrogen; impurity diffusion; interdiffusion; lanthanum; liquid metal diffusion; lithium; lutetium; magnesium; manganese; molybdenum; niobium; plutonium; potassium; praseodymium; promethium; rhenium; rubidium; sodium; surface diffusion; tantalum; terbium; ternary diffusion; thermomigration; thulium; titanium; tungsten; uranium; vanadium; zirconium.

Contents

List of Tables

Cu-Be

Cu-Ce

Cu-Eu

Cu-H

Cu-La

Cu-Li

Cu-Lu

Cu-Mg

Cu-Mn

Cu-Mo

Cu-Nb

Cu-Pm

Cu-Pr

Cu-Tb

Cu-Ti

Cu-Tm

Cu-U

Cu-W

Cu-Zr

List of Figures

Cu-Be

Cu-Ce

Cu-Cr

Cu-Eu

Cu-H

Cu-Li

Cu-Lu

Cu-Mn

Cu-Mo

Cu-Nb

Cu-Pm

Cu-Pr

Cu-Tb

Cu-Ti

Cu-Tm

Cu-U

Cu-Zr

1. Introduction

1.1. Organization of Review According to Alloy System

The present review is the third in a series designed to provide data on diffusion in copper and copper alloys. The first paper [1] [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 present paper continues with the coverage of diffusion in copper alloy systems. Data on diffusion in

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[1] Figures in brackets indicate literature references.

systems which involve elements of the groups IA, IIA, IIIB, IVB, VB, VIB, and VIIB are presented in the present paper. Succeeding papers in this series will cover the remaining copper alloy systems.

Each Cu-X alloy system 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-Be system includes all diffusion situations which involve both copper and beryllium. This same format will be followed for all Cu-X systems. According to this format, the Cu-Be review treats:

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

To present the data in as systematic a form as possible, diffusion situations which involve only copper and beryllium (items 1, 2, and 3 in the above list) are discussed first and are presented in separate subsections under the Cu-Be system. Then, situations involving a third element in addition to copper and beryllium are presented. A separate subsection of this type appears for each third element. These subsections appear in alphabetical order according to the chemical symbol of the third element. If no diffusion data are available on a given three-component system, say Cu-Be-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. For easy reference, a list of subsections is provided in the table of contents for each alloy system.

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-Be-X. References to diffusion in multicomponent systems also are provided in the Cu-Be-M ternary system discussions.

The organization of the data by alloy systems should aid the reader in finding specific items of data desired. However, to avoid unnecessary fragmentation, all diffusion data for systems which include, for example, copper, beryllium, and a given third element M, are listed under the single ternary system, Cu-Be-M. This procedure effectively combines in a single set of subsections items 4, 5, 6, and 7 of the above listing. Thus, diffusion of M into Cu-Be alloys, diffusion in Cu-Be-M alloys, diffusion of copper into Be-M alloys, and diffusion of beryllium into Cu-M alloys all would be included in the Cu-Be-M subsection. Combining items 4 to 7 seems reasonable since, when an impurity, even in very dilute concentration, diffuses in a binary alloy, the resulting three-component system can be regarded as forming a ternary alloy. It is logical to discuss all such ternary Cu-Be-M alloys together, regardless of the concentrations of the species (i.e., Cu, Be, and M).

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

$$J=-D(\partial c/\partial x), \tag{1}$$

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,

$$D=D_0 \exp(-Q/RT). \tag{2}$$

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 $1.3806 \times 10^{-20} J \cdot K^{-1}$ 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 large number of these graphs are shown in the present review.

The textual discussion provides commentary on the experiments reported and, wherever possible, provides a further 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 behaviour in that system.

At temperatures near the melting point, volume diffusion through regions of good crystal structure is normally predominant. In substitutional copper alloys, volume diffusion usually occurs by a vacancy mechanism where atoms move by exchanging with neighboring vacancies. Thus, vacancy jump frequencies, vacancy concentrations, and non-random vacancy diffusion effects have an important influence on diffusion in these alloys. In addition, if interstitial atoms are present in an alloy, they may diffuse rapidly in volume diffusion by jumping directly from one interstitial site to another. Here, non-random effects can disappear.

At lower temperatures, diffusion along the easy paths provided by grain boundaries often becomes important. 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 as 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 defined 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 number of atoms c' per unit area (rather than 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, for example references [1 to 7]. In addition, specific references and comments are provided at points in the textural commentary where results from some of the less standard types of measurements are discussed.

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 usually 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 usually are considered more reliable (in the absence of other considerations) and are more easily evaluated.

1.3. Special Considerations in Alloys—Different Types of Diffusion Coefficients

For diffusion in alloys, one must be particularly careful to establish the kind of diffusion coefficient which is reported. There are at least two main types of diffusion experiments in alloys frequently reported in the literature, tracer diffusion and interdiffusion. These experiments, which are described in more detail below, yield "tracer diffusion coefficients" and "chemical interdiffusion coefficients", respectively. Also, a number of other types of diffusion measurements can yield still other types of "diffusion coefficients". Since the physical conditions defining these experiments differ from one another, the "diffusion coefficient" value measured in one type of experiment often differs from the "diffusion coefficient" measured in other experiments.

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 coefficients for the two constituents in a binary alloy 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 major 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. By contrast, J for the interdiffusion coefficient is the flux with respect to the ends of the specimen. 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^*. Equations relating D_i^I to these other diffusion coefficients are given, for example, in reference [8].

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 non-symmetric concentration-versus-distance profiles in some interdiffusion experiments. If a non-symmetric 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.

When $\langle v \rangle_F$ arises from a known driving force, F, it is found [9] that $\langle v \rangle_F = F \psi^{-1} D^*/kT$. For impurity diffusion or for diffusion in alloys, ψ^{-1} can be a rather complex quantity depending, for example, on the vacancy jump frequency ratios near an impurity, and sometimes even being negative. When the force, F, arises from a temperature gradient, one can define a "measured heat of transport", Q^{**}, such that $F = Q^{**}\psi \, T^{-1} \, (\partial T/\partial x)$, as described in reference [1]. Then, Q^{**} can be calculated directly from the ratio $\langle v \rangle_F/D^*$ as measured at temperature, T, and temperature gradient, $\partial T/\partial x$. Similarly, when the force, F, arises from an electric field, E, one can define a "measured effective charge," q^{**}, such that $F = q^{**}\psi E$. Here, q^{**} is the effective charge which appears in a conventional Nernst-Einstein relation, $\langle v \rangle_F/D^* = q^{**}E(kT)^{-1}$. Use of q^{**} provides a convenient means of reporting experimental results. However, q^{**} may differ greatly from the actual charge of the diffusing species.

In ternary and higher order multicomponent alloys, there will be more than one independent 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 coefficients, D_{ij}, where

$$J_i = -\sum D_{ij}\frac{\partial c_j}{\partial x}. \qquad (5)$$

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,

$$J_i = -\sum_{j\neq n} D^n_{ij}\frac{\partial c_j}{\partial x}, \qquad (6)$$

where

$$D^n_{ij} = D_{ij} - D_{in}. \qquad (7)$$

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

In interdiffusion experiments, the velocity, v_k, of the original interface lattice plane with respect to the ends of the specimen normally is proportional to $\tau^{-1/2}$, where τ is the diffusion time. Here, it is assumed that the original composition profile was a step function with a single step occurring at the original interface, and that the interdiffusion couple was held at a constant temperature for time, τ. The net shift in position of the original interface lattice plane, which can be measured for example by placing inert wires or other markers at this plane, is called the Kirkendall shift, x_k. For normal parabolic diffusion, where v_k is proportional to $\tau^{-1/2}$, the Kirkendall shift will be proportional to $\tau^{+1/2}$, since $x_k = \int_0^\tau v_k\,dt$. Then, for simple interdiffusion in a binary A–B alloy,

$$x_k = 2\tau(D^I_{\mathrm{A}} - D^I_{\mathrm{B}})\,(\partial N_{\mathrm{A}}/\partial x)_\tau. \qquad (8)$$

From this equation, it is apparent that there is no Kirkendall shift when the intrinsic diffusion coefficient, D^I_{A}, of species A equals the intrinsic diffusion coefficient, D^I_{B}, of species B. Also, in parabolic diffusion, $\partial N_{\mathrm{A}}/\partial x$ is proportional to $\tau^{-1/2}$, so eq (8) yields $x_k \propto \tau^{1/2}$, as expected.

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

$$\tilde{D} = N_{\mathrm{A}}D^I_{\mathrm{B}} + N_{\mathrm{B}}D^I_{\mathrm{A}}. \qquad (9)$$

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 (8) and (9).

The tracer diffusion coefficient, D^*_i, is directly related to the atom jump frequency for atoms of species i and also to the average displacement of an individual atom. According to kinetic diffusion theory, atom jump frequencies are expected to depend exponentially on reciprocal absolute temperature. Thus, there is a direct reason from kinetic theory to expect D^*_i to depend exponentially on reciprocal absolute temperature, as in eq (2). By contrast, the temperature dependence of D^I or $\tilde{D}$ may be more complex. Even so, eq (2) is commonly used in the literature to express the temperature dependence of these other diffusion coefficients, too.

Since tracer measurement usually can be made more accurately than other types of diffusion coefficient measurements, special attention is paid to tracer measurements in this review. In practical applications where one wants to know the probability of an individual atom penetrating through a thin homogeneous film or where diffusion of a very dilute constituent is of interest, knowledge of D^*_i is directly needed. In other applications, D^I or $\tilde{D}$ may more directly provide the information needed. As discussed above, these other diffusion coefficients, D^I and $\tilde{D}$, can often be related to the more fundamental quantity, D^*.

The intrinsic diffusion coefficients, D^I, also can be interpreted on an atomic level. In a simple interdiffusion experiment, the flux of atoms of species i across a given atomic lattice plane is proportional to D^I_i. The D^I thus determines the net transport of material across this lattice plane and the value of v_k at this plane.

The interdiffusion coefficient, $\tilde{D}$, is proportional to the rate at which an original concentration gradient in an interdiffusion experiment tends to smooth itself out. Thus, $\tilde{D}$ has an easily visualized macroscopic meaning. Since in most metallurgical applications one is concerned with interdiffusion between two bulk samples or in the rate of alloy homogenization, interdiffusion coefficients are of considerable technological importance.

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.

1.4. Diffusivity, Permeation, and Solubility of Gases in Metals and Alloys

In this paper, for the first time in the series, a fair amount of space is devoted to the diffusivity and permeability of a gas (hydrogen) in copper and its alloys. The experimental methods employed for the measurement of the diffusivity and permeability of gases in metals can generally be divided into two categories:

1. infusion/outgassing techniques
2. membrane techniques.

The general feature in infusion/outgassing experiments is that a solid specimen is allowed to equilibrate with a given gas pressure at a fixed temperature, and then permitted to outgas (in a vacuum) at the same temperature. The outgassing rate is measured versus time and allows for the calculation of the diffusivity of the gas (and the measurement of the total quantity of the gas desorbed allows for the calculation of the solubility).

The membrane techniques involve the measurement of gas transport through a solid membrane from a region of high gas concentration to one of a lower gas concentration. The details of membrane techniques will vary from laboratory to laboratory, but all the methods will have this common denominator.

It should be remembered that diffusion is only one of the mechanistic aspects of permeation. The gas permeation process involves several other essential steps, of which the lattice diffusion of the gas atom is only one. For example, in the permeation of a diatomic gas (such as H_2) through a metallic membrane, the following steps (in consecutive order) are part of the permeation process:

1. Transfer of molecule from the gas phase to the surface (Van der Waal's adsorption).
2. Attraction of the molecule or single atoms on the surface (chemisorption).
3. Transfer of an atom from the surface to the bulk of the metal (dissolution of the gas in the metal).
4. *Diffusion* (lattice) of the gas atoms through the membrane.
5. Transfer of atoms from the solid solution at the low pressure side to the surface.
6. Recombination of atoms to form molecules on the low pressure surface.
7. Desorption of the gas from the low pressure surface.

In general (for those membranes which are not too thin), permeability is diffusion-controlled, and since all steps are consecutive, the rates at which all others proceed will become equal to the diffusion rate when the steady state is reached.

The diffusivity (D), permeability (K), and solubility (S) of hydrogen in metals (at dilute hydrogen concentrations) depend exponentially on temperature according to the following Arrhenius-type equations [10, 11]:

$$D = D_0 \exp(-Q_D/RT), \tag{10}$$

$$S = S_0 \exp(-Q_S/RT), \tag{11}$$

$$K = DS = K_0 \exp(-Q_K/RT). \tag{12}$$

The pre-exponential, K_0, is equal to the product, D_0S_0, and the activation energy, Q_K, is equal to the sum, $Q_D + Q_S$. The units of permeability and solubility (like diffusivity) are expressed in the literature in a wide variety of ways. In this review, permeability data usually have been converted to the units of

$$\mathrm{cm^3(STP)\ s^{-1}\ cm^{-1}\ atm^{-n}}. \tag{13}$$

One cm^3(STP) is that quantity of an ideal gas which would occupy a volume of 1 cm^3 at standard temperature and pressure (STP) conditions of 0 °C and 1 atmosphere. Sieverts' Law [10, 11] allows $n = 1/2$ for the permeation of hydrogen or nitrogen through metals.

Solubilities in this paper have the following units:

$$\mathrm{cm^3(STP)\ cm^{-3}\ atm^{-n}} \tag{14}$$

for the purposes of data comparison. As with permeabilities, one cm^3(STP) and n have the same meaning here.

Diffusivities are expressed in the same units (cm^2/s) as elsewhere in this review.

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; British Iron and Steel Industry Translation Service (BISI), The Iron and Steel Institute, 39 Victoria Street, London, S.W. 1, England; National Translation Center (NTC), 35 West 33rd Street, Chicago, Illinois 61606.

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2. Copper-Beryllium

2.1. Be → Cu

The impurity diffusion of beryllium into pure polycrystalline copper in the temperature range 1075 to 700 °C has been investigated [1]. The beryllium impurity was diffused from a thin film deposited on the surface of a copper substrate and the changes in beryllium surface concentration were followed by an X-ray diffraction technique [2]. A relationship between the changes in surface concentration and lattice parameters allowed a beryllium diffusion coefficient to be calculated. The average values of these diffusion coefficients are listed in table 1. When plotted as a function of reciprocal absolute temperature, a straight line can be fitted to the data (see fig. 1). The resulting Arrhenius expression (with the

TABLE 1. Beryllium impurity diffusion coefficients in polycrystalline copper. Data excerpted from [1].

T(°C)	D(cm^2/s)
1075	2.1×10^{-8}
1050	1.1×10^{-8}
1000	5.7×10^{-9}
950	2.9×10^{-9}
900	1.2×10^{-9}
850	4.3×10^{-10}
800	1.7×10^{-10}
762	1.0×10^{-10}
700	2.4×10^{-11}

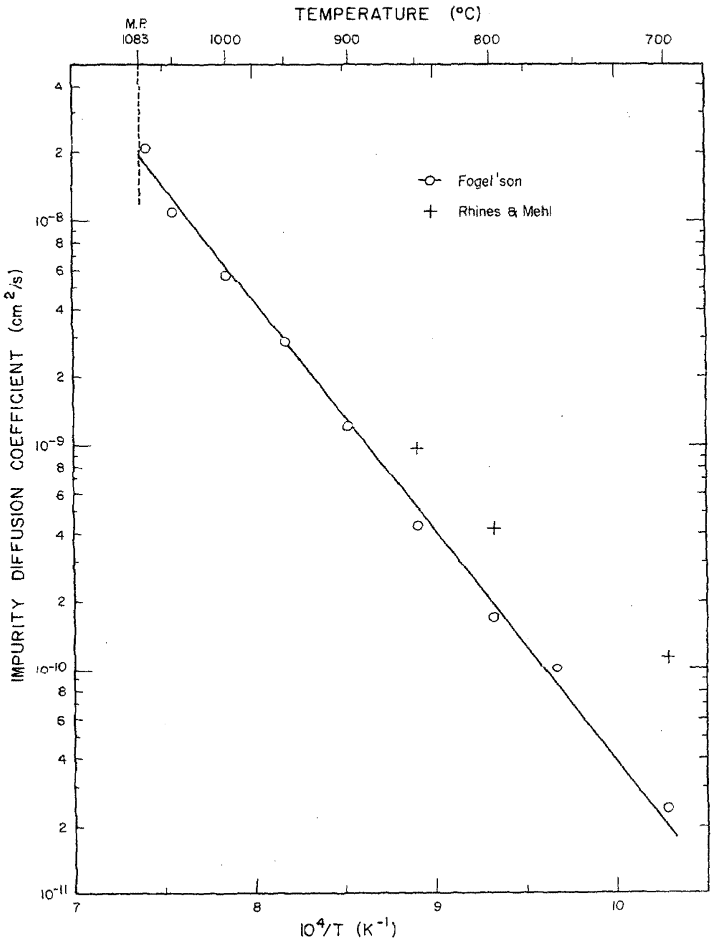

FIGURE 1. The beryllium impurity diffusion coefficient in copper as a function of reciprocal absolute temperature.

Data extracted from the papers of Fogel'son [1] and Rhines and Mehl [3].

author's calculated errors) for the impurity diffusion of beryllium in copper is

$$D = (0.66^{+0.38}_{-0.24}) \exp[-(46{,}800 \pm 1040 \text{ cal} \cdot \text{mol}^{-1})/RT] \text{ cm}^2/\text{s}.$$

Although not as accurate as tracer methods, the above technique does afford some measure of beryllium diffusion rates.

The interdiffusion data of Rhines and Mehl [3] was extrapolated to zero beryllium concentration to obtain estimated diffusion coefficients for beryllium in pure copper. These values are plotted in figure 1 with the above data for comparison

2.2. Cu* → Be

Measurements of the diffusion of radioactive ^{64}Cu into beryllium has been reported [4]. The tracer diffusion coefficients were determined both perpendicular ($D_\perp$) and parallel ($D_\parallel$) to the c-axis of the hexagonal close-packed structure of beryllium.

The ^{64}Cu was deposited onto the single crystals of "super-refined" beryllium. After diffusion, the Gruzin method of analysis [5] was used to determine the concentration gradient. The calculated values of the diffusion coefficients are listed in table 2. A plot of the log $D_\perp$ and log $D_\parallel$ vs. $(1/T)$ is shown in figure 2.

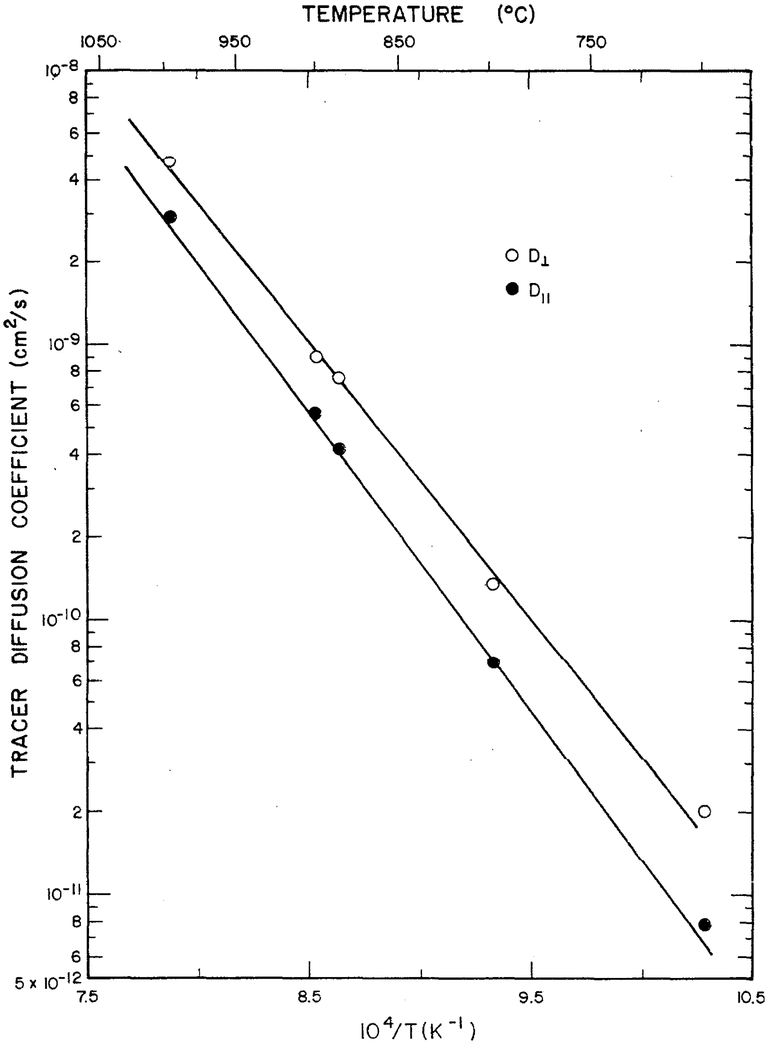

FIGURE 2. The tracer diffusion coefficient of ^{64}Cu in pure, single crystals of beryllium as a function of reciprocal absolute temperature.

The anisotropy of diffusion is apparent. Data taken from [4].

TABLE 2. Copper-64 tracer diffusion coefficients in beryllium. Data excerpted from [4]

T(°C)	D^*(cm^2/s) Perpendicular to c-axis	D^*(cm^2/s) Parallel to c-axis	$D_\perp/D_\parallel$
1000	4.70×10^{-9}	2.92×10^{-9}	1.60
900	9.37×10^{-10}	5.76×10^{-10}	1.62
883	7.7×10^{-10}	4.17×10^{-10}	1.85
799	1.35×10^{-10}	7.11×10^{-11}	1.90
699	2.05×10^{-11}	7.94×10^{-12}	2.59

It is interesting to note that if the lowest temperature point is ignored, the two lines could be easily drawn parallel (and thus no anisotropy in activation energy revealed). Assuming the data at the lowest temperature point are correct, the anisotropy of the diffusion of ^{64}Cu in beryllium can be expressed by the relations

$$D_\perp = 0.35 \exp\ (-45{,}900\ \mathrm{cal \cdot mol^{-1}}/RT)\ \mathrm{cm^2/s},$$

and

$$D_\parallel = 0.90 \exp\ (-49{,}500\ \mathrm{cal \cdot mol^{-1}}/RT)\ \mathrm{cm^2/s}.$$

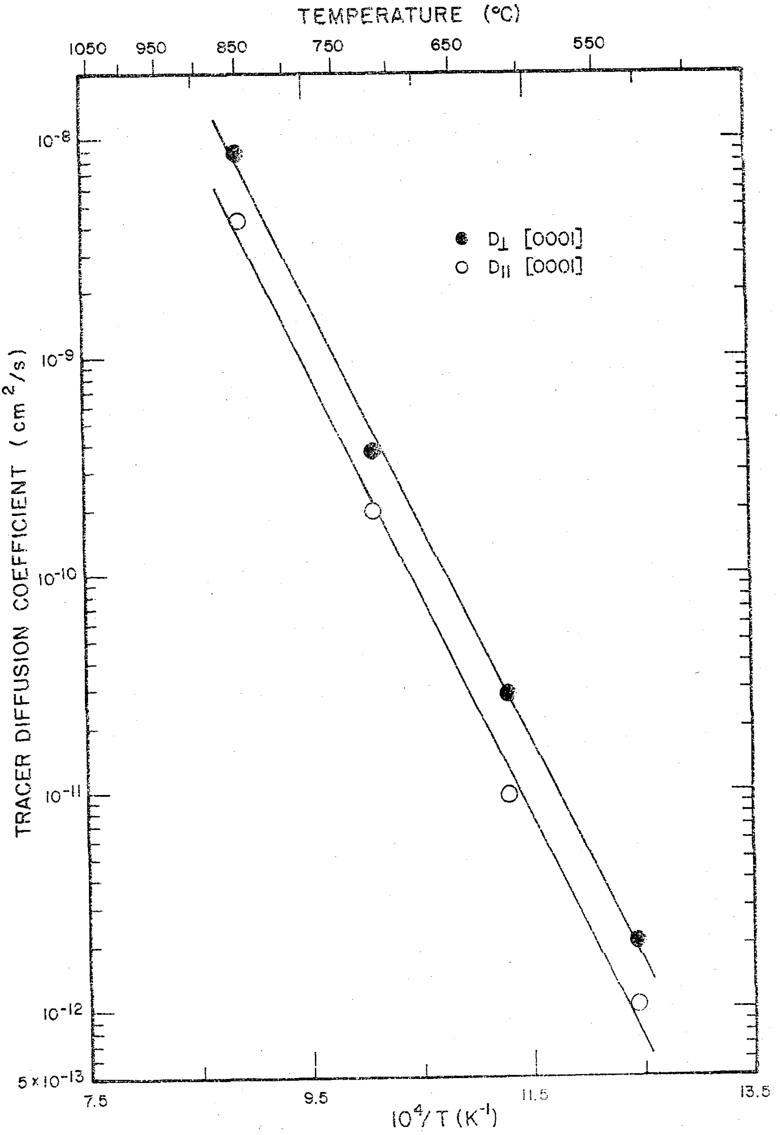

FIGURE 3. The tracer diffusion of beryllium in Be-Cu (10.3 wt%) alloys as a function of reciprocal absolute temperature.

Diffusion rates were measured both parallel and perpendicular to the c axis in the hexagonal-structured single crystals. Data excerpted from [7].

There have been no other tracer experiments in this system for comparison with these results, although low-temperature (420–640 °C) results [6] obtained from ion-backscattering experiments are consistent with the above-mentioned data.

2.3. Be* → Be-Cu

Concurrent with some high temperature creep studies of Be-Cu alloys, Le Hazif and co-workers [7] measured beryllium tracer diffusion coefficients in alloys containing 10.3 wt% (44.7 at.%) copper. Diffusion rates were measured both parallel ($D_{\parallel}$) and perpendicular ($D_{\perp}$) to the *c*-axis in the hexagonal-structured single crystals. The Gruzin formula [5] was used to calculate the tracer diffusion coefficients in the temperature range 850 to 500 °C. We have obtained the unpublished values of the tracer diffusion coefficients from the above-mentioned authors and plotted them in figure 3 as a function of reciprocal absolute temperature. Our least squares fit of the data yields straight lines which can be described by the following Arrhenius expressions:

perpendicular to the [0001],

$$D_{\perp}^{*}[0001]=9.03 \exp(-46.6 \text{ kcal}\cdot\text{mol}^{-1}/RT) \text{ cm}^2/\text{s},$$

and parallel to the [0001],

$$D_{\parallel}^{*}[0001]=5.99 \exp(-47.3 \text{ kcal}\cdot\text{mol}^{-1}/RT) \text{ cm}^2/\text{s}.$$

The above values for the pre-exponential factors and activation energies differ slightly from those published by Le Hazif et al.

Relative to self-diffusion rates in pure beryllium, the copper alloying additions reduce the mobility of the beryllium.

2.4. Cu-Be Interdiffusion

The most important of the early interdiffusion studies was the now "classic" investigation of the rates of diffusion of a number of solutes (including Be) in the α-solid solutions of copper by Rhines and Mehl [3]. Their results are often referred to, although their experiments were fraught with difficulties; most notably, those of recrystallization and grain growth in the diffusion zone. The data are presented here, although its reliability is open to question.

Their polycrystalline diffusion couples were composed of copper electrodeposited onto Cu-Be alloys (9.52–10.05 at.%/1.47–1.56 wt% Be). The diffusion temperatures ranged from 701 to 851 °C. The time of diffusion varied from 8.82 to 34.71 days. A Matano analysis [8] of the beryllium penetration data allowed for the evaluation of the interdiffusion coefficient. These calculated values are plotted in figure 4 with small extrapolations at either end of the curves. The log D vs. $(1/T)$ was plotted for a series of concentrations, and the activation energy, Q, was determined from the slopes. The relationships between Q and the solute concentrations are summarized in figure 5. Data contained in the diffusion-concentration plots were extrapolated to zero beryllium concentration to give an estimate of the impurity diffusion coefficients and are compared to the data of Fogel'son [1] in figure 1.

Nowick [9] was one of the first to question the data of Rhines and Mehl. Since the validity of the Rhines-Mehl data above is questionable, its use should be with caution.

A multiphase, interdiffusion study in the copper-beryllium system has been reported [10]. Diffusion data were obtained for all phases (α, β, γ, δ, ε) existing in the binary phase diagrams (as displayed in Hansen, Elliott, and Shunk [11]).

The diffusion couples were composed of pure copper (cathode Cu of 99.95 wt% Cu, containing less than 0.001 wt% O) bonded to relatively pure beryllium (which contained 0.13 wt% Fe, 0.07 wt% Cu, 0.03 wt% Si, 0.03 wt% Mg, 0.08 wt% Ca, 0.011 wt% Al, 0.02 wt% C, and an undetermined amount of O). Additional diffusion couples were made of pure copper and Cu-Be alloys of 12.0 wt% (49 at.%) beryllium for diffusion studies pertaining to the γ-phase, and Cu-Be alloys of 6.2 wt% (32 at.%) beryllium for diffusion studies relative to the β-phase. The diffusion anneals took place at 550, 650, 750, and 840 °C for 5 to 2000 hours.

The concentration gradients brought about by interdiffusion were determined, unfortunately, only from microhardness readings. The phases in the diffusion zone were examined metallographically. The growth of the phases was proportional to the square root of the time at temperature.

Interdiffusion coefficients were calculated via the Matano method and are listed in table 3.

The Arrhenius plot of log D vs. $(1/T)$ for these data is shown in figure 6.

The straight-line temperature-dependence of the interdiffusion coefficient allows the calculation of an activation energy, Q, and a pre-exponential, D_0, in the Arrhenius equation. These are listed in table 4.

The intrinsic diffusion coefficients were calculated according to Darken [12] for copper and beryllium for the β-phase only and are listed in table 5.

Values for the pre-exponential and the activation energy as obtained only from the pure-copper/pure-beryllium configuration are listed in table 6.

The motion of the weld-interface for a number of diffusion couple configurations was recorded by the authors.

The results of this multiphase interdiffusion study of Reinback and Krietsch do not agree with those of Rhines and Mehl [3] in the α-phase, although they are in agreement with Nowick's [9] calculations (who made use of the data of Rhines and Mehl). This agreement must be considered to be strictly fortuitous in view of the experimental difficulties experienced by Rhines and Mehl and the rather imprecise microhardness method of concentration analysis used by Reinbech and Krietsch.

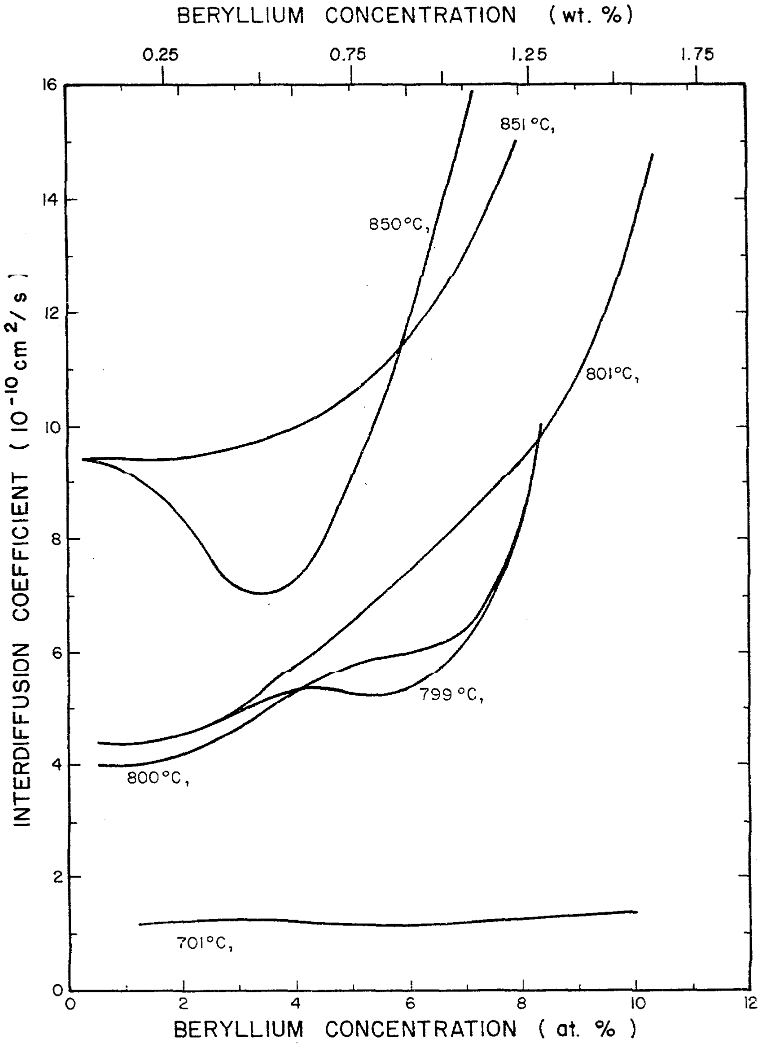

FIGURE 4. The interdiffusion coefficient of pure copper and Cu-Be alloys as a function of beryllium concentration at near 700, 800, and 850 °C for varying lengths of time.

Data taken from Rhines and Mehl [3].

TABLE 3. Interdiffusion coefficients in the copper-beryllium system. Data extracted from [10]

Diffusion Pair	Phase	$\tilde{D}$(cm^2/s)			
		840 °C	750 °C	650 °C	550 °C
Cu/Be	α	1.5×10^{-9}	2.8×10^{-10}	2.9×10^{-11}	3.2×10^{-12}
	β	6.7×10^{-8}	2.3×10^{-8}	5.1×10^{-9}	
	γ	4.7×10^{-8}	1.4×10^{-8}	1.9×10^{-9}	3.7×10^{-10}
	δ	4.5×10^{-10}	1.2×10^{-10}	1.9×10^{-11}	2.6×10^{-12}
	ε	5.1×10^{-10}			
Cu/Cu-Be(49 at.%)	α	2.3×10^{-9}	5.3×10^{-10}	2.4×10^{-11}	
	β	1.1×10^{-7}	3.5×10^{-8}	$2.4 \times 10^{-}$[illegible]	
Cu/Cu-Be(32 at.%)	α	2.5×10^{-10}	8.0×10^{-11}	$5.7 \times 10^{-}$[illegible]	

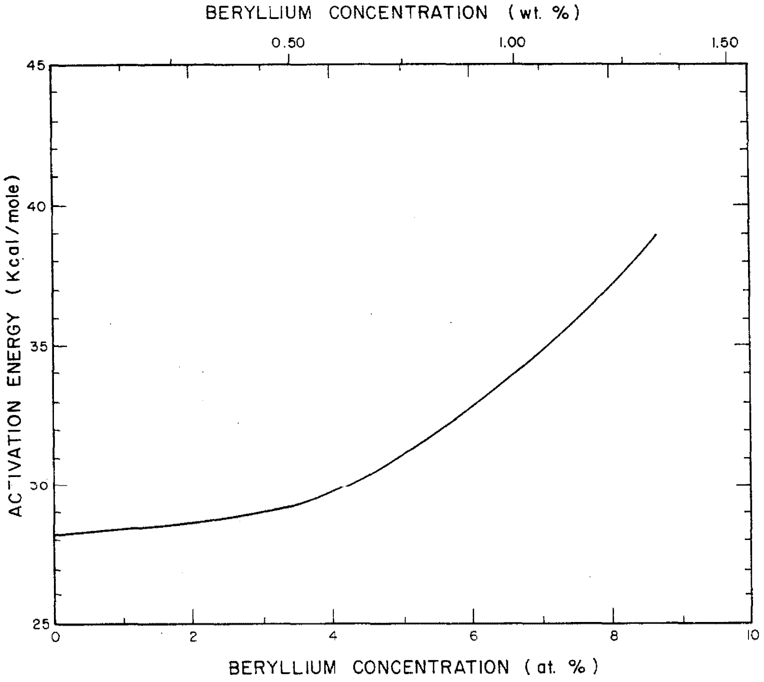

FIGURE 5. The activation energy for interdiffusion between copper and Cu-Be alloys (α-phase) as a function of beryllium concentration.

Data taken from [3].

Diffusion couples of zone-refined beryllium and high-purity copper foil were used to study the beryllium-rich end of the Be-Cu phase diagram [13, 14]. No diffusion data were reported, nor is enough data presented to calculate such.

Beryllium diffusion into copper has been studied by packing copper specimens in beryllium powder and annealing at 600 to 800 °C [15]. Hardness readings and metallographic examination were used to determine the beryllium penetration into the copper. The results are not very conclusive, other than that maximum diffusion was attained at 800 °C in 10 hours; the diffusion depth being 1 mm.

Heating copper in a beryllium chloride atmosphere has been employed in creating diffusion coatings [16].

In view of the few experiments devoted to the interdiffusion of copper and beryllium and the results obtained, it is clear that some additional experimentation is needed to clear up some of the doubts existing in the data.

2.5. Age-Hardening

Copper beryllium alloys have been used for strain-enhanced diffusion investigations [17–19]. The growth of age-hardening precipitates in these alloys allows one to observe diffusion at very small values of (Dt), utilizing polycrystalline alloy specimens. Ultrasonic vibrations were found to slightly accelerate the pre-

TABLE 4. Diffusion parameters for interdiffusion in the copper-beryllium system. Data taken from [10]

Phase	D_0 (cm²/s)	Q (kcal/mol)
α	1.9×10^{-1}	41.5
β	8.4×10^{-2}	27.5
γ	5.4×10^{-2}	31
δ	1.2×10^{-3}	33

TABLE 5. Beryllium and copper intrinsic diffusion coefficients in the β-phase of the copper-beryllium system. Data excerpted from [10]

Diffusion Configuration	T(°C)	D(cm²/s) Beryllium	D(cm²/s) Copper
Cu/Be	840	7.2×10^{-8}	5.8×10^{-8}
	750	2.4×10^{-8}	2.1×10^{-8}
	650	4.9×10^{-9}	5.7×10^{-9}
Cu/Cu-Be(49 at.%)	840	1.4×10^{-7}	5.0×10^{-8}
	750	4.1×10^{-8}	2.2×10^{-8}

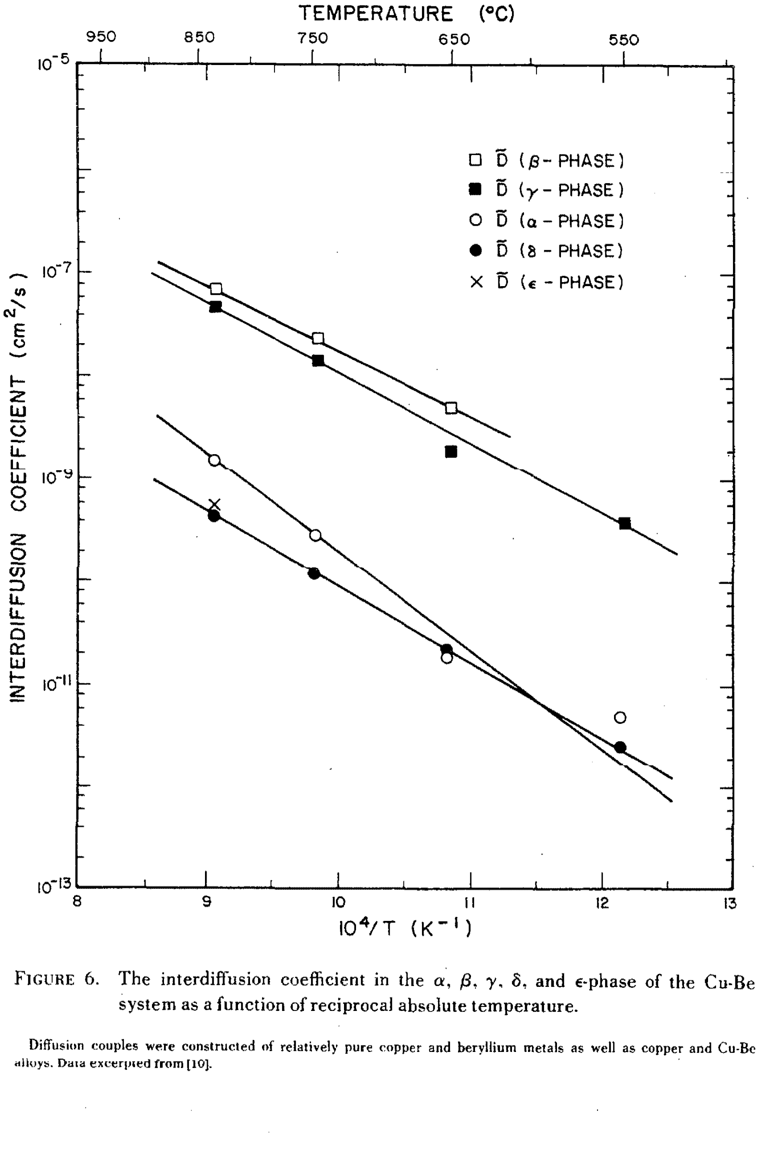

FIGURE 6. The interdiffusion coefficient in the α, β, γ, δ, and ε-phase of the Cu-Be system as a function of reciprocal absolute temperature.

Diffusion couples were constructed of relatively pure copper and beryllium metals as well as copper and Cu-Be alloys. Data excerpted from [10].

TABLE 6. Intrinsic diffusion parameters in β-phase for the diffusion pair Cu/Be. Data taken from [10]

Diffusing Species	D_0 (cm^2/s)	Q (kcal/mol)
Be	3.5×10^{-2}	29
Cu	4.5×10^{-3}	25

cipitation hardening in Cu-Be alloys in the early stages of irradiation. This small increase in the hardening rate can probably be ascribed entirely to the acoustic enhancement of grain boundary precipitation, rather than to the sonic energy setting dislocations in motion and the consequent production of vacancies. It is not likely that acoustic energy in the kHz frequency range, used in these experiments, will be absorbed by and produce the to-and-fro motion of dislocations (although this acoustic energy can be absorbed at grain boundaries) [20]. However, when defects are introduced into a system by strain, hardness measurement is not a reliable method of monitoring diffusion, since other effects, such as enhanced nucleation or dislocation production, could also be altering the hardness.

2.6 Cu-Be-Ag

Studies have been made on the effect of beryllium additions on the grain boundary diffusion of silver in polycrystalline copper [21, 22]. The results conflict, but the earlier results (which claimed that beryllium retards both the volume and grain-boundary diffusion of silver in copper) are believed to be in error because of the rather inaccurate method of analysis (microstructure comparisons). The more recent investigation utilized a radioactive tracer (^{110}Ag) vacuum sputtered onto the Cu-Be alloy specimens. After diffusion anneals, the specimens were analyzed using Gruzin's method [23]. Grain boundary diffusion coefficients were calculated using Fisher's analysis [24]. The calculations assumed a grain boundary width of approximately 10^{-6} cm and a volume diffusion coefficient for ^{110}Ag in the Cu-Be alloys of approximately 10^{-12} cm^2/s at 590 °C. The volume diffusion coefficient assumption was based on similar work in Cu-Sb alloys [25].

All the diffusion studies were performed at 590 °C for 100 hours, although prediffusion heat treatments were different for each specimen. The results are given in table 7 and seem to indicate that minor additions of beryllium (of the order of 0.1 wt%/0.7 at.%) accelerate the grain boundary diffusion of silver in copper. Special note should be taken that results are based upon a "less-than rigorous" calculation.

TABLE 7. Grain boundary diffusion coefficients of silver in a Cu-Be (0.1 wt%) alloy at 590°C. Data extracted from [21,22]

Pre-diffusion Heat Treatment	D_{gb}(cm^2/s)
None	3.7×10^{-8}
100 h @ 863 °C	2.4×10^{-8}
100 h @ 863 °C and 50 h @ 590 °C	3.3×10^{-8}

2.7. Cu-Be-Al

Copper-aluminum alloys have been heated in beryllium powders at 600–800 °C for 2 to 10 hours, and the depth of the beryllium diffusion determined from hardness measurements and micrographic observations [15]. The authors report that maximum diffusion occurred at 800 °C (and 10 hours of annealing), and the depth of diffusion was 3 mm.

2.8. Cu-Be-Fe

Copper containing 19.15 at.% (3.25 wt%) beryllium has been interdiffused with iron in the temperature range 1000 to 1100 °C [26, 27]. The beryllium alloying addition reduced the iron grain boundary penetration of copper.

2.9. Cu-Be-H

The addition of 2 at.% (0.3 wt%) beryllium to copper causes the hydrogen permeability to decrease by a factor of three (relative to pure Cu) in the temperature range 700–500 °C [28].

2.10. Cu-Be-O

The high temperature oxidation characteristic of Cu-Be alloys has been reported [29–32]. Although no diffusion coefficients were measured, the quantitative data taken did allow the authors to speculate on the relative rates of diffusion of copper and beryllium through the oxide layers of their specimens.

2.11. Cu-Be-X

The interdiffusion of permalloy-coated Cu Be alloy wires has been qualitatively investigated [33], and no diffusion coefficients were reported.

The very high affinity of beryllium for oxygen and nitrogen has made the fusion welding of beryllium and beryllium-alloys difficult and complicated. As a consequence, much study has been directed towards the solid phase welding of these materials and a great deal of literature generated. The bulk of these investigations were concerned with obtaining a reasonably sound bond between the metals, rather than a study of the diffusion processes which took place. In view of the fact that most of this literature is not "diffusion studies per se," we will not go into the details of the results presented in this literature, but rather refer the reader to the review literature which already exists in this area [34–37] for the extraction of any data he might need.

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3. Copper-Cerium

3.1. $Ce^* \rightarrow Cu$

The tracer diffusion coefficient of the rare earth metal isotope ^{141}Ce in copper has been studied in the temperature interval 752 to 970 °C [1]. The values of the tracer diffusion coefficients were obtained by two different experimental methods, the residual activity method (Gruzin's technique [2]) and serial-sectioning with analyses of the sections removed (as described by Makin et al. [3]). In these experiments, the cerium isotope was dissolved in water, then transferred to the polished surface of the polycrystalline copper specimens where it was allowed to dry. During the vacuum diffusion anneals, the hydrated rare earth chloride decomposed to an oxide from which the cerium isotopes diffused into the copper. All but the measurements at 950 °C (which used the serial-sectioning technique) utilized the residual activity method. The plots of the residual activity versus the corresponding penetration distance showed steep slopes near the specimen surface (up to a penetration distance of 0.2 to 0.3 μm) after which there was a more gradual decline. It was assumed, therefore, that a constant concentration, c_0, of the tracer was maintained at a position, x_0, near the surface (this resulted in a small deviation of $\leqq 10\%$ in the diffusion coefficients). The concentration-penetration plots could be fitted to error function curves, and tracer diffusion coefficients were calculated using values of c_0 obtained by extrapolating the residual activity curves.

To check the validity of this residual activity analysis, serial-sectioning experiments also were performed. High activity was found at the surface. The remaining points in a plot of log specific activity versus penetration distance could be fitted by two straight lines. The first straight line segment extended from near the surface to a depth of ~20 μm. If a Gaussian penetration profile was assumed (rather than the error function assumed for the residual activity measurement) and the diffusion coefficient then calculated from the slope of this first line, results in agreement with the residual activity measurements were obtained. These values are also given in table 8.

TABLE 8. Cerium-141 tracer diffusion coefficients in copper [1].

T(°C)	D^*(cm^2/s)
950	$^a4.35 \times 10^{-13}$
950	$^a4.02 \times 10^{-13}$
950	$^a3.91 \times 10^{-13}$
947	3.91×10^{-13}
947	3.71×10^{-13}
900	2.76×10^{-13}
861	1.87×10^{-13}
861	1.66×10^{-13}
800	7.87×10^{-14}
800	7.51×10^{-14}
760	5.86×10^{-14}
760	5.73×10^{-14}

[a] These values were determined from serial sectioning of the specimens whereas the remaining values were determined from residual activity measurements.

The second straight line segment in the log concentration versus square of penetration plot from the serial-sectioning experiments covered the remaining points in the profile and showed a smaller slope than the first segment. Diffusion coefficients calculated from this segment varied greatly from one specimen to another and were larger than those quoted in the table, perhaps reflecting diffusion along short-circuiting paths, such as dislocations.

Diffusion coefficients from the table are plotted in figure 7. Our least squares analysis of these values yields the following expression,

$$D^*_{\mathrm{Ce}} = 2.38 \times 10^{-8} \exp(-26.7\ \mathrm{kcal \cdot mol^{-1}}/RT)\ \mathrm{cm^2/s},$$

represented by the solid line on figure 7. It should be noted that the D_0 and Q contained in the above expression differ somewhat from the authors' published values.

It is apparent from these results that, even at temperatures close to the melting point, the diffusion of cerium in copper takes place only very slowly. Also, the D_0 value of 2.38×10^{-8} cm^2/s is unusually low. Nevertheless, similar results (with D^* actually a factor of 10 lower) were found by the same authors for tracer diffusion of other rare earths (Lu, Pm, Tb, and Tm) in copper. Qualitatively, similar results were also found previously by Williams and Slifkin [4] for diffusion of rare earths in silver and lead. The authors of these papers propose that the large size of the rare earth atoms, which makes solubility difficult, also impedes volume diffusion and makes the segregation of rare earth atoms on dislocations or other structural defects more likely.

3.2. Cu → Ce (Electromigration)

The solid-state electromigration of copper in γ-cerium has been observed in purification studies [5, 6]. The cerium specimens were cut from sheet rolled from ingots obtained from molten salt-metal equilibrations during which radioactive copper tracers were introduced. Specimens were electrolyzed between nickel electrodes containing resistance heaters and no gradient in temperature exceeding 10 °C was observed. Specimen temperatures were controlled to within ±3 °C or 4 °C. Although the electromigration chamber was evacuated, a slight amount of surface oxidation was observed. After 242 hours of electromigration at 600 °C, the concentration profile of copper was determined from spectrographic analysis. The data show very slight diffusion of copper to the anode. The authors speculated that the anode-directed diffusion of copper is primarily due to the potential field effect and that any contribution from electron momentum transfer forces, if present, is minimal.

More recent experiments [7], utilizing electromigration to purify cerium, have found copper being transported to the cathode. It is not clear why the disagreement exists.

3.3. Cu-Ce References

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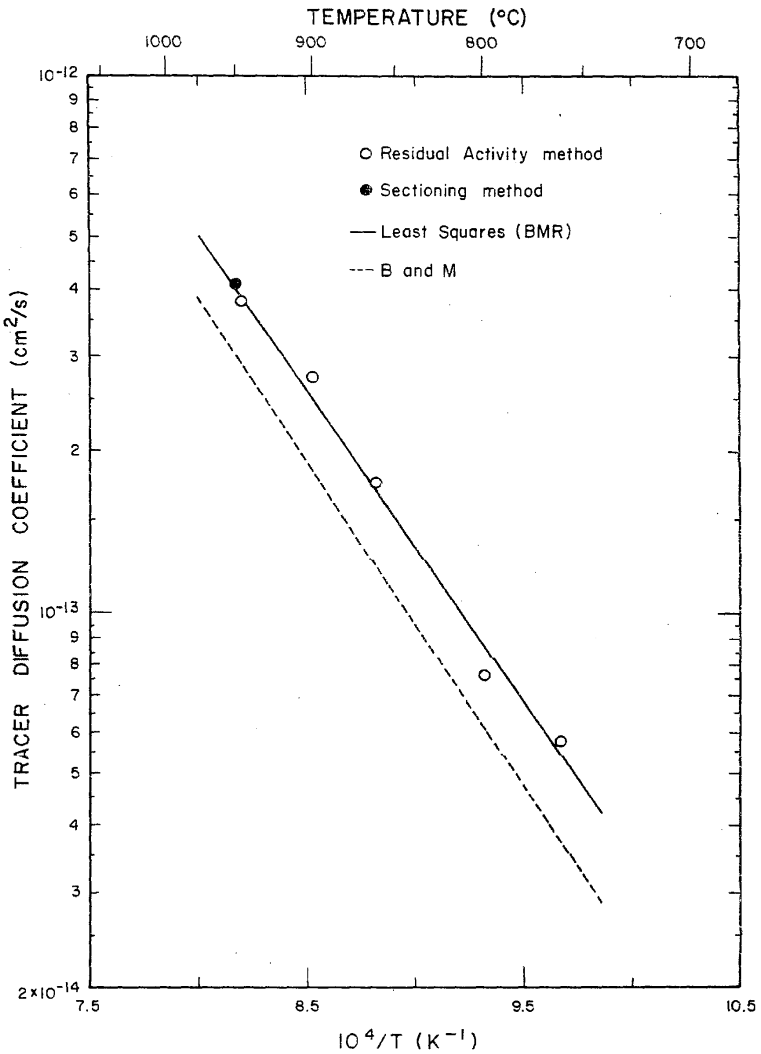

FIGURE 7. The tracer diffusion coefficient of ^{141}Ce in polycrystalline copper as a function of reciprocal absolute temperature.

Diffusion coefficients were determined by a residual activity and serial sectioning technique. Data taken from [1]. The dashed line is obtained from the D_0 and Q values listed by Badrinarayanan and Mathur [B and M] in reference 1. The solid line is obtained from the values $D_0 = 2.38 \times 10^{-8}$ cm^2/s and $Q = 26.7$ kcal · mol^{-1} resulting from our least squares analysis of the data given in table 8.

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4. Copper-Chromium

4.1. Cr* → Cu

Three different sets of tracer measurements [1–4] have been made of the diffusion of ^{51}Cr in pure copper. The activation energies reported in two of the studies are almost exactly the same [1–3], but the actual tracer diffusion coefficients and D_0 values differ by nearly a factor of four (see fig. 8). The third group of measurements [4] not only yielded coefficients that differed in absolute values but gave a higher-valued activation energy.

Seitz [1] electroplated ^{51}Cr (half-life 27.8 days) onto single crystal copper specimens, diffusion-annealed the specimens at four temperatures ranging from 796 to 1035 °C with the temperature controlled to ±0.5 °C, sectioned the specimens after diffusion, and determined the specific activity of each section. His results can be expressed as:

$$D^* = 3.1 \exp(-53.4 \text{ kcal} \cdot \text{mol}^{-1}/RT) \text{ cm}^2/\text{s}.$$

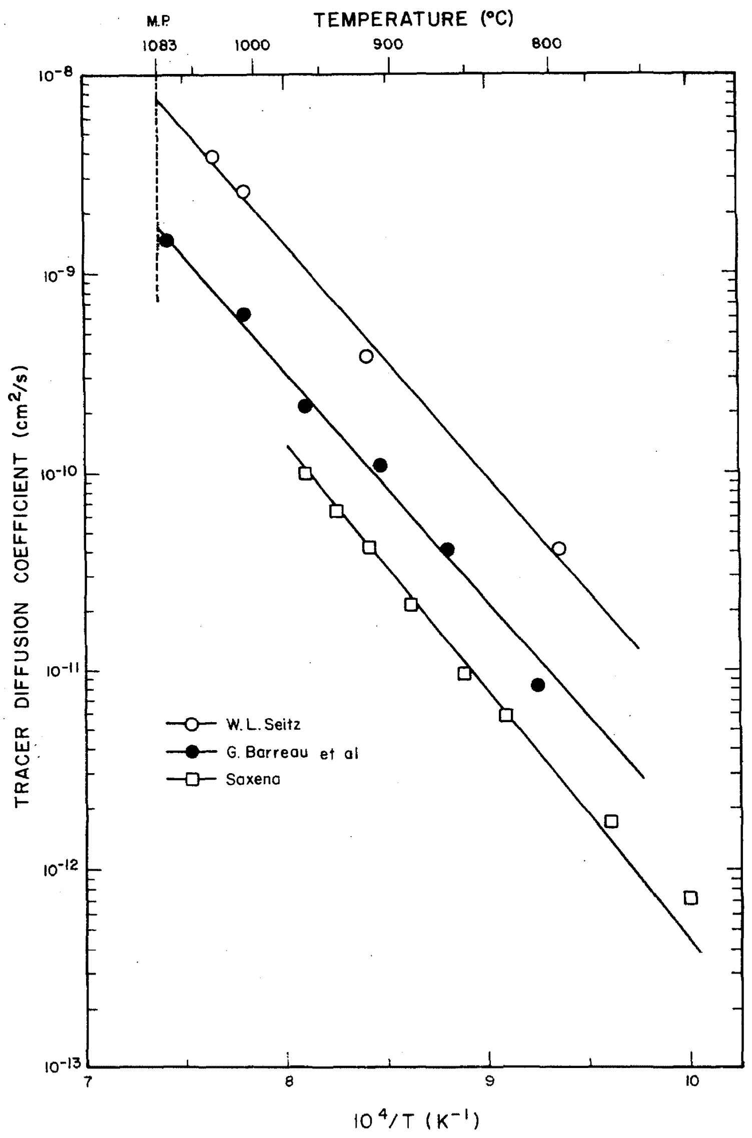

FIGURE 8. The tracer diffusion coefficient of ^{51}Cr in copper as a function of reciprocal absolute temperature.

Data of Seitz [1, 2] obtained from serial sectioning experiments, data of Barreau et al. [3] and Saxena [4] obtained from measurement of residual activity.

The author quoted uncertainties of ±2.9 cm^2/s in D_0, and ±2.0 kcal in the activation energy.

Barreau et al. [3] deposited ^{51}Cr isotope on polycrystalline O.F.H.C. copper and, after diffusion at temperatures in the range 800 to 1070 °C, used the residual activity method of Gruzin to determine diffusion coefficients. They quote an activation energy of 53.5 kcal/mol, almost identical with that of Seitz, but with a large uncertainty (±5 kcal/mol). With this activation energy, their published Arrhenius line drawn through their data, which is reproduced in figure 8, can be represented as:

$$D^* = 0.78 \exp(-53.5 \text{ kcal}\cdot\text{mol}^{-1}/RT) \text{ cm}^2/\text{s}.$$

By contrast, the authors published the somewhat different D_0 value of 1.02 cm^2/s, and the D_0 from the experiments of Seitz is 3.1 cm^2/s.

Saxena [4] also electrodeposited the ^{51}Cr isotope on polycrystalline copper, diffused in the temperature range 700 to 960 °C, and used the residual activity technique in his counting procedure. His tracer coefficients (mean values) are shown plotted in figure 8. The lower temperatures exhibit higher-valued coefficients (probably due to diffusion along grain boundaries, dislocations, etc.) than would be expected from a linear extrapolation of the higher temperature values. If data below 800 °C are disregarded, a straight line can be fitted to the remaining data and an Arrhenius expression determined. The expression

$$D^* = 1.6 \exp(-57{,}500\ \mathrm{cal \cdot mol^{-1}}/RT)\ \mathrm{cm^2/s},$$

has an accuracy in the pre-exponential of 30%, and in the activation energy of 2%, according to the author.

The difference in diffusion coefficients, pre-exponentials, and activation energies between the three investigations above are much greater than normal experimental error. Seitz mentions that he experienced difficulties with an oxidized layer on the surface of his specimens. This tended to tie up the tracer isotope near the surface and resulted in several cases of poorly defined profiles for volume diffusion. Saxena also noted concentration anomalies in the first 5 microns of his specimen's surface. These effects also may have occurred in the experiments of Barreau et al. Analysis by the residual activity method, used by both Saxena and Barreau et al., would then very likely yield tracer diffusion coefficients which were too low. From this line of reasoning, Saxena's experiments should be particularly suspect in view of his especially low-valued coefficients.

4.2. Cu-Cr Interdiffusion

There has been no quantitative study of the interdiffusion of binary Cu-Cr alloys. The few studies undertaken [5–8] are qualitative in nature, dealing with interdiffusion between electro-deposited coatings or in vapor-deposited layers and (or) substrates. Such experiments generally involve low temperatures, polycrystalline specimens, thin layers, short annealing times, and in some cases, poorly-characterized materials. In those instances where the interdiffusion process was monitored, chromium diffused through the copper much more easily than the copper through the chromium [7].

A study of the growth kinetics of chromium precipitates in a Cu-Cr (0.35 wt%/0.43 at.%) alloy yielded data which indicated that the coarsening process was controlled by volume diffusion of the solute and required an activation energy of approximately 48 kcal/mol [9].

4.3. Cu-Cr-Al

The interdiffusion of copper at 500 °C in couples constructed of an aluminum-copper (1 wt%/0.43 at.%) alloy and an aluminum-chromium (1 wt%/0.5 at.%) alloy has been studied [10]. The interdiffusion coefficients were found to be approximately 6×10^{-10} cm²/s.

Diffusion coatings produced on copper surfaces (by interdiffusing Al and Cr simultaneously into Cu) have been found to be oxidation-resistant at temperatures up to 900 °C [11].

4.4. Cu-Cr-Fe

The tracer diffusion of ^{59}Fe in Cu-Cr alloys (0.8% chromium) was found by Barreau and co-workers [3] to be essentially the same as the lattice diffusion rate of iron in unalloyed O.F.H.C. copper.

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 [12, 13]. 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 of Cu-Fe-Cr alloys (containing 2 to 18% chromium and 4% copper) has been reported by Ahmed and coworkers [14–16].

4.5. Cu-Cr-Ni

The addition of small quantities of chromium (0.8%) to pure copper does not have any measureable effect on the nickel tracer diffusion coefficient [17].

4.6. Cu-Cr-X

Sirca [12, 13], in addition to his interdiffusion studies with liquid copper and iron, also interdiffused molten copper with a number of austenitic 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 austenitic steels (18–8 stainless, Mn-steels, nonmagnetic steels, and Ni-Cr-steels). Preferential diffusion of the copper down grain boundaries was absent in the ferritic steels (Cr-, Si-, and V-steels) employed in the investigation.

Hume and co-workers [18, 19] interdiffused copper and several selected stainless steels over the temperature range 600 to 1050 °C. The stainless steels chosen had nominal compositions of 17 chromium–13 nickel–2.5 molybdenum, 25 chromium–20 nickel, and 25 chromium–12 nickel–3 tungsten. 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.

4.7. Molten Metal Studies

The dissolution rate of chromium in molten copper has been studied [20, 21]. The dissolution rate has been found to be restricted by diffusion. The diffusion coefficient of chromium in copper, calculated from kinetic data, at 1373 K is 0.30×10^{-5} cm²/s.

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5. Copper-Cesium

Like the other copper-alkali metal systems, the behavior of copper may be expected to exhibit a very high rate of diffusion in cesium, although no experimental evidence has been published.

6. Copper-Europium

6.1. Eu* → Cu

The tracer diffusion coefficient of the rare earth metal isotopes $^{152+154}$Eu in copper has been studied in the temperature interval 752 to 970 °C [1]. The values of the tracer diffusion coefficients were obtained by two different experimental methods: the residual activity method (Gruzin's technique [2]) and serial-sectioning with analyses of the sections removed (as described by Makin et al. [3]). In these experiments, a mixture of europium isotopes was dissolved in water, then transferred to the polished surface of the polycrystalline copper specimens where it was allowed to dry. During the diffusion anneal the hydrated europium chloride decomposed to an oxide from which the europium isotopes diffused into the copper.

TABLE 9. Tracer diffusion coefficients of Eu-152+154 in copper. Data taken from [1]

T(°C)	D*(cm^2/s)
970	3.02×10^{-12}
970	[a]2.75×10^{-12}
970	2.73×10^{-12}
970	2.43×10^{-12}
950	2.20×10^{-12}
950	1.80×10^{-12}
895	1.34×10^{-12}
895	1.14×10^{-12}
860	[a]7.56×10^{-13}
855	8.31×10^{-13}
855	7.96×10^{-13}
820	6.03×10^{-13}
752	[a]2.77×10^{-13}

[a] These values were determined from residual activity method of the specimens whereas the remaining values were determined from serial sectioning.

Since reasonably high energy γ-radiation (0.34 MeV), whose linear absorption coefficient in copper is small, was counted to detect the isotope, no absorption correction was found necessary, even with the residual activity method. However, it was found that the readings starting at the surface and up to 0.2 to 0.3 μm from the surface showed a sharp drop, after which they declined more gradually. This was attributed to the poor solubility of the rare earth in copper which would allow only a certain amount of europium into the copper. It was assumed, therefore, that a constant concentration, c_0, of the tracer was maintained at position x_0 near the surface. The concentration-penetration plots were found to fit the error function curves fairly well, and diffusion coefficients were calculated on this basis, using values of c_0 obtained by extrapolating the residual activity curves. The values are summarized in table 9. A small deviation (usually smaller than ±10%) from these calculated diffusion coefficients was found when an alternate fit of the data, not assuming that c_0 was known, was used.

To check the validity of this residual activity analysis, serial-sectioning experiments also were performed. These again showed a high point at the surface. The remaining points in a plot of log specific activity versus penetration distance could be fitted by two straight lines. The first straight line segment extended from near the surface to a depth of < 20 μm. If a Gaussian penetration profile was assumed (rather than the error function assumed for the residual activity measurement) and the diffusion coefficient then calculated from the slope of this first line, results in agreement with the residual activity measurements were obtained. These values are also given in table 9.

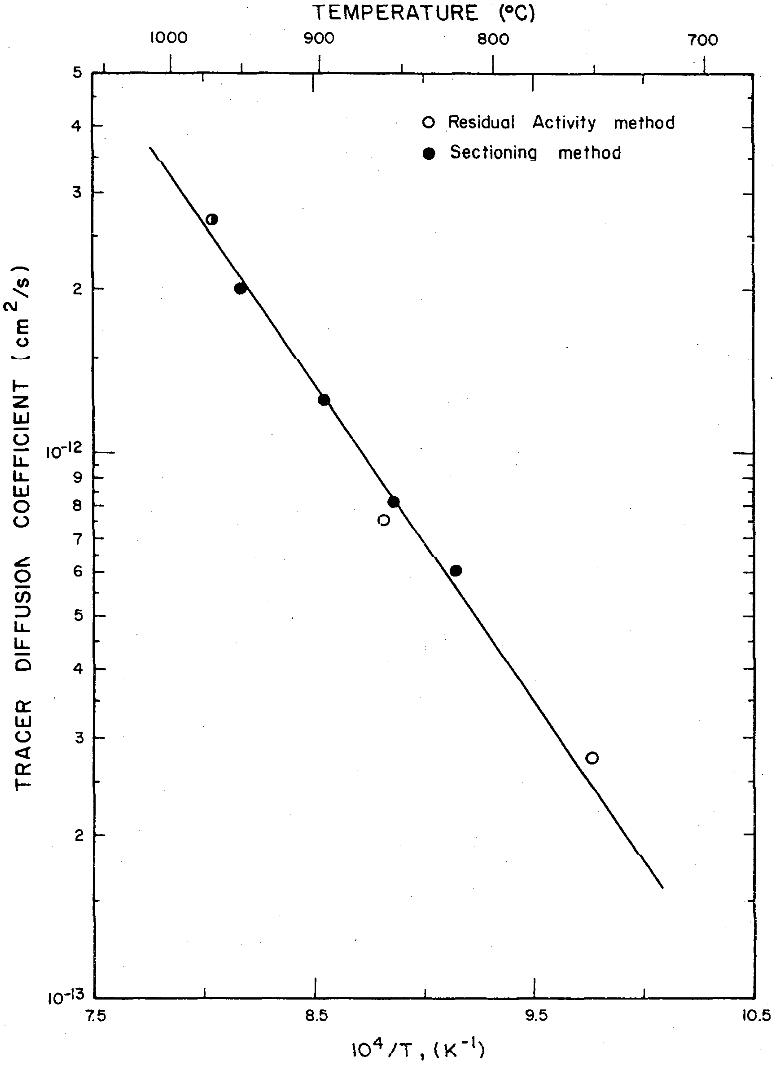

FIGURE 9. The tracer diffusion coefficients of the isotopes $^{152+154}$Eu in polycrystalline copper as a function of reciprocal absolute temperature.

Data obtained from the paper of Badrinarayanan and Mathur [1].

The second straight line segment in the log concentration versus square of penetration plot from the serial-sectioning experiments covered the remaining points in the profile (up to a depth of 70 μm) and showed a smaller slope than the first segment. Diffusion coefficients calculated from this segment varied greatly from one specimen to another and were 4 to 40 times larger than those quoted in the table, perhaps reflecting diffusion along short-circuiting paths, such as dislocations. Diffusion coefficients from the table are plotted in figure 9. Our least squares analysis of these values yields the expression,

$$D^*_{\mathrm{Eu}} = 1.36 \times 10^{-7} \exp(-26.9 \text{ kcal} \cdot \text{mol}^{-1}/RT) \text{ cm}^2/\text{s},$$

represented by the solid line in figure 9. The D_0 and Q in this expression differ slightly from the authors' published values.

It is apparent from these results that, even at temperatures close to the melting point, the diffusion of europium in copper takes place only very slowly. Also, the D_0 value of 1.36×10^{-7} cm^2/s is unusually low. Nevertheless, similar results (with D_0 actually a factor of 10 lower) were found by the same authors for tracer diffusion of other rare earths (Ce, Lu, Pm, Tb, and Tm) in copper. Qualitatively, similar results were also found previously by Williams and Slifkin [4] for diffusion of rare earths in silver and lead. The authors of these papers propose that the large size of the rare earth atoms which makes solubility difficult also impedes volume diffusion and makes the segregation of rare earth atoms on dislocations or other structural defects more likely.

6.2. Cu-Eu References

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7. Copper-Hydrogen

7.1. Cu→H

The diffusivity and permeability of hydrogen (and its isotopes) in copper, in part because of its great practical importance, has been the topic of study by many researchers [1–53]. Attention here will be devoted to those experiments that are directly concerned with the measurement of diffusion (or permeation) rather than on the effects of hydrogen (e.g., embrittlement). Additionally, attention will be devoted only to the experiments of recent vintage because of the problems faced by early experimenters which have been largely overcome by the availability of better materials, technology, etc. It has only been the most recent of developments which have given us reliable hydrogen diffusion coefficients in pure copper over a reasonable temperature range.

In the assessment of these more recent diffusion data, one may note that the experiments of Eichenauer and coworkers [1, 2], Katz et al. [3], Perkins and Begeal [4, 5], Aschan [8], Belyakov and coworkers [23, 31], Ransley and Talbot [11], and Schenck and Lange [10] yield results which are of the same order of magnitude (see fig. 10).

Good absolute agreement is obtained between the high temperature measurements (950 to 450 °C) of Eichenauer and Pebler [1], and Katz, Guinan and Borg [3]; the latter being an isotope effect measurement. This agreement must be considered fortuitous since Eichenauer in subsequent experiments [2], which employed both hydrogen and deuterium, obtained lower-valued diffusion coefficients when compared to those obtained by Katz and coworkers [3]. Other high temperature experiments [8, 10, 23, 31, 38] were performed in a more limited temperature range and yielded results possessing considerable scatter. Ransley and Talbot's data [11] lack the consistency displayed by the other results. Demin et al. [54] made diffusion calculations that are inconsistent with nearly all experimental results. The low temperature investigations of Cazade et al. [35] are strictly qualitative. Carnuth's experiments on the effects of cold deformation on hydrogen diffusion rates in copper yield only effective diffusion coefficients which involve a host of other variables [27].

Low temperature hydrogen diffusion data have been taken by Perkins and Begeal [4, 5] in the range 440 to 200 °C. These results are in excellent agreement with the high temperature data of Katz and coworkers [3]. It is interesting to note that such agreement exists in view of the fact that two very different techniques of experimentation were used. Katz and coworkers measured the rate of outgassing of hydrogen from spherical single crystals of copper, whereas Perkins and Begeal, in their low temperature studies, employed a permeation method and polycrystalline copper specimens.

A least squares analysis was made [4, 5] on all of the light hydrogen data of Katz et al., and Perkins and Begeal (see table 10), and the resulting straight line is shown plotted in figure 10. The expression describing this dependence is given by:

$$D_{\mathrm{H}\to\mathrm{Cu}} = (1.06 \pm 0.05) \times 10^{-2} \exp[(-9180 \pm 60) \text{ cal} \cdot \text{mol}^{-1}/RT] \text{ cm}^2/\text{s}.$$

Diffusion coefficients for deuterium (D_2) and tritium (T_2) have also been determined [2, 3, 26], and a mass dependence is quite apparent (see fig. 11). Agreement is not good between the two principal experiments [2, 3], although ratios of the diffusion coefficients are consistent. Both of these studies were based on measure-

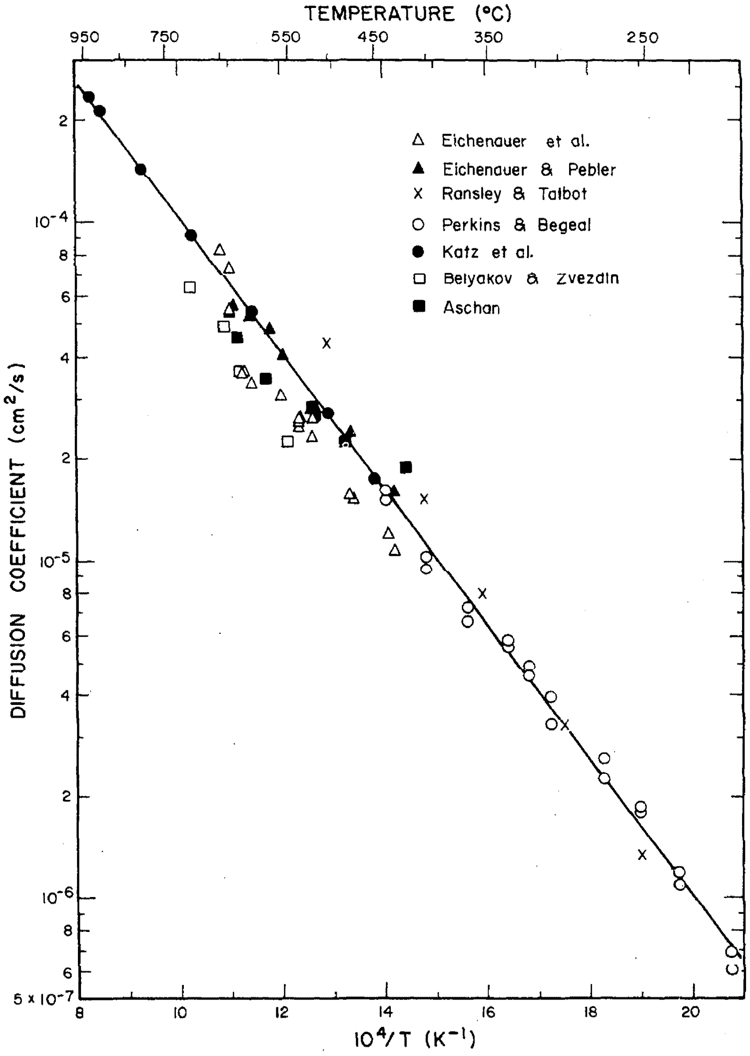

FIGURE 10. The diffusion coefficient of hydrogen (mass one) in copper as a function of reciprocal absolute temperature.

Data extracted from Eichenauer and coworkers [1, 2], Katz et al. [3], Perkins and Begeal [4, 5], Aschan [8], Belyakov and coworkers [23, 31], and Ransley and Talbot [11]. The straight line shown is a least squares analysis of the data of Katz et al. [3] and Perkins and Begeal [4, 5].

ment of the rate at which a gas-saturated copper single crystal outgasses. Reasons for the disagreement are not readily apparent, although systematic differences between laboratories may in large part be responsible. Values of the diffusion parameters, D_0 and Q, for the diffusion of deuterium and tritium in pure copper are listed in table 11 (along with the respective authors' determinations made with hydrogen of mass 1 for comparison).

It is interesting to note that in the above-mentioned experiments the measured values of D_H/D_D and D_H/D_T are much smaller than predicted by absolute-rate theory (in its simplest, nonquantum-mechanical form, absolute-rate theory yields a mass dependence of D given by the expression $D_a/D_b = (M_b/M_a)$, where M is the mass of diffusing atom). Another anomaly is the substantial dependence on temperature shown by the ratio of the diffusion coefficients. To adequately explain these deviations from simple theory, one probably has to consider anharmonic effects as well as making quantum-mechanical corrections, both of which are beyond the scope of this review.

The diffusion of deuterium in deuteron-irradiated copper in the temperature range −46 to +20 °C has also been studied [26]. A nontraditional experimental technique was employed in these investigations—that of measuring the counting rate of neutrons from the D(d, n) H^3 reaction occurring in metals irradiated with

TABLE 10. The diffusion coefficients of light hydrogen in pure copper as determined by Katz et al. [3], and Perkins and Begeal [4]

T(°C)	D(cm^2/s)	Reference
925	2.32×10^{-4}	[3]
900	2.13×10^{-4}	[3]
800	1.42×10^{-4}	[3]
700	9.18×10^{-5}	[3]
600	5.42×10^{-5}	[3]
500	2.72×10^{-5}	[3]
450	1.75×10^{-5}	[3]
438	1.6×10^{-5} 1.5×10^{-5}	[4] "
402	1.05×10^{-5} 9.6×10^{-6}	[4] "
366	7.3×10^{-6} 6.6×10^{-6}	[4] "
336	5.8×10^{-6} 5.5×10^{-6}	[4] "
322	4.9×10^{-6} 4.6×10^{-6}	[4] "
307	3.9×10^{-6} 3.3×10^{-6}	[4] "
274	2.6×10^{-6} 2.3×10^{-6}	[4] "
254	1.8×10^{-6} 1.8×10^{-6}	[4] "
233	1.2×10^{-6} 1.05×10^{-6}	[4] "
208	7.0×10^{-7} 6.0×10^{-7}	[4] "

low energy deuterons. The experimental results indicated that grain boundary diffusion of deuterium was the principal transport mechanism and chemical purity was also a factor (there was a slower deuterium diffusion rate in the less pure copper) to be considered. An apparent activation energy of approximately 2.8 kcal/mol (0.12 eV) was calculated for the diffusion of deuterium in polycrystalline copper in this temperature range in spite of a considerable uncertainty in the coefficients.

The same experimental techniques employed for the measurement of hydrogen diffusivity often allow for the determination of the gas solubility and permeability (the product of diffusivity, D, and solubility, S, equals the permeability or permeation constant, K). Hydrogen permeation measurements in pure copper have usually accompanied the above-mentioned diffusion studies, and some of the more recent data [2, 4, 5, 23, 31, 55] are plotted in figure 12. Agreement is generally only fair. The constants calculated from membrane measurements by Belyakov and Zvezdin [23, 31] are taken over a somewhat limited temperature range, with the results for both pure and O.F.H.C. copper being very close to each other. Gorman and Nardella [55] measured hydrogen transport through a polycrystalline O.F.H.C. copper membrane over a somewhat more extensive temperature range (700 to 350 °C) and obtained activation energies and pre-exponential factors close to those of Eichenauer and coworkers [2]. Perkins and Begeal [4, 5] have also measured hydrogen permeation through a polycrystalline O.F.H.C. copper membrane and have reported the permeability constant (in the temperature range 200–440 °C) as being defined by:

$$K = 60.0 \times 10^{-3} \exp\left(-18.5 \text{ kcal}\cdot\text{mol}^{-1}/RT\right) \quad \text{cm}^3(\text{STP})\ \text{s}^{-1}\ \text{cm}^{-1}\ \text{atm}^{-1/2}.$$

The relationship is shown plotted in figure 12. The constants for the permeability equations as determined by the various authors are summarized in table 12.

Ehrmann et al. [22], working in a very narrow temperature range (260–160 °C), obtained an activation energy of only ~15 kcal/mol, somewhat lower than other researchers.

The influence of surface impurities on the low pressure surface of polycrystalline copper did not appear to have a significant effect on the hydrogen permeation rate [6, 7].

It has been reported that a tensile stress increases hydrogen permeability, while a compressive stress reduces permeation [57].

Technological interest in laminated materials has resulted in several investigations where the copper layer was found to dominate the temperature dependence of hydrogen permeation in the laminate [4, 5, 22, 56].

7.2 Cu-H-Au

Gol'tsov and coworkers [58] measured hydrogen diffusion coefficients, permeability, and solubility in the alloy Cu_3Au, as well as the effect of isothermal ordering (at 350 °C) on these quantities. The data were taken with one of the conventional experimental techniques [59] used in permeability studies where a thin membrane of the alloy is subjected to a differential hydrogen pressure while being heated. Alloy specimens were annealed at 700 °C and then step-cooled (at a mean rate of 5 °/h). The influence of ordering was determined by making measurements in the temperature range 350 to 280 °C. The calculated hydrogen diffusion coefficients are plotted in figure 13 as a function of reciprocal absolute temperature. Where possible, straight lines were fitted to the data, and pre-exponential factors (D_0) and activation energies (Q) calculated for the hydrogen diffusion process (see table 13). The data for the hydrogen permeability are also plotted as a function of the reciprocal absolute temperature in figure 14, revealing different exponential temperature dependencies. The pre-exponential factor (K_0) and activation energies (Q_K) calculated for the permeation process are listed in table 13. Near the critical temperature (~400 °C), abrupt changes occur in the hydrogen diffusion and permeability rates. The influence of ordering on both quantities is apparent after prolonged isothermal anneals at 350 °C. A model (which is really an extension of Krivoglaz and Smirnov's theory [60]) to describe the anomalous changes in the hydrogen diffusion coefficients at the order-disorder transformation has been proposed by the same authors [61–64].

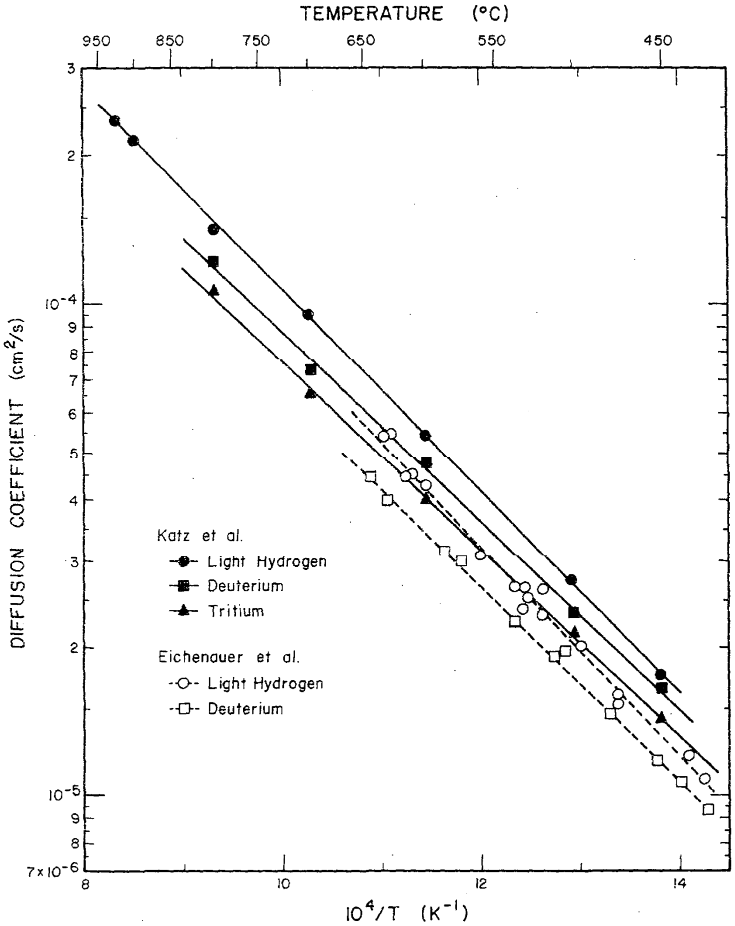

FIGURE 11. Diffusion coefficients of light hydrogen, deuterium, and tritium in copper as a function of reciprocal absolute temperature.

Data extracted from the results of Eichenauer et al. [2] and Katz et al. [3].

TABLE 11. Diffusion parameters (with errors) for the Arrhenius equation describing the diffusion of hydrogen, deuterium and tritium in single crystals of copper. Data taken from Katz et al. [3] and Eichenauer et al. [2]

Authors	Parameters	Hydrogen	Deuterium	Tritium
Eichenauer, Loser and Witte (errors shown are mean square errors)	D_0(cm²/s)	0.0115 ± 6.5%	0.00620 ± 3.8%	
	Q(cal/mol)	9750 ± 2.5%	9040 ± 1.5%	
Katz, Guinan, and Borg	D_0(cm²/s)	11.31 ± 0.40	7.30 ± 1.05	6.12 ± 0.51
	Q(cal/mol)	9286 ± 65	8794 ± 244	8717 ± 141
	(standard deviation)	±1.72%	±4.55%	±2.62%

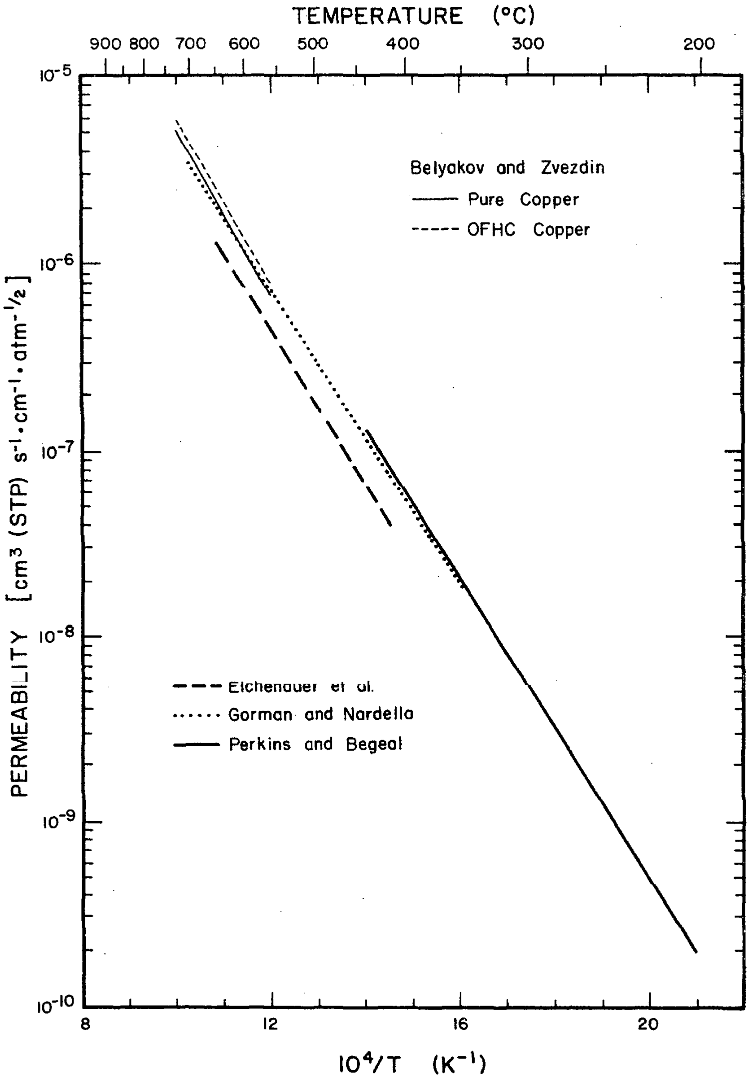

FIGURE 12. The permeability, K, of hydrogen in copper as a function of reciprocal absolute temperature.

Data extracted from the papers of Belyakov and Zvezdin [23, 31], Gorman and Nardella [55], Perkins and Begeal [4, 5], and Eichenauer and coworkers [2].

TABLE 12. Permeability data for hydrogen in copper

T(°C)	Pressure Range (Torr)	Pre-exponential Factor (K_0) $\left(\frac{cm^3\ (STP)}{s \cdot cm \cdot atm^{1/2}}\right)$	Activation Energy, Q_k ($kcal \cdot mol^{-1}$)	Material	Technique	Reference
700 - 350	760	3.80×10^{-2}	18.0	Polycrystalline OFHC Membrane	Permeation	[55]
650 - 425	100 - 700	3.70×10^{-2}	18.8	Single Crystal Cylinder	Outgassing	[2]
440 - 200	10 - 1000	6.00×10^{-2}	18.5	Polycrystalline OFHC Membrane	Permeation	[56]
700 - 550		0.119	20.0	Membrane	Permeation	[23, 31]
700 - 550		0.134	20.0	OFHC Membrane	Permeation	[23]
260 - 160	26 - 504		15.4	OFHC Membrane	Permeation	[22]
1050 - 850			~19.5	Polycrystalline Membrane	Permeation	[6, 7]

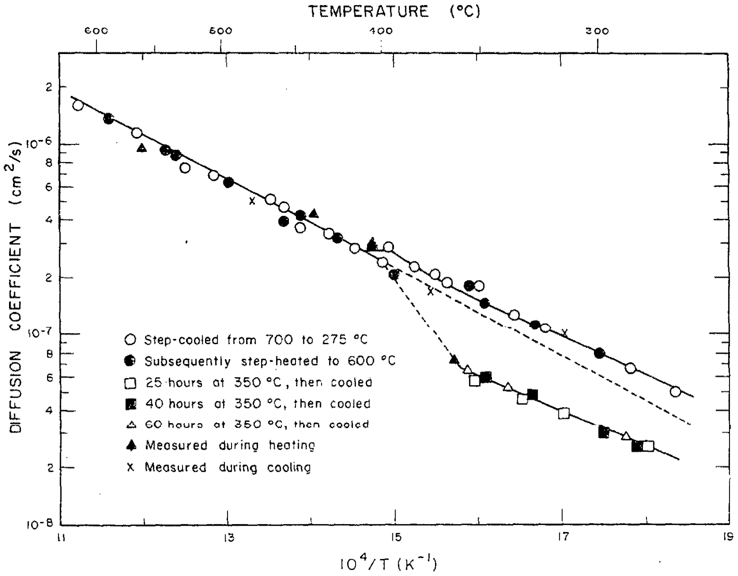

FIGURE 13. The diffusion of hydrogen through a thin alloy membrane of Cu_3Au as a function of reciprocal absolute temperature.

The influence of ordering is apparent. All data taken from the permeability experiments of Gol'tsov and coworkers [58].

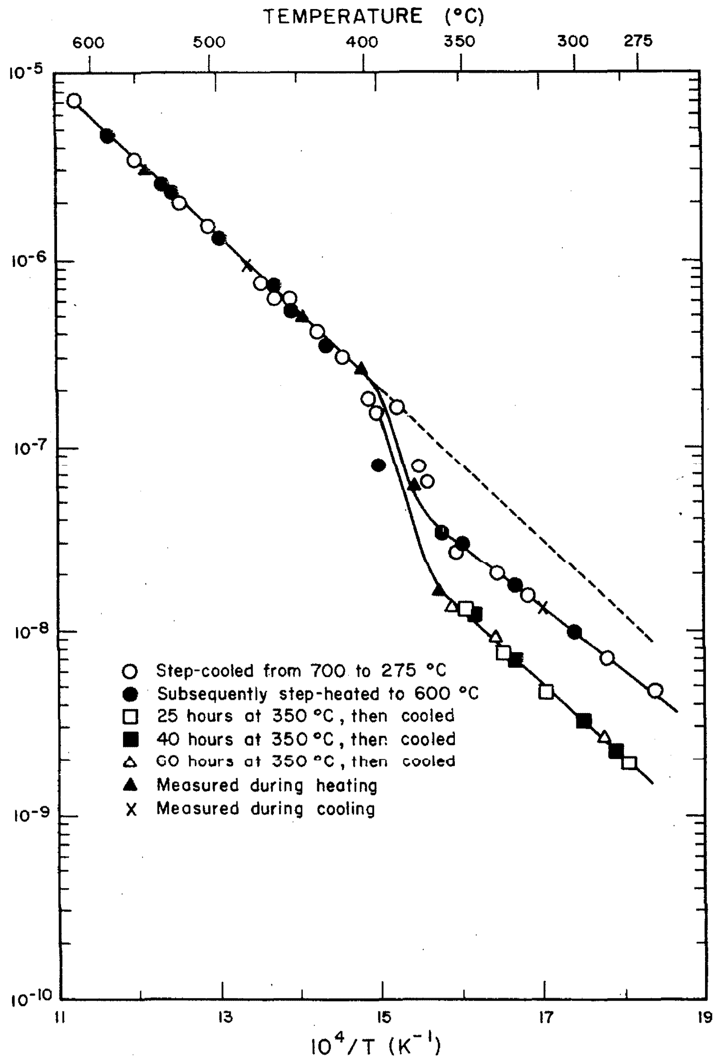

FIGURE 14. The permeability of hydrogen through a thin alloy membrane of Cu_3Au as a function of reciprocal absolute temperature.

The influence of ordering on the permeability rate is apparent. All data taken from the permeability experiments of Gol'tsov and coworkers [58].

TABLE 13. Hydrogen diffusion and permeation parameters in Cu_3Au. Data extracted from [58]. Note units of the pre-exponential, K_0

T(°C)	Diffusion Parameters		Permeation Parameters	
	D_0 (cm^2/s)	Q (kcal/mol)	K_0 $\left(\frac{cm^3(H_2) \cdot mm \cdot}{cm^2 \cdot s \cdot atm^{1/2}}\right)$	Q (kcal/mol)
600 - 430[a]	5.14×10^{-4}	10.25	2.42×10^{-1}	18.6
380 - 275[a]	3.16×10^{-4}	9.50	1.9×10^{-2}	16.6
350 - 280[b]	5.1×10^{-4}	8.50	8.16×10^{-2}	19.5

[a] Prior annealing at 700 °C, then step-cooled at a mean rate of 5 °C/h.

[b] Prior isothermal annealing at 350 °C for 25, 40, and 60 hours.

7.3. Cu-H-Be

The addition of 2 at.% (0.3 wt%) beryllium to copper causes the hydrogen permeability to decrease by a factor of three (relative to pure copper) in the temperature range 700–500 °C [23].

7.4. Cu-H-Pd

Dresler and Frohberg [65] examined the behavior of the hydrogen diffusion coefficient as a function of composition within bcc and fcc structures of this binary system and found that there was a significant increase in the diffusivity in going from a completely disordered to an ordered structure.

In the temperature range 700 to 300 °C, the effect of ordering on hydrogen movement in the alloy Cu_3Pd has been investigated [66]. Both the temperature dependence of the permeability $K(cm^3 \cdot mm/cm^2 \cdot s\ atm^{1/2})$, and the diffusion coefficients, $D(cm^2/s)$, were reported. The experimental procedures and apparatus employed (see references 67–69) yielded errors of ±3 and ±5% in the measurement of penetration rates and diffusion coefficients according to the authors. The results of the experiments are plotted in figures 15 and 16 as a function of reciprocal absolute temperature. The influence of ordering on the penetration rates and diffusion coefficients is evident in the figure. Measurements made with alloy specimens that had been heated to and

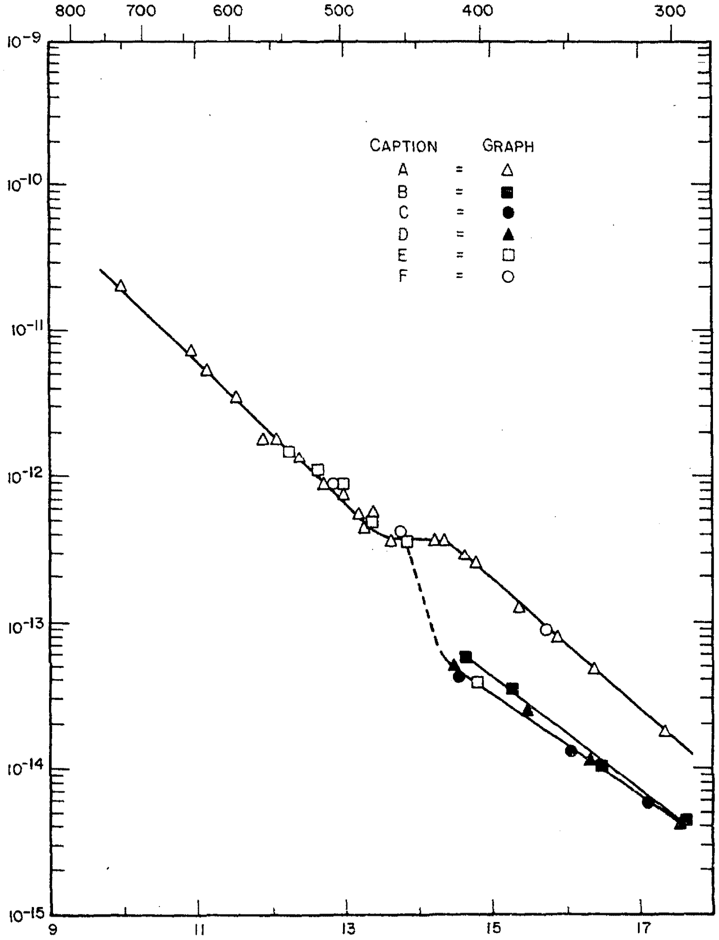

FIGURE 15. The temperature dependence of the diffusion coefficient, $D(cm^2/s)$, of hydrogen in Cu_3Pd alloy.

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 75 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 [66].

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 effects 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. The parameters for the two equations are listed in tables 14 and 15.

The diffusion of hydrogen (and deuterium) in Cu-Pd alloys at relatively low temperatures (25 to 130 °C) has been investigated [71]. The alloys ranged in copper content from 0 to 58 at.% (70 wt%). 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 [72], but at lower temperatures, 400 to 600 °C, ordering takes place at compositions above approximately 50 at.% (63 wt%) 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 speci-

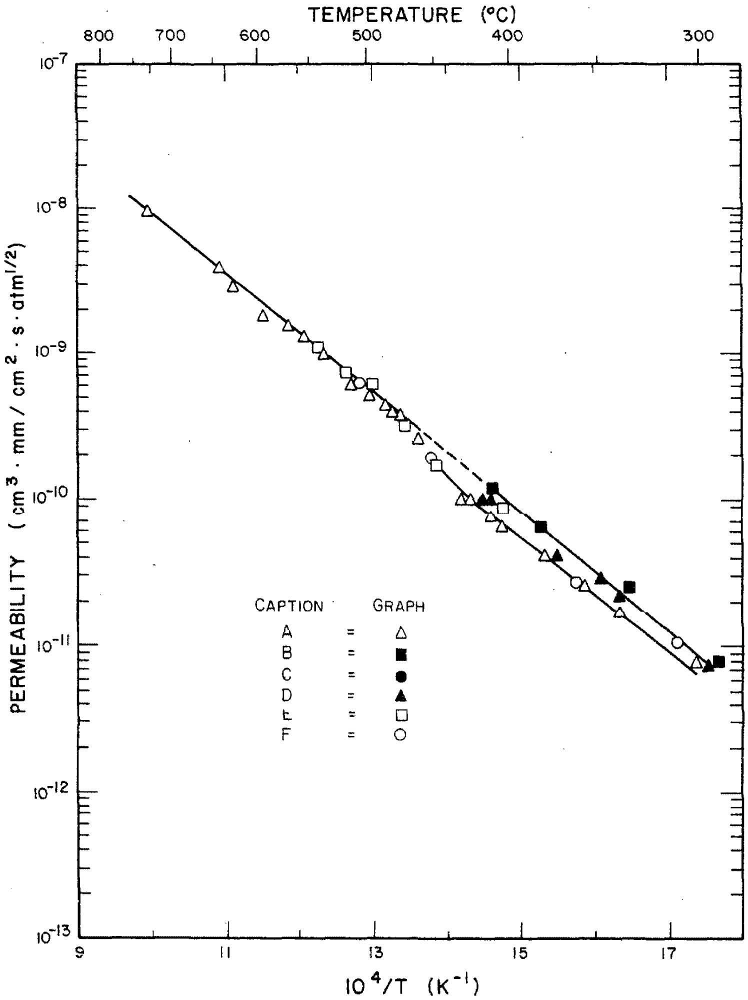

FIGURE 16. The temperature dependence of the permeability (or rate of permeation), K(cm^3 · mm/cm^2 · s · atm$^{1/2}$), of hydrogen in a Cu_3Pd alloy.

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 75 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 [66].

TABLE 14 Parameters for the rates of permeation and diffusion of hydrogen in a disordered alloy of Cu_3Pd. Data taken from [66

Temperature (°C)	K_0 $\left(\frac{cm^3 \cdot mm}{cm^2 \cdot s \cdot atm^{1/2}}\right)$	Q_K (cal/mol)	D_0 (cm²/s)	Q_D (cal/mol)
> 480	2.5×10^{-2}	8300	2.80×10^{-3}	9650
< 410	1.06×10^{-2}	7770	1.80×10^{-3}	8500

TABLE 15. 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 [66]

Annealing Time (hours)	K_0 $\left(\frac{cm^3 \cdot mm}{cm^2 \cdot s \cdot atm^{1/2}}\right)$	Q_K (cal/mol)	D_0 (cm²/s)	Q_D (cal/mol)
20	2.5×10^{-2}	8300	5.30×10^{-4}	7750
45	1.60×10^{-2}	8000	3.35×10^{-4}	7300
70	1.60×10^{-2}	8000	3.35×10^{-4}	7300

TABLE 16. 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 [71]

Alloy Composition (at.% Cu)	Pre-Diffusion Heat Treatment			Phase Present in Alloys	Hydrogen Diffusion Coefficient (cm²/s) (at 25 °C)
	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	< 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	$2^{1/2}$ wks	α,β	2.4×10^{-5}
					2.5×10^{-5}[a]
47.8	350	0	1 wk	α,β	9.0×10^{-6}
	350	5	1 wk	α,β	2.3×10^{-5}
	350	120	$2^{1/2}$ 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	4.5×10^{-5}
	350	120	$2^{1/2}$ 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	$3^{1/2}$ 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	5.2×10^{-5}[b]

[a] Specimen rebuilt and experiment repeated.

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

TABLE 17. Diffusion coefficients of hydrogen at elevated temperatures (~130 °C) in an alloy of Cu-Pd (47.5 at.% Pd) compared to room temperature (25 °C) values. Pre-diffusion heat treatments are listed in addition. From the data of [71].

Pre-Diffusion Heat Treatment			Diffusion Measurements	
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 weeks	25	4.9×10^{-5}
350	6.7	3 weeks	121	13.2×10^{-5}
350	6.7	3 weeks	133	15.2×10^{-5}

mens, with the resistivity being related to the hydrogen concentration. The room temperature (25 °C) diffusion coefficients are listed in table 16 along with alloy compositions, prediffusion heat treatments of the specimens (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 17 for the alloy composition Cu-Pd (47.5 at.%/60 wt%). The large increase in the hydrogen diffusion coefficient at the α/β transition is 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).

7.5. Cu-H-Si

The addition of 3 at.% (1.35 wt%) silicon to pure copper has been found to reduce hydrogen permeability by a factor of six [23]. The effect of the silicon alloying addition was on the pre-exponential factor, the activation energy remaining nearly unchanged compared to pure copper. The experiments, which were performed in the temperature range 700–500 °C, employed copper alloy membranes whose principal alloying constituents were either 1.5 or 3.0 at.% (0.67 or 1.35 wt%) silicon.

7.6. Cu-H-Ti

The interdiffusion of thin films of titanium (charged by deuteron bombardment) and a copper substrate has been followed with an electron microprobe [67]. The role of diffusion in degassing the specimens was explored.

7.7. Cu-H-Zn

Aschan [8] has measured hydrogen diffusion coefficients in hot-rolled commercial purity cartridge brass (72% Cu, 28% Zn) using a saturation-desorption technique [1]. The temperature range of his study varied from 600 to 400 °C. Below 550 °C, the hydrogen diffusion coefficients were nearly the same as those obtained in pure copper specimens. At higher temperatures, the values of the coefficients were comparatively lower than those found for pure copper.

7.8. Cu-H-X

The addition of aluminum (9 at.%) and iron (4 at.%) to pure copper causes the hydrogen permeability to decrease by a factor of 100 in the very narrow temperature range 700–600 °C [23].

Other significant reductions in hydrogen permeability rates were noted in copper alloys containing silicon (3%) and manganese (1%) or tin (7%) and phosphorous (0.2%) as major alloying constituents.

7.9. Electrotransport

It has been noted that within the temperature range 1000–900 °C, the electrotransport of hydrogen in copper is directed primarily toward the anode [73].

7.10. Molten Metal Studies

The diffusion of hydrogen in molten copper has been experimentally investigated in the temperature range 1450–1100 °C by Sacris and Parlee using both steady and nonsteady-state techniques [74]. A combination of both sets of data yielded the following Arrhenius expression describing the hydrogen diffusion process:

$$D = 10.91 \times 10^{-3} \exp(-2148 \pm 349 \text{ cal} \cdot \text{mol}^{-1}/RT) \text{ cm}^2/\text{s}.$$

More recently, Wright and Hocking [75] made experimental determinations at 1101 and 1201 °C and obtained coefficients that are in agreement with those of Von Hofsten [76] but in poor agreement with the above data of Sacris and Parlee [74].

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8. Copper-Potassium

8.1. General Comments

Impurity diffusion studies in the copper-potassium study are lacking. Like in sodium, copper is believed to be a fast diffuser, moving as an interstitial and dissolving at least partly interstitially [1]. The only noble metal diffusion investigations have been those diffusing gold tracers into potassium [2–4]. As in sodium, gold tracers diffused very fast ($\sim 7\times10^{-6}$ cm^2/s at room temperature).

8.2. Cu-K References

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9. Copper-Lanthanum

9.1. La → Cu

Krishtal et al. [1] measured internal friction in copper containing 0.005 and 0.01 wt% lanthanum in the temperature range 20–450 °C. The results were interpreted in terms of a dislocation damping model with diffusion of lanthanum assumed to occur along dislocation pipes. Activation energies for the dislocation pipe diffusion of lanthanum in copper derived from these experiments are given in table 18.

TABLE 18. Activation energy for dislocation pipe diffusion of lanthanum in copper. Data extracted from [1].

La Concentration (wt%)	Q (kcal/mol)	
	Recovery Results	Excitation Results
0.005	31.0	32.0
0.01	35.6	38.2

9.2. Cu-La-B

Attempts to measure impurity diffusion rates of copper in lanthanum hexaborite at 1125 °C were unsuccessful [2]. No detectable copper penetration could be observed for diffusion anneals of up to 18.5 hours.

9.3. Cu-La References

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10. Copper-Lithium

10.1. Cu*→ Li

The diffusion of copper into lithium has generated a fair amount of recent interest because of its relatively high diffusivity rate. Ott [1, 2] has studied the tracer diffusion of ^{64}Cu in lithium between 50 and 120 °C and found that copper diffuses faster than any other hitherto

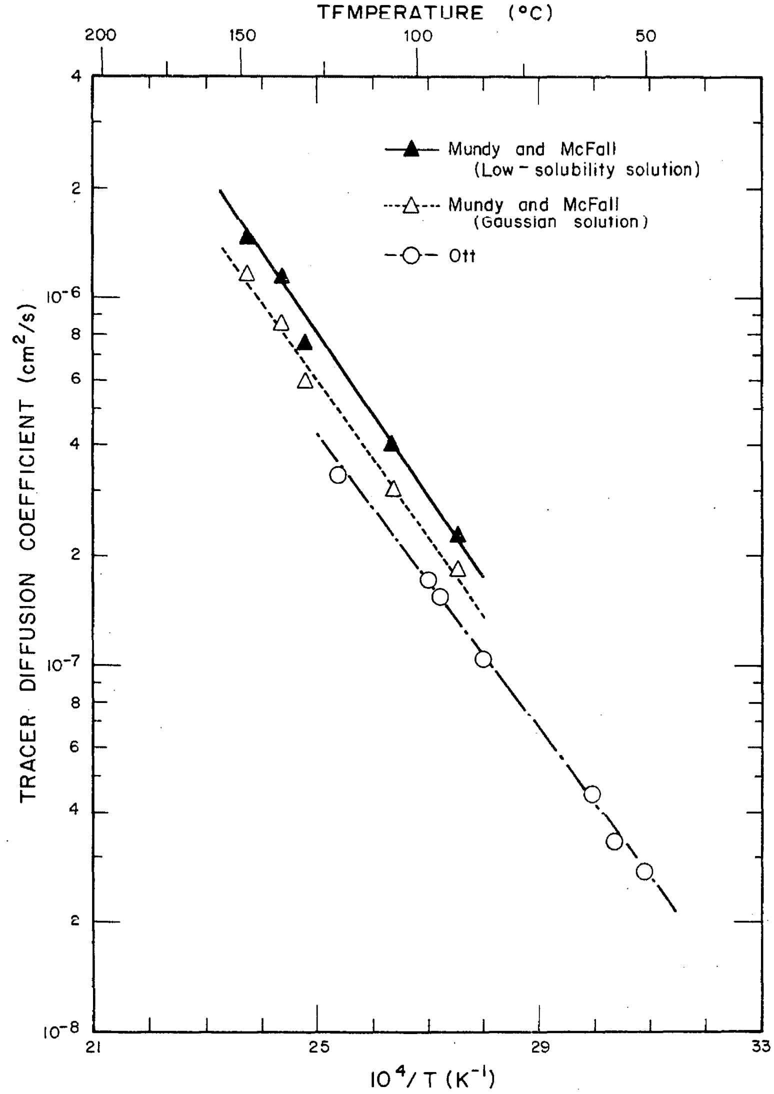

FIGURE 17. The tracer diffusion coefficient of copper in pure lithium as a function of reciprocal absolute temperature.

Data extracted from works of Ott [1, 2], and Mundy and McFall [4]. The latter's diffusion coefficients were computed by two different methods. The dashed line shown is the result of our unweighted least squares analysis of their computed diffusion coefficients. The solid line represents the most reliable values (see text).

investigated impurity in lithium. The lithium metal was 99.98% pure, and a thin-film evaporating-sectioning technique was employed. The experimental results yielded the diffusion coefficients listed in table 19 and plotted in figure 17. A least squares analysis of the experimental results from the Arrhenius plot yielded the following expression:

$$D^* = (0.047 \pm 0.011) \exp(-9.22 \pm 0.22 \text{ kcal} \cdot \text{mol}^{-1}/RT) \text{ cm}^2/\text{s}.$$

An error in Ott's paper shows the pre-exponential as 0.47 cm^2/s. Even though there is little scatter in the data, regular systematic errors may have occurred in this work because of the low copper solubility.

More recently, an isotope effect experiment for copper diffusing into lithium has been reported by Mundy and McFall [3, 4]. Measurements were taken in the temperature range 90 to 147 °C. Their rather careful experimental techniques (in part described in [4–7]) yielded curved penetration profiles, as well as an anomalously high-valued initial point. Because of the low solubility of copper in lithium, the data were computed by two methods: a least squares fit of the data to the traditional Gaussian solution, and a least squares fit of the data to the solution given by Malkovich [8]. The results of both of these computations are listed in table 20 (along with the values of χ^2). Since the latter method yields smaller values of χ^2 and takes into consideration the very low solubility of copper in lithium, one must consider the tracer diffusion coefficients yielded by this means of computation as the most reliable. The solid line in figure 17 is the result of a "weighted" least squares analysis of the data calculated with the low solubility solution [9] and probably is the most reliable representation of ^{64}Cu diffusing in lithium. The Arrhenius expression for this line is:

TABLE 19. Copper-64 tracer diffusion coefficients in lithium. Data taken from [1, 2].

T(°C)	D*(cm^2/s)
120.4	(3.312 ± 0.195) × 10^{-7}
96.5	(1.720 ± 0.070) × 10^{-7}
93.9	(1.567 ± 0.070) × 10^{-7}
83.9	(1.042 ± 0.038) × 10^{-7}
60.9	(4.523 ± 0.020) × 10^{-8}
56.3	(3.332 ± 0.040) × 10^{-8}
50.8	(2.769 ± 0.020) × 10^{-8}

$$D^*_{\text{Cu}\rightarrow\text{Li}} = (0.3_3 \pm 0.2_4) \exp(-10{,}270 \pm 630 \text{ cal} \cdot \text{mol}^{-1}/RT) \text{ cm}^2/\text{s}.$$

These D_0 and Q values differ somewhat from the initial published values [4] of $D_0 = 0.3 \pm 0.2$ cm^2/s and $Q = 10{,}000$ cal · mol^{-1}.

The nonsolid lines shown in figure 17 were obtained from our unweighted least squares analyses of the various authors' data. These lines through data points not corrected for solubility lie significantly lower than the solid line.

The isotope effect for the diffusion of copper in lithium is small [4] showing only 0.11 ± 0.03 of the inverse square root of mass dependence predicted by classical rate theory. This effect of mass on the diffusion rate was measured only at one temperature, 147.5 °C.

Just below the melting point, the value of the copper tracer diffusion coefficient is extrapolated to be of the order of 10^{-6} cm^2/s. In view of the anomalously high magnitude of the copper diffusivity, these results should be interpreted along with the similarly high impurity diffusivities found in other metals [10–27] over the last eight or nine years. Interpretation of the mechanism of this fast impurity diffusion have been offered by a number of researchers [3, 4, 15, 20, 28, 29], although which mechanism, or mechanisms, is/are operating is not clear.

10.2. Cu-Li Interdiffusion

The interdiffusion of lithium and copper has not been studied in detail. In a very qualitative study, lithium-rich coatings have been produced on copper by electrodeposition from molten lithium fluoride [30]. The authors postulated that diffusion of lithium into the copper samples was the rate-controlling step during the deposi-

TABLE 20. Diffusion of ^{64}Cu into lithium as a function of temperature (after Mundy and McFall [3]).

T(°C)	Gaussian Solution D*(cm^2/s)	χ^2	Malkovich Low-Solubility Solution D*(cm^2/s)	χ^2
147.5	1.17 × 10^{-6}	51.4	1.46 × 10^{-6}	3.1
137.0	8.36 × 10^{-7}	411.1	1.14 × 10^{-6}	392.4
130.0	5.87 × 10^{-7}	2905.2	7.42 × 10^{-7}	161.0
106.0	3.01 × 10^{-7}	10.4	3.98 × 10^{-7}	6.8
90.0	1.82 × 10^{-7}	4835.6	2.26 × 10^{-7}	85.4

tion process at 900 °C. No diffusion coefficients were calculated. Also, assorted copper alloys have been diffusion bonded with the aid of lithium alloys (which may also contain Ag, Bi, Cu, Mg, Pb and (or) Tl) at temperatures as high as 600 °C (with or without pressure) [31].

10.3. Dislocation Pipe Diffusion

The motion of lithium impurity atoms along dislocation pipes in copper has been investigated by following the time dependence of internal friction [32]. The temperature range of the study was 20 to 450 °C. Lithium alloying additions varied from 0.01 to 0.001 wt% (0.1 to 0.01 at.%). An activation energy of ~ 20 kcal/mol was calculated for the pipe diffusion process in each of the alloys.

10.4. Thermotransport

The thermotransport of radioactive copper in pure lithium has been investigated by Thernquist [33]. His measurements were taken using a steady-state vacuum technique [34, 35], in spite of the relatively short half-life of the ^{64}Cu isotope (≈ 13 h). His semiquantitive results allowed for the computation of a heat of transport of approximately 5 kcal/mol. The computation takes into account self-transport but not defect flow effects.

10.5. Cu-Li References

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11. Copper-Lutetium

11.1. Lu* → Cu

The tracer diffusion coefficient of the rare earth metal isotope ^{177}Lu in copper has been studied in the temperature interval 850 to 1010 °C [1]. The measurement and calculation of the lutetium tracer diffusion coefficients were obtained in the same manner described in earlier sections for the cerium and europium tracers in copper (except that no serial sectioning of specimens was involved). The data are listed in table 21, and the coefficients are plotted as a function of reciprocal absolute temperature in figure 18. In the temperature interval studied, the ^{177}Lu tracer diffuses in copper according to the expression,

$$D^*_{\mathrm{Lu}} = 1.2 \times 10^{-8} \exp(-28 \text{ kcal} \cdot \text{mol}^{-1}/RT) \text{ cm}^2/\text{s}.$$

Both D^* and D_0 values here are lower than is usual for impurity diffusion in copper. The same comments as for the europium tracer results discussed previously are applicable to these lutetium results.

TABLE 21. Lutetium-177 tracer diffusion coefficients in copper [1].

T(°C)	D^*(cm^2/s)
1010	2.07×10^{-13}
1010	1.77×10^{-13}
945	1.30×10^{-13}
945	1.12×10^{-13}
895	6.56×10^{-14}
895	6.33×10^{-14}
850	4.26×10^{-14}
850	4.04×10^{-14}

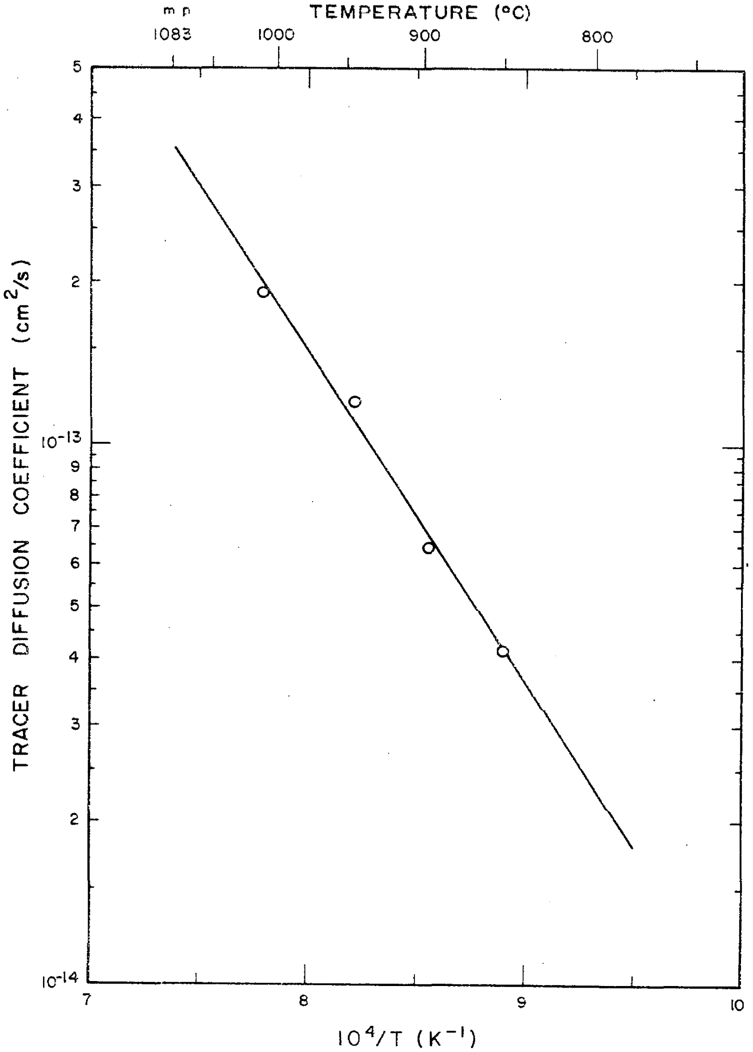

FIGURE 18. The tracer diffusion coefficient of ^{177}Lu in pure copper as a function of reciprocal absolute temperature.

Data taken from [1].

11.2. Cu-Lu Reference

[1] Badrinarayanan, S., and Mathur, H. B., "Impurity Diffusion of Rare Earth Metals in Copper," Indian J. Pure Appl. Phys. **8**, 324–330 (1970).

12. Copper-Magnesium

12.1. General Comments

Few investigations have been made into copper-magnesium binary alloys, the interest being principally in ternary, and higher order alloys that exhibit ageing. Bergner [1] has recently summarized some of the theoretical concepts and experimental data on the diffusion of copper, magnesium, and other technically important alloying metals (Si, Zn, Fe) in aluminum.

12.2. Cu-Mg-Al and Cu-Mg-X

Renouard [2] constructed diffusion couples which were formed with Al (99.5 at.%) and Al-Cu (4 at.%)-Mg (0.8 at.%). These couples were annealed at 380, 420, 460, and 500 °C and the diffusion of copper and magnesium was determined spectrographically. Similarly, diffusion couples constructed of an Al-Zn (2 at.%) alloy and an Al-Zn (8 at.%)–Mg (2.5 at.%)–Cu (1.5 at.%) alloy were also annealed at the same temperatures and analyzed accordingly. The data contained much scatter. The author's calculated values of D are tabulated in table 22.

In view of the low temperature and polycrystalline specimens, grain boundary effects may have played an important role in these experiments.

Koltsova and coworkers [3] studied the kinetics of diffusion processes in aluminum-base alloys (containing Cu and Mg) with a particular emphasis on formation of intermetallic compound $CuAl_2$.

During homogenization (to remove dendritic segregation) anneals (at ~ 500 °C) performed with aluminum-based alloys (containing 4–5% Cu, ~ 1.5% Mg, 0.60% Mn, and 0.12% Zr), Verdier [4] noted that magnesium diffused more quickly than copper.

The diffusion bonding of aluminum and magnesium alloys has been accomplished with the aid of moderate pressures and temperatures [5].

12.3. Cu-Mg References

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13. Copper-Manganese

13.1. Mn* → Cu

The impurity diffusion of the tracer ^{54}Mn into single crystals of pure (99.99%) copper has been experimentally studied by Mackliet [1] and Ikushima [2].

The experimental techniques employed by both authors were similar (the tracer was electrodeposited only with difficulty, diffused at temperature, and then sectioned to determine the penetration), although Mackliet did all his studies at only one temperature (1069 °C). The results of their studies are listed in table 23. When these diffusion coefficients are plotted versus the inverse of the absolute temperature, a straight line results, as shown in figure 19.

The straight line, as determined by Ikushima [2] using a least square calculation, represents the diffusion coefficient as:

$$D^* = D_0 \exp(-Q/RT) = 10^7 \exp(-91{,}400 \text{ cal} \cdot \text{mol}^{-1}/RT) \text{ cm}^2/\text{s}.$$

The probable error in the activation energy (Q) is ±1600 cal/mol, and in the pre-exponential (D_0) is $10^{\pm 0.32}$ or (0.48 to 2.09). These values for D_0 and Q are quite large, and the existing theories of diffusion cannot easily account for them, especially that of D_0.

Although Mackliet measured his diffusion coefficient at only one temperature, he estimated a value for D_0 and Q using Zener's elastic model of diffusion [3, 4].

TABLE 22. Copper and magnesium interdiffusion coefficients from AlCuMg and AlCuMgZn alloys. Data excerpted from [2]

T(°C)	$\tilde{D}_{Cu}$ (cm²/s) Couple 1[a]	$\tilde{D}_{Cu}$ (cm²/s) Couple 2[b]	$\tilde{D}_{Mg}$ (cm²/s) Couple 1[a]	$\tilde{D}_{Mg}$ (cm²/s) Couple 2[b]
500	2.4×10^{-9}	1.1×10^{-9}		2.2×10^{-9}
460	1.3×10^{-9}	5.0×10^{-10}	5.8×10^{-10}	8.1×10^{-10}
420	6.7×10^{-10}	2.1×10^{-10}	1.9×10^{-10}	2.5×10^{-10}
380	3.3×10^{-10}	1.1×10^{-10}		9.7×10^{-11}

[a] Al/AlCuMg.

[b] AlZn/AlCuMgZn.

Using these estimates, he found that, for the most extreme variations that might be expected, the diffusion coefficient of the tracer ^{54}Mn in copper would be predicted to lie within a rather narrow range (shown as the shaded range in Figure 19), with the limits of this range given by the expressions:

$$D^* \cong \begin{Bmatrix} 0.08 \exp(-41{,}000 \text{ cal} \cdot \text{mol}^{-1}/RT) \\ 0.5 \ \ \exp(-46{,}000 \text{ cal} \cdot \text{mol}^{-1}/RT) \end{Bmatrix} \text{cm}^2/\text{s}.$$

Why such a radical difference should exist between this result and the activation energy and the pre-exponential factor reported by Ikushima is not readily apparent, although the penetration curves obtained by Ikushima do show a fair amount of scatter, and both authors had difficulty in electrodepositing their ^{54}Mn tracer on their copper specimens. Mackliet's activation energy and D_0 values are in fair agreement with other impurity diffusion data in copper [5]. Also, they are consistent with the diffusion coefficient, Kirkendall shift, and interdiffusion in Cu-Mn alloys (which contain dilute amounts of manganese), whereas Ikushima's results are not.

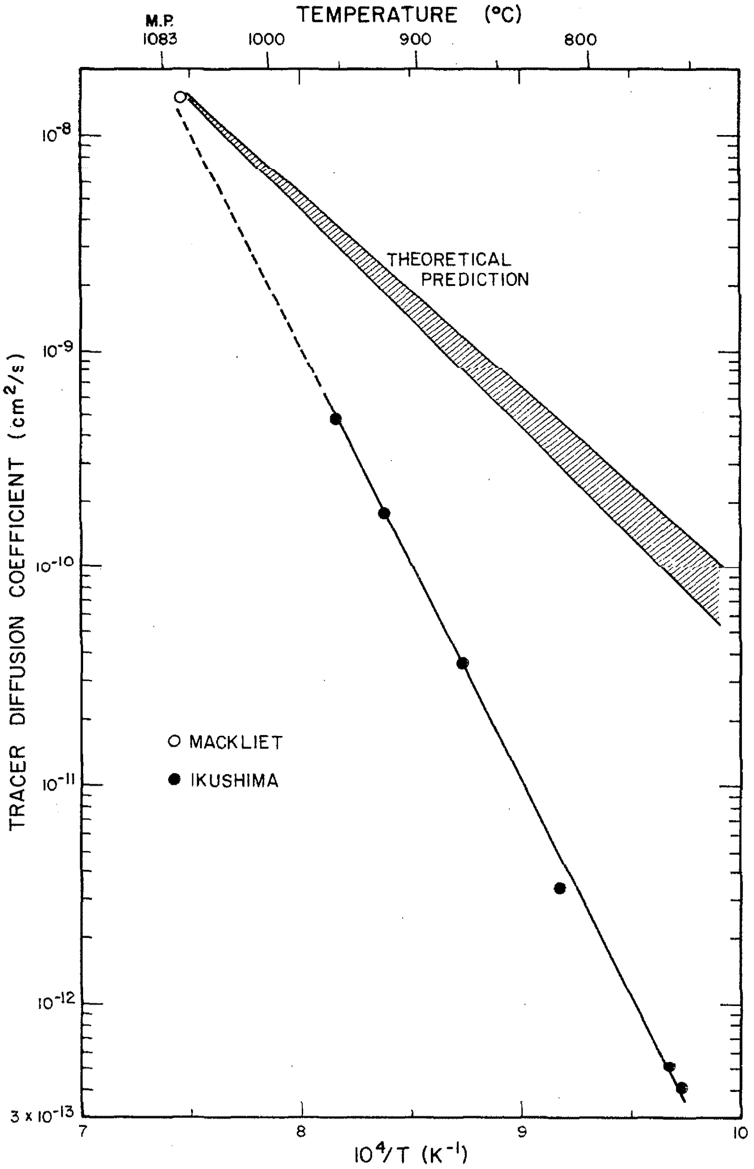

FIGURE 19. The tracer diffusion coefficient of ^{54}Mn in pure copper as a function of reciprocal absolute temperature.

All measurements made on single crystals of copper. Experimental data taken from papers of Mackliet [1] and Ikushima [2]. Theoretical predictions calculated from Zener's model [3, 4].

TABLE 23. Manganese-54 tracer diffusion coefficients in copper. Data extracted from [1, 2].

T(°C)	D*(cm²/s)
1069 ± 1[a]	1.49×10^{-8}
950 ± 1	4.82×10^{-10}
918 ± 1	1.79×10^{-10}
871 ± 1	3.59×10^{-11}
817 ± 1	3.32×10^{-12}
761 ± 1	5.07×10^{-13}
754 ± 2	4.09×10^{-13}

[a] Single measurement of Mackliet; the remaining measurements are by Ikushima.

13.2. Cu-Mn Interdiffusion

Interdiffusion in the Cu-Mn system has been the subject of several investigations [6–8]. Matano [6] carried out his studies with Cu-Mn alloys of 7 to 10 wt% (8 to 11 at.%) manganese over a temperature range of 400 to 950 °C. The concentration profiles determined from lattice parameter measurements [9] yielded the diffusion coefficients in table 24. These results should be used with caution since recrystallization occurred during the diffusion anneals in some of the samples. Grain boundary diffusion was also probably contributing greatly at the lower temperatures in his polycrystalline samples.

More recently Cu-Mn interdiffusion kinetics in 28 wt% (31 at.%) manganese alloys have been studied by Caloni et al. [7] with an X-ray microprobe. The chemical analysis of the materials used to prepare the polycrystalline diffusion couples is shown in table 25. All the diffusion heat treatments were performed under a dynamic vacuum, between 640 and 820 °C, and for times varying from 2 to 32 hours. After diffusion, the copper and manganese concentrations were determined on a plane surface, normal to the welded interface and parallel to the direction of diffusion. The interdiffusion coefficients were calculated using Grube's method [10] and are listed in table 26. Linear probability plots of the data indicated that the interdiffusion coefficient, $\tilde{D}$, is independent of concentration over a wide range of composition. To represent the data in terms of an activation energy (Q) and pre-exponential (D_0), the diffusion coefficients were plotted on a log scale as a function of the reciprocal of the absolute temperature, as in figure 20. The author's quoted line, fitted by a least square calculation, is expressed as,

$$\tilde{D}=D_0 \exp(-Q/RT)=$$

$$0.58 \exp(-42{,}400 \text{ cal}\cdot\text{mol}^{-1}/RT) \text{ cm}^2/\text{s}.$$

TABLE 24. Interdiffusion coefficients in copper-manganese (7-10 wt%) alloys. Data extracted from Matano [6]

T(°C)	Time(s)	$\tilde{D}$(cm²/s)
950	3.60×10^{3}	6.48×10^{-10}
890	7.20×10^{3}	1.85×10^{-10}
850	2.40×10^{3}	1.27×10^{-10}
650	6.00×10^{2}	3.70×10^{-11}
500	1.86×10^{4}	9.49×10^{-13}
500	9.00×10^{3}	1.62×10^{-12}
500	1.80×10^{3}	3.59×10^{-12}
400	8.64×10^{4}	1.97×10^{-13}

TABLE 25. Chemical analysis of materials by Caloni et al. [7].

Material	Composition (wt%)			
	Cu	Mn	Fe	Si
Copper	99.98	0.001	0.002	
Cu-Mn Alloy	71.74	28.03	0.08	0.15

TABLE 26. Interdiffusion coefficients in a copper-manganese (28 wt%) alloy (after Caloni et al. [7]).

T(°C)[a]	$\tilde{D}$(cm²/s)
820	1.84×10^{-9}
790	1.14×10^{-9}
770	6.22×10^{-10}
740	3.55×10^{-10}
690	1.26×10^{-10}
640	3.18×10^{-11}

[a] All temperatures measured to ±2 °C.

It should be noted that our least squares analysis of the same data yielded a pre-exponential factor of 1.43 cm²/s and an activation energy of 44,500 cal/mol. This temperature dependence is plotted in figure 20 for comparison. It is also interesting to note that the line

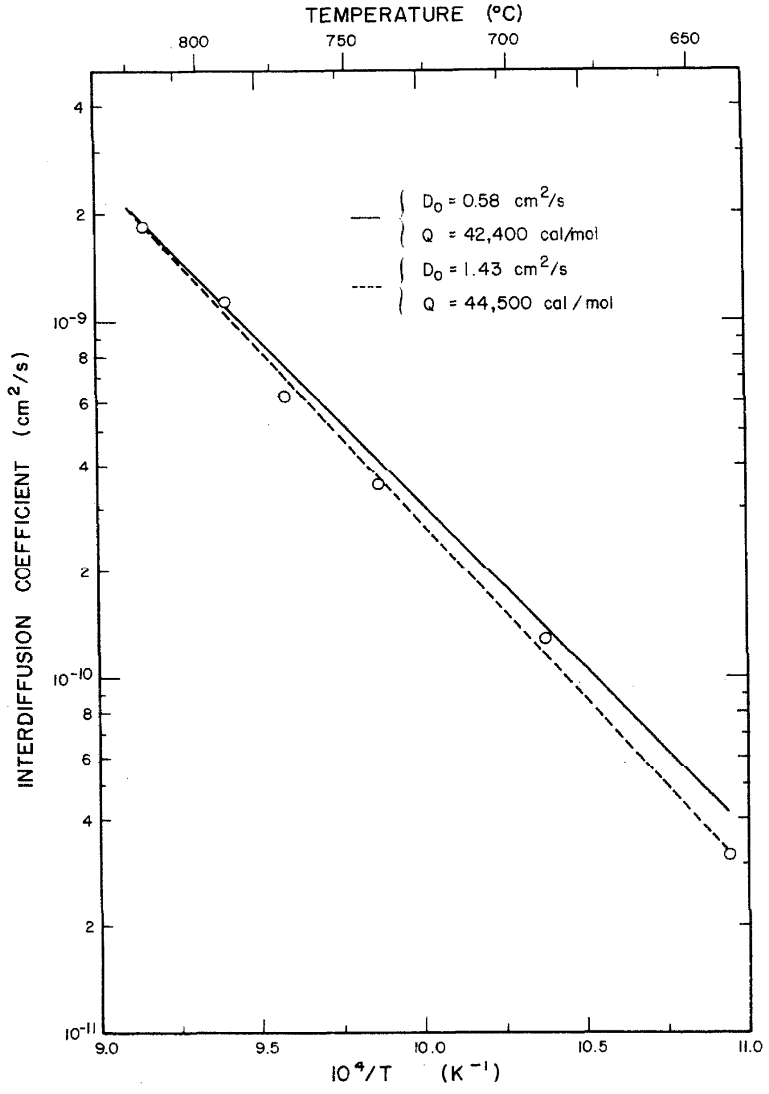

FIGURE 20. The interdiffusion coefficient as a function of reciprocal absolute temperature in copper-rich Cu-Mn.

Cu-Mn (28 wt%) alloys interdiffused against pure copper. The solid line represents the results as published by Caloni and Ferrari [7]. The dashed line represents the results obtained from our least squares analysis of Caloni and Ferrari's data. The dashed line appears to be the same as the line drawn in the researchers published Arrhenius plot, although it does not correspond to their published D_0 and Q values.

plotted in Caloni and Ferrari's paper [7] is the same (with respect to the data points) as the dashed line we have shown in figure 20. In any event, both calculated results are probably within the limits of error of the experiments.

A very brief interdiffusion study at a single temperature (850 °C) has been reported [8, 11]. The study employed vapor-solid as well as solid-solid diffusion couples. In the solid-solid couples, alloys containing 10.9 at.% (9.6 wt%) and 5.7 at.% (5.0 wt%) manganese were bonded to OFHC copper. The vapor-solid diffusion couple utilized chips of an alloy of 10.9 at.% manganese packed around OFHC copper. The diffusion anneals were for three days duration.

After diffusion, metallographic examination revealed porosity, mostly on the alloy side in the diffusion zone of the solid-solid couple. No porosity was found in the diffusion zone of the vapor-solid couple. The Kirkendall shifts indicated that manganese moved faster than the copper.

The manganese concentration profiles in the diffusion zone were determined with an electron-microprobe. From these profiles the interdiffusion coefficient, $\tilde{D}$, was calculated as a function of composition by a Matano analysis [12]. The results of these calculations for selected manganese concentrations are given in table 27. It is of interest to note that the solid-solid and vapor-solid couples show such good agreement.

TABLE 27. Interdiffusion coefficients in the copper-manganese system at 850 °C (after Wittenberger et al. [8, 11]).

Mn Conc. (at.%)	$\tilde{D}(10^{-10}cm^2/s)$		
	Couple A	Couple B	Couple C
5.5	5.2		5.6
6.0		6.1	6.1
6.85		7.0	7.2
9.0		11.8	11.8

A: Solid/Solid, Cu/Cu-Mn(5.7 at.%).

B: Solid/Solid, Cu/Cu-Mn(10.9 at.%).

C: Solid/Vapor, Cu/Cu-Mn(10.9 at.%).

13.3. Cu-Mn-Al

Interdiffusion studies have been performed with alloys in the aluminum-rich, single-phase corner of the ternary constitution diagram [13]. All diffusion couples were annealed at 556.5 °C for 1.238×10^6 seconds. After diffusion, the diffusion couples were sectioned and irradiated in a nuclear reactor. Activation analysis for copper and manganese allowed their concentration-penetration curves to be determined.

The nominal compositions of the alloys used to make the diffusion couples are listed in table 28. The configuration of the diffusion couples and the chemical interdiffusion coefficients resulting from the anneal are listed in table 29.

There was no concentration dependence of $\tilde{D}^3_{11}$ found.

TABLE 28. Compositions of alloys used by Kirkaldy et al. [13].

Alloy Number	Composition (wt%)		
	Al	Cu	Mn
A	99.99	0.005	
B	94.87	3.95	1.15
C	95.97	4.00	
M	98.78	0.004	1.18

The value of $\tilde{D}^3_{12}$ was determined from an experiment where the copper concentration was initially almost uniform, with Kirkaldy's solution [14] being applied to the differential equations encountered. The significance of the negative value of $\tilde{D}^3_{12}$ is that copper diffuses up a manganese gradient [15]. This type of interaction also was found in the other ternary configurations (*C*/*E*, *B*/*A*).

A single mean interdiffusion coefficient, $\tilde{D}^3_{22}$, was determined for the diffusion of manganese from several configurations because of the limited number of data points obtainable due to the small penetration distances. Under these circumstances, it is not obvious whether the different copper configurations had any influence on the manganese diffusion.

In the authors' assessment of the neutron activation method of interdiffusion analysis, they claim a precision of 1.3% and an absolute accuracy of 1% for an individual point. Most of their error was attributed to inhomogeneities in their standard samples.

Mitani and Yakota [16], in a study of the sintering behavior of Cu-γ_2(Cu_9Al_4)-Mn mixed powder compacts at ~ 900 °C, found that the addition of manganese to the Cu-γ_2 system enhanced interdiffusion.

13.4. Cu-Mn-Ni

The rate of diffusion of manganese in Cu-Mn-Ni alloys was measured over a temperature range of 846 to 1046 °C [17]. The experimental technique [18] employed involved the evaporating 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 managanese from the surface produces a concentration gradient in the alloy, thus requiring additional managanese 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

TABLE 29. Partial interdiffusion coefficients in the Al-Cu-Mn ternary system at 556.5 °C. Data excerpted from [13]

Couple Configuration	$\tilde{D}^3_{ij}$ (cm²/s)$^{(a)}$		
	$\tilde{D}^3_{11}$	$\tilde{D}^3_{12}$	$\tilde{D}^3_{22}$
C/A	1.78×10^{-9} (*b*)	—	—
B/C	—	-0.8×10^{-9} (*b*)	—
A/B, B/C, A/M, C/M	—	—	9.0×10^{-12} (*c*) (mean value)
C/M, A/B	—	(*d*)	

[a] 1 = Cu, 2 = Mn, 3 = Al.

[b] Determined from copper profile.

[c] Determined from manganese profile.

[d] Complex copper concentration profiles consistent with above values of $\tilde{D}^3_{11}$ and $\tilde{D}^3_{12}$.

zero manganese concentration, this value is only an average figure over the manganese composition range 0 to 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 [19]. 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 [20]. The concentration-penetration curves revealed nonideal thermodynamic behavior and "uphill" diffusion of manganese in which manganese 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.

13.5. Cu-Mn-Zn

Interdiffusion coefficients have been measured in a study of ternary diffusion in the large single-phase copper-rich corner of the Cu-Mn-Zn system at 850 °C [21–22].

A vapor-solid diffusion couple where the two solutes (Mn and Zn) diffuse from a vapor source into a ternary solid solution was employed. Inert markers were initially placed at the vapor-solid interface to assist in the determination of the intrinsic diffusion coefficients.

The concentration-penetration profiles were determined from X-ray fluorescence analyses for manganese and zinc. Partial interdiffusion coefficients were calculated at three different compositions and are listed in table 30. Independent evaluations of the interdiffusion coefficients reflect a variation of less than 10% in the values of $\tilde{D}^3_{11}$ and $\tilde{D}^3_{22}$. The coefficient $\tilde{D}^3_{12}$ varied by less than 40%, whereas $\tilde{D}^3_{21}$ changed by as much as 100%. The negative value for the partial interdiffusion coefficient $\tilde{D}^3_{21}$ results from the small value of the intrinsic diffusion coefficient D^3_{21}.

Where the inert marker motion was significant, partial intrinsic diffusion coefficients were calculated using the method of Philibert and Guy [23], and these are listed in table 31. Because of the difficulty the authors experienced in accurately evaluating the concentration gradient at the inert marker plane, they estimate that the partial intrinsic diffusion coefficients D^3_{11} and D^3_{22} vary within about 20%, while D^3_{31} and D^3_{32} vary about 50%. The cross coefficients, D^3_{12} and D^3_{21}, varied as much as 100%.

A reanalysis of these data [24] confirmed the earlier conclusions [21] that zinc diffuses faster than manganese and copper diffuses the slowest of all in the Cu-Mn-Zn system at 850 °C.

In addition to the nonsteady state, semi-infinite diffusion couple studies [21–24] described above, steady-state substitutional diffusion studies [11, 25] also were performed. Thin membranes of copper were exposed to zinc and manganese vapors at 850 °C to obtain steady-state concentration profiles that were invariant with time. Electron-microprobe analysis of the membrane yielded the concentration profiles of the manganese and zinc in the copper-rich phase of the Cu-Mn-Zn system. The burial of inert markers was also measured where possible. Assuming that the diffusion of copper is zero at steady-state, the results indicate for all vapor-source compositions employed (see table 32) that manganese still diffuses slower than the zinc in the copper matrix.

TABLE 30. Partial interdiffusion coefficients in the Cu-Zn-Mn ternary systems at 850 °C. Data taken from [21, 22].

Composition	$\tilde{D}^3(10^{-10}\mathrm{cm}^2/\mathrm{s})$			
	$\tilde{D}^3_{11}$	$\tilde{D}^3_{12}$	$\tilde{D}^3_{21}$	$\tilde{D}^3_{22}$
Cu-Zn(6.9 at.%)-Mn(1.2 at.%)	8.7	0.68	-0.02	9.0
Cu-Zn(8.1 at.%)-Mn(2.4 at.%)	11.4	2.6	-0.08	12.2
Cu-Zn(10.3 at.%)-Mn(1.8 at.%)	18.2	1.1	-0.17	14.6

1 = Zn; 2 = Mn; 3 = Cu.

TABLE 31. Partial intrinsic diffusion coefficients in the Cu-Zn-Mn system at 850 °C. Data extracted from [21, 22].

Composition	$D^3_{ij}(10^{-9}\mathrm{cm}^2/\mathrm{s})$					
	D^3_{11}	D^3_{12}	D^3_{21}	D^3_{22}	D^3_{31}	D^3_{32}
Cu-Zn(13.5 at.%)-Mn(4.1 at.%)	10.1	1.5	0.04	3.5	-1.0	-0.3
Cu-Zn(19.2 at.%)-Mn(4.1 at.%)	14.2	1.5	0.2	4.8	-0.6	-1.5

1 = Zn; 2 = Mn; 3 = Cu.

TABLE 32. Composition of alloys used as vapor sources by Wittenberger et al. [11, 25].

Composition (at.%)		
Cu	Mn	Zn
94.4	5.6	–
92.6	–	7.4
89.1	–	10.9
88.1	–	11.9
86.7	10.5	2.8
80.7	17.1	2.2
79.4	5.7	14.9

13.6. Cu-Mn-X

The diffusion of copper in manganese-steels has been the subject of a cursory study [26]. The aim of these qualitative investigations was to determine the effect of alpha-forming elements on the intergranular diffusion of copper into γ-iron. The results indicated that copper diffused primarily along the grain boundaries at 1100 °C in the austenitic (18/8 stainless, manganese-Hadfield, etc. steels.

13.7. Molten Metals

The diffusion of manganese in liquid Cu-Mn alloys at 1110, 1150, and 1250 °C has been reported [27]. In a 2.44 wt% (2.81 at.%) liquid alloy, the diffusion of manganese can be expressed as:

$$D = 1.62 \times 10^{-3} \exp(-9550 \text{ cal} \cdot \text{mol}^{-1}/RT) \text{ cm}^2/\text{s},$$

with stated errors of ± 2000 cal/mol in activation energy, and $\pm 1 \times 10^{-3}$ cm^2/s in the pre-exponential factor. In an alloy containing 5.1 wt% (5.9 at.%) manganese, the diffusion coefficient at 1150 °C was found to be $(6.2 + 1.0) \times 10^{-5}$ cm^2/s, which is comparable to the value $(5.5 \pm 0.2) \times 10^{-5}$ cm^2/s measured at this temperature for manganese diffusion in the 2.44 wt% alloy.

Studies of the chemical compositions in the melt close to the solidification front yield diffusion data that are in essential agreement with the above expression [28].

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14. Copper-Molybdenum

14.1. Cu-Mo Interdiffusion

Quantitative lattice diffusion data in this binary system are lacking. In one group of experiments, pure, deoxidized, polycrystalline, copper specimens were annealed in pure molybdenum shavings for as long as 100 and 200 hours at temperatures of 950 to 980 °C [1]. The molybdenum penetration was followed metallographically and by microhardness readings, as well as by thermal emf measurements. No diffusion coefficients were calculated.

The diffusion bonding of pure polycrystalline copper and molybdenum has been accomplished at 900 °C [2]. Maximum interdiffusion rates of the order of 10^{-11} cm^2/s were calculated.

14.2. Cu-Mo-Fe

Lazarev and Golikov have, in a series of papers [3–5], reported rates of volume and grain boundary diffusion of radioactive ^{64}Cu in polycrystalline Fe-Mo alloys (alloying additions were either 0.7 or 1.0 wt% Mo). Experiments were performed (using a residual activity technique [6, 7] over the temperature range 1000 to 700 °C and thus in both the α- and γ-phases of the alloys. Experiments in the α-phase utilized an alloy containing 1.0 wt% Mo, (0.58 at.%), and in the γ-phase, a 0.7 wt% (0.41 at.%) Mo alloy. The results indicate that the molybdenum alloying addition had no measureable effect on the lattice diffusion rate of ^{64}Cu relative to diffusion in pure iron. (The data are not plotted here since the results obtained by Rothman et al. [8] are deemed more reliable.) A method of calculation [7] was employed to process the experimental results which did yield ^{64}Cu grain boundary diffusion coefficients from the same concentration-penetration curves. These data are shown plotted in figure 21 as the product of the half-width of the grain boundary, δ, and the grain boundary diffusion coefficient, D_{gb}. The temperature dependence shows a discontinuity at the α/γ phase transition (910 °C). It is apparent that the molybdenum alloying additions reduce the grain boundary mobility of ^{64}Cu, the effect becoming more pronounced at lower temperatures.

Sirca, in a series of experiments [9–11], examined the lattice and grain boundary diffusion of copper in molybdenum-alloy steels. These investigations in the temperature range 1000 to 1100 °C were very qualitative in nature.

14.3. Cu-Mo-X

Hume and coworkers [12, 13] interdiffused copper and several selected stainless steels over the temperature range 600 to 1050 °C. The stainless steels chosen had nominal compositions of 17 Cr-13 Ni-2.5 Mo (wt%), 25 Cr-20 Ni (wt%), and 25 Cr-12 Ni-3 W (wt%). The results revealed that, in the solid state, copper interdiffuses very slowly (maximum penetration at 1050 °C after 10,000 h was only 3 mm; at 700 °C, less than 30 μm in 10,000 h). 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.

The radiation enhancement of diffusion in Ni-Fe-Cu-Mo alloys has been reported by Ferro and Soardo [14]. 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.

14.4. Surface Diffusion

The surface diffusion of copper atoms on molybdenum has been reported [15]. The phenomenon of secondary ion emission [16, 17] was employed to follow the surface diffusion of copper atoms out of a copper film deposited on a molybdenum substrate. The surface diffusion coefficients were calculated using the mathematical treatment of [17]. The results in the temperature range of 500 to 800 °C are listed in table 33. These same data are plotted in figure 22 along with the straight line (dashed) given by the author's published pre-exponential factor (8.7×10^{-4} cm^2/s) and activation energy (12.5 kcal/mol). His data points are far- removed from this line. There is no apparent reason for such a discrepancy, and we have recalculated D_0 and Q using a least squares analysis. The temperature dependence we arrive at is given by,

$$D_{\mathrm{surf}} = 2.50 \times 10^{-3} \exp(-13{,}900\ \mathrm{cal} \cdot \mathrm{mol}^{-1}/RT)\ \mathrm{cm}^2/\mathrm{s}.$$

The formation of copper islands during the diffusion of copper over molybdenum has been directly observed by optical and electrical microscopy [18]. When a

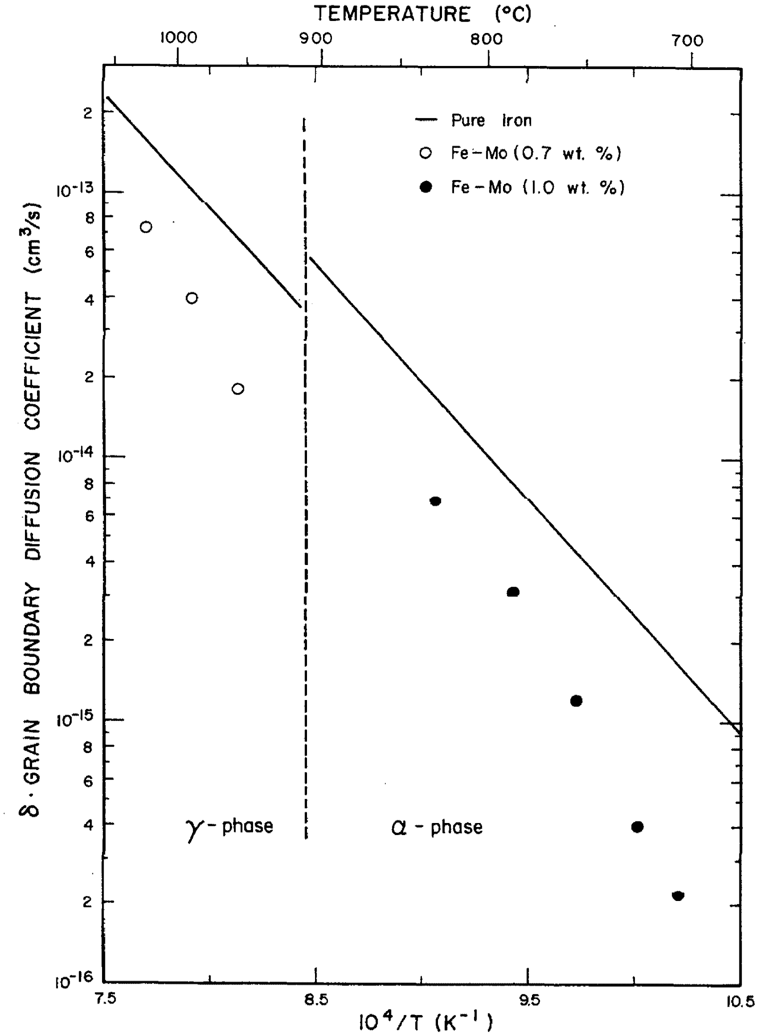

FIGURE 21. The product $\delta \cdot D_{gb}$ as a function of reciprocal absolute temperature for Cu in Fe and Fe-Mo alloys.

δ is defined as the half-width of the grain boundary in Fe and Fe-Mo alloys. D_{gb} is the grain boundary diffusion coefficient of radioactive ^{64}Cu in these alloys. Data extracted from the papers of Lazarev and Golikov [3-5].

TABLE 33. Copper surface diffusion coefficients on molybdenum. Data taken from [15]

T(°C)	D_{surf}(cm^2/s)
800	4×10^{-6}
700	1.77×10^{-6}
600	6.8×10^{-7}
500	3.2×10^{-7}

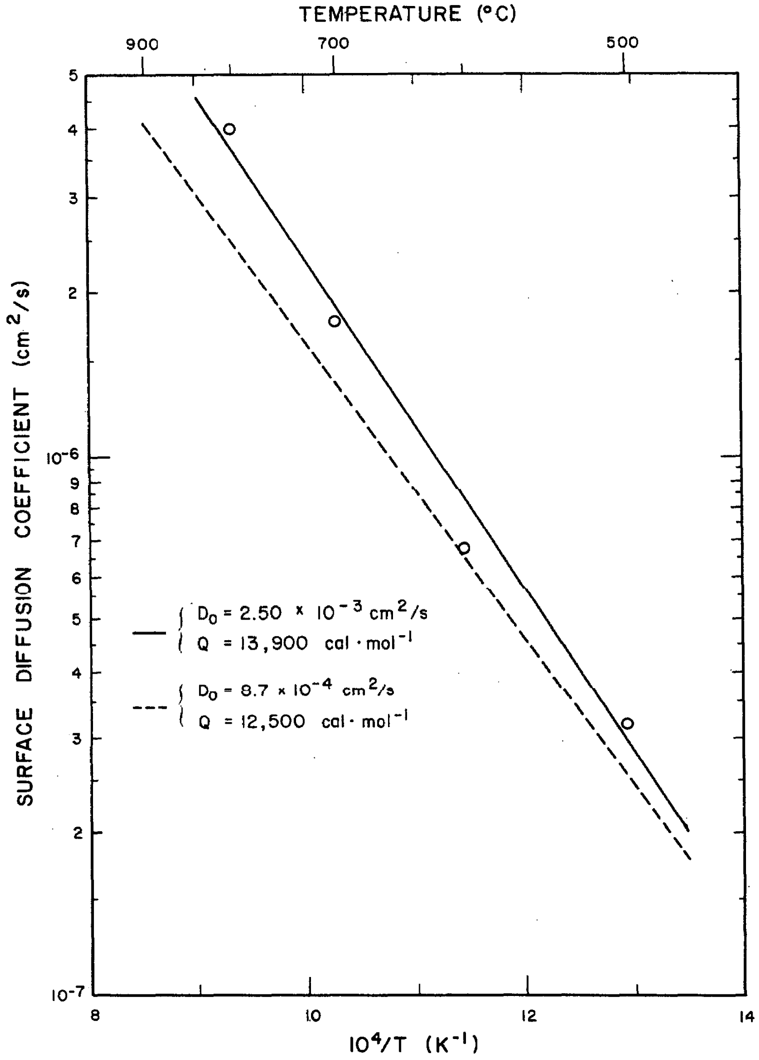

FIGURE 22. Surface diffusion coefficient of copper on molybdenum as a function of reciprocal absolute temperature.

Author's data [15] do not agree with his Arrhenius expression (represented by dashed line). Solid line represents our recalculation using his data points.

copper film (~ 5000 Å thick) was vacuum-evaporated onto a molybdenum foil and then given a diffusion anneal for 45 minutes at 700 °C, a redistribution of the copper to islets was noted.

14.5. Grain Boundary Diffusion

Grain boundary diffusion has been studied in a few ternary copper-molbdenum-iron alloys and these are discussed in a preceding section.

14.6. Cu-Mo References

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15. Copper-Sodium

15.1. General Comments

The diffusion rate of copper into sodium, or vice versa, has not been experimentally determined. There are, though, strong indications [1] that copper (similar to the other noble metals) in sodium diffuses very fast interstitially (and hence forms at least a partial interstitial solid solution in sodium). The diffusion of radioactive gold in sodium has been measured between 0 °C and 77 °C and was found to be very fast [2, 3], and can be expressed by the following equation:

$$D^*_{\mathrm{Au}} = (3.34 \pm 1.0) \times 10^{-4} \exp(-2.21 \pm 0.2\ \mathrm{kcal \cdot mol^{-1}}/RT)\ \mathrm{cm^2/s}.$$

Tracer studies of silver diffusing in sodium reveal silver to be a fast diffuser also [3, 4], although not quite as fast as gold, and can be expressed by the following equation:

$$D^*_{\mathrm{Ag}} = 1.8 \times 10^{-2}\ \exp(-5.3\ \mathrm{kcal \cdot mol^{-1}}/RT)\ \mathrm{cm^2/s}.$$

15.2. Cu-Na References

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16. Copper-Niobium

16.1. Nb* → Cu

The impurity diffusion of ^{95}Nb into pure (99.999%), polycrystalline copper has been studied over the temperature range of 807 to 906 °C [1]. The residual activity method of analysis was employed to determine the concentration profile of the diffused isotope. The specimen was sectioned by grinding, and the thickness of the removed layer was estimated by weight difference. The resulting tracer diffusion coefficients for ^{95}Nb in copper are listed in table 34. Figure 23 shows the temperature dependence of this data. The following relationship was found from the best fit of the data:

TABLE 34. Niobium-95 tracer diffusion coefficients in copper [1].

T(°C)	D*(cm^2/s)
906	1.46×10^{-11}
865	5.63×10^{-12}
856	4.17×10^{-12}
827	2.21×10^{-12}
807	1.56×10^{-12}

$$D^* = 2.04 \exp\left[-60{,}060\ \mathrm{cal \cdot mol^{-1}}/RT\right]\ (\mathrm{cm^2/s}).$$

The accuracy of the frequency factor ($D_0 = 2.04$ cm^2/s) is quoted as ±30%, and of the activation energy (Q = 60.06 kcal/mol), as ±2%.

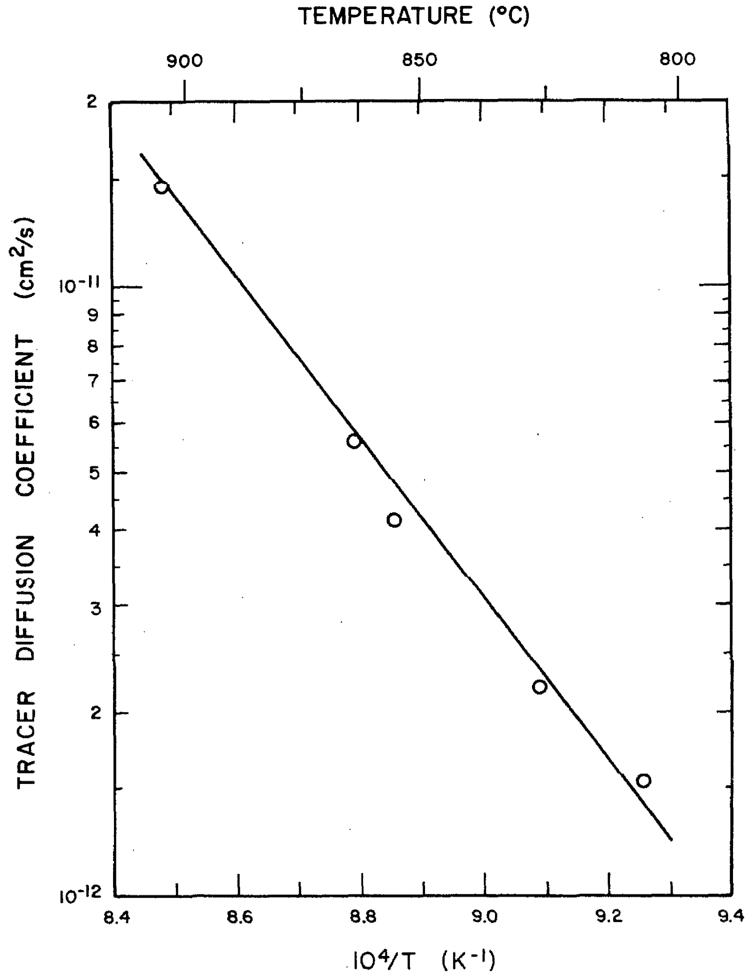

FIGURE 23. The tracer diffusion coefficient of ^{95}Nb in pure copper as a function of reciprocal absolute temperature.
Data taken from [1].

Although the minimal scatter in the plot indicates the care taken in performing the experiment, the temperature range of the investigation is rather narrow. The activation energy is a little higher than the values for other transition solutes in copper ($Q_{\mathrm{Pd}}=54.37$ kcal/mol, $Q_{\mathrm{Ni}}=$ 56.6 kcal/mol, and $Q_{\mathrm{Co}}=54.1$ kcal/mol).

16.2. Cu-Nb Interdiffusion

The interdiffusion occurring between a niobium-coated wire covering a copper core has been investigated in the temperature range 907 to 800 °C [2]. The degree of interdiffusion occurring in the bimetallic wire was followed with electrical resistance measurements. The technique has been employed before [3], and calculations were developed by Bokshtein et al. [4]. Interdiffusion was assumed to be concentration-dependent in the rather narrow temperature range of the study, and the following parameters for an Arrhenius expression were arrived at:

$$D_0=4.91\pm0.22\ \mathrm{cm}^2/\mathrm{s},$$

$$Q=52.6\pm10.3\ \mathrm{kcal/mol}.$$

No individual interdiffusion coefficients were reported, and lack of experimental details (e.g., the role of a second phase in the interdiffusion process) makes an assessment of these results difficult.

Interdiffusion investigations at somewhat higher temperatures (1100 to 1740 °C) have yielded only very qualitative data [5]. The diffusion couples were prepared by melting pure copper around a pure niobium core. Second phase precipitation and relative solubilities were noted, but no interdiffusion coefficients were calculated.

Solid state diffusion couples of pure copper and niobium that were annealed at 1000 °C for as long as 14 days revealed little or no interdiffusion [5].

16.3. Cu-Nb-Zr

Interdiffusion of copper and Zr-Nb alloys is described in the Cu-Zr-Nb section where it is compared with Cu-Zr interdiffusion.

16.4. Cu-Nb References

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17. Copper-Promethium

17.1. Pm* → Cu

The tracer diffusion coefficient of the rare earth, metal isotope ^{147}Pm in polycrystalline copper has been measured in the temperature range 720 to 955 °C [1]. The measurements and calculation of ^{147}Pm diffusion coefficients were done in the same manner described above for ^{141}Ce and $^{152+154}$Eu tracers diffusing in pure copper except that all measurements were obtained by using a residual activity method, and a correction was made for absorption in the samples of the ^{147}Pm beta particle (0.22 MeV) used to count the activity. The results are summarized in table 35. The temperature dependence of the coefficients is illustrated in figure 24. The straight line drawn through the data points can be described by the following Arrhenius relation obtained from a least square analysis,

TABLE 35. Promethium-147 tracer diffusion coefficients in copper. Data extracted from [1].

T(°C)	D*(cm^2/s)
955	5.74×10^{-13}
955	5.35×10^{-13}
902	2.65×10^{-13}
851	1.85×10^{-13}
851	1.63×10^{-13}
805	1.08×10^{-13}
805	9.98×10^{-14}
765	6.06×10^{-14}
720	3.59×10^{-14}
720	3.44×10^{-14}

$$D^* = 5\times 10^{-8} \exp(-28 \text{ kcal}\cdot\text{mol}^{-1}/RT) \text{ cm}^2/\text{s}.$$

The D_0 *and* Q *values in this* expression differ only slightly from the authors' published values. It may be noted that both D_0 and D^* values are very low. These results are subject to the same comments made in an earlier section where tracer diffusion coefficients of the rare earth metal europium in copper were reported.

17.2. Cu-Pm Referenc

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18. Copper-Praseodymium

18.1. Cu* → Pr

The tracer diffusion coefficient of ^{64}Cu in the body-centered cubic and double-hexagonal, close-packed phases of praseodymium has been measured [1]. The radioactive copper, deposited onto the surfaces of the polycrystalline (average grain diameter, 0.2 to 0.3 mm) praseodymium, was found to diffuse at extremely rapid rates ($\sim 10^{-5}$ to 10^{-6} cm^2/s). The experimental technique [2] called for the serial sectioning of the specimens after the relatively short diffusion anneals (~10 min.). The copper concentration profiles obeyed a Gaussian distribution. The values of the ^{64}Cu diffusion coefficients calculated from the slopes of the penetration profiles are listed in table 36. The temperature dependence of the coefficients is shown in figure 25. Straight lines can be fitted to the data points, allowing pre-exponential terms and activation energies to be determined. The resulting *Arrhenius expression for the diffusion of* ^{64}Cu in double-hexagonal, close-packed praseodymium is:

$$D^*_{\text{Cu}} = (8.4^{+2.5}_{-1.9}) \times 10^{-2} \exp(-18.1 \pm 0.5 \text{ kcal}\cdot\text{mol}^{-1}/RT) \text{ cm}^2/\text{s}.$$

and in body-centered cubic praseodymium is:

$$D^*_{\text{Cu}} = (5.7^{+2.1}_{-1.5}) \times 10^{-2} \exp(-17.8 \pm 0.7 \text{ kcal}\cdot\text{mol}^{-1}/RT) \text{cm}^2/\text{s}.$$

This phase transformation, from double-hcp to be bcc structure, only slightly decreases the measured mobility of copper (as has also been observed for gold diffusion in praseodymium [2].

The measured copper diffusion in the low temperature phase (double-hcp) represents an average of the diffusivities along nonequivalent crystallographic axes. The author does present arguments to support the assumption that atomic transport properties should not be very different along the *a* and *c* axes in praseodymium.

The ultra-fast diffusion of copper observed here is similar to the diffusion rates exhibited by the other noble metals [2], zinc [3], and cobalt [2] in praseodymium as

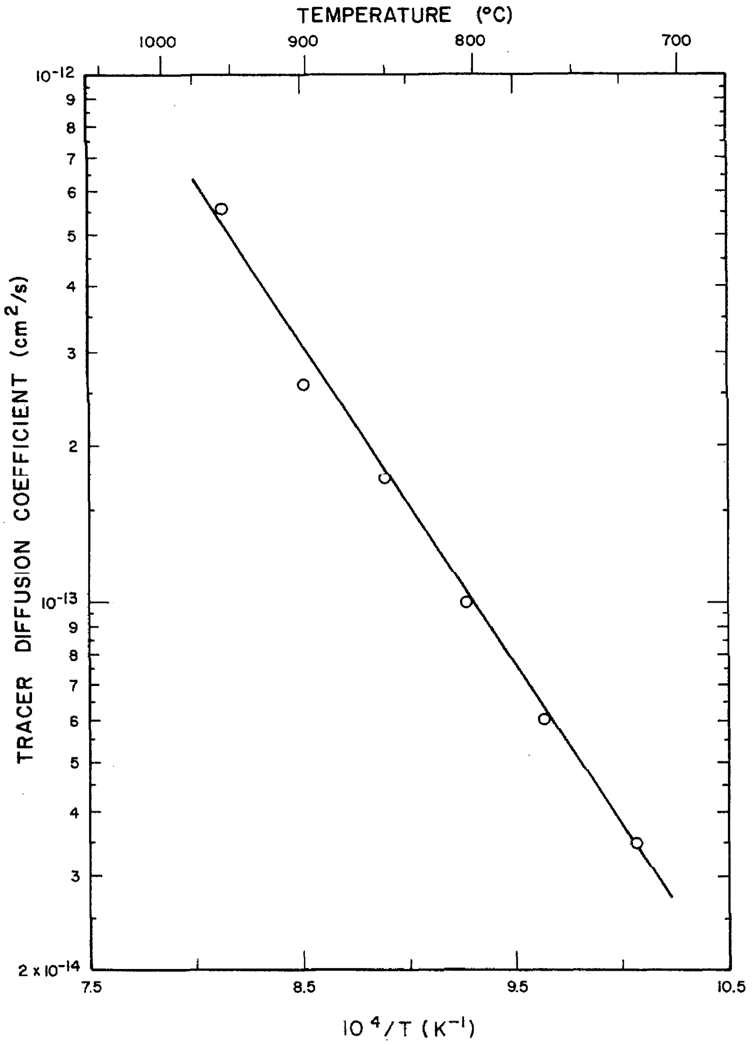

FIGURE 24. The tracer diffusion coefficient of ^{147}Pm in polycrystalline copper as a function of reciprocal absolute temperature.

Data extracted from [1].

TABLE 36. Copper-64 tracer diffusion coefficients in praseodymium. Data taken from [1]

T(°C)	D*(cm^2/s)	Structure
914.0	2.98×10^{-5}	b.c.c.
899.4	2.68×10^{-5}	b.c.c.
880.5	2.29×10^{-5}	b.c.c.
866.5	2.15×10^{-5}	b.c.c.
850.7	1.96×10^{-5}	b.c.c.
832.0	1.81×10^{-5}	b.c.c.
830.5	1.59×10^{-5}	b.c.c.
815.0	1.43×10^{-5}	b.c.c.
786.0	1.60×10^{-5}	double h.c.p.
740.8	1.08×10^{-5}	double h.c.p.
727.0	8.94×10^{-6}	double h.c.p.
697.5	7.34×10^{-6}	double h.c.p.
681.0	6.42×10^{-6}	double h.c.p.
653.5	4.52×10^{-6}	double h.c.p.

well as all three of the noble metals in lithium [4–6], lead [7, 8], and tin [9, 10]. The occurrence of such high diffusivities usually has been ascribed to the solutes being partly dissolved in interstitial positions and partly as substitutionals [11], or to the formation of solute interstitial-vacancy pairs [12].

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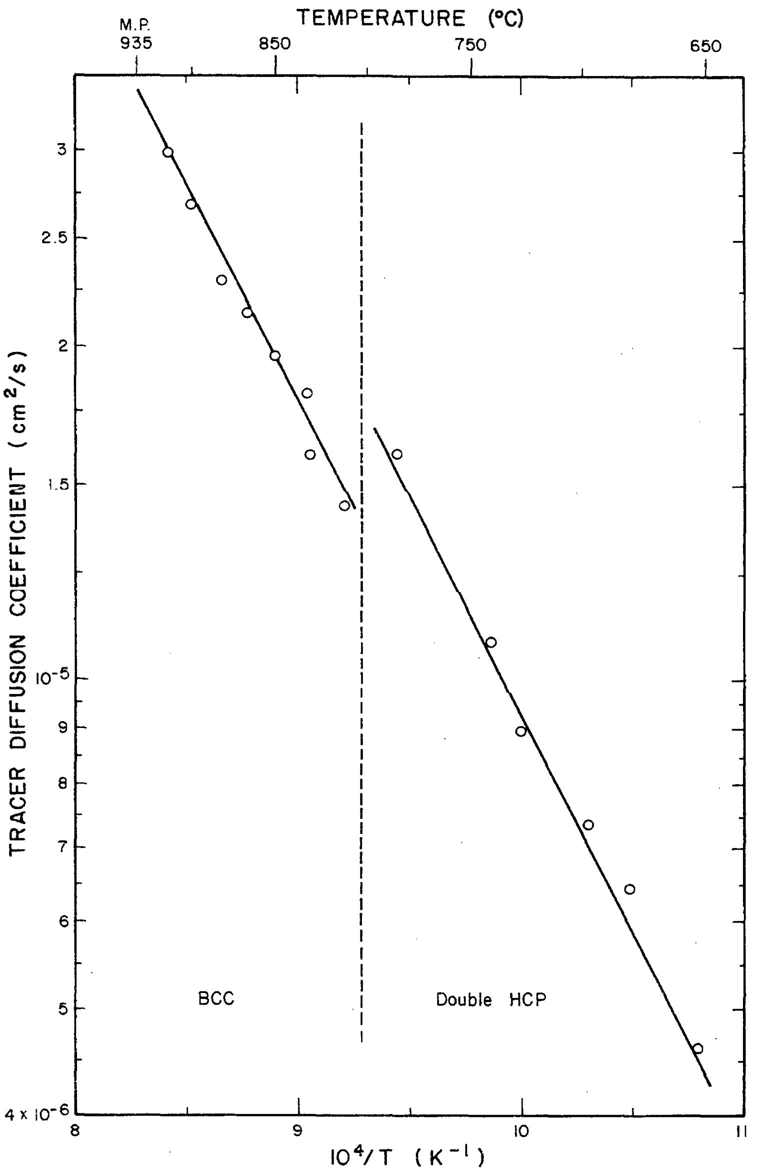

FIGURE 25. The tracer diffusion coefficient of ^{64}Cu in praseodymium as a function of reciprocal absolute temperature.

Data extracted from [1].

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19. Copper-Plutonium

19.1. Cu-Pu Interdiffusion

Jamet [1] interdiffused pure copper with a Pu-Cu alloy (5 at.% Cu/1.4 wt%) at 500 °C for varying time intervals. The intermetallic compounds $PuCu_2$, $PuCu_4$, and $PuCu_{11}$ were found in the interdiffusion zones which were examined with an electron probe microanalyzer and a microhardness reading.

Lataillade and coworkers [2] bonded pure copper to Pu-Cu (5 and 20 at.%/1.4 and 6 wt%) alloys and interdiffused them at temperatures from 500 to 580 °C.

The intermetallic compounds $PuCu_2$ and $PuCu_4$ were observed and identified in the interdiffusion zone. The growth kinetics (believed to be diffusion-controlled) of these two phases were studied, revealing an activation energy of 28,000 cal/mol for the process.

19.2. Cu-Pu-Ga

Concurrent with the above experiments in the Cu-Pu binary system, both authors formed interdiffusion couples of pure copper and Pu-Ga alloys and studied the diffusion. Jamet [1], utilizing Pu-Ga alloys containing 1.5 to 6 at.% (0.44 to 1.8 wt%) gallium, detected the compounds $Pu(CuGa)_3$ and $Pu(CuGa)_2$ after anneals at 500 °C. Lataillade et al. [2] formed interdiffusion couples of pure copper and Pu-Ga (1.5 and 6 at.%) alloys. The couple was designed so that the intermetallic compound $PuCu_3(Ga)$ would form in the interdiffusion zone at 500 and 800 °C. The gallium content of the ternary compound was found to be variable.

19.3. Cu-Pu References

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20. Copper-Rubidium

There have been no experimental investigations determining the rates of diffusion of copper in rubidium, or vice versa. Pure speculation would predict copper to diffuse very fast in rubidium for the same considerations discussed in the Cu-K and Cu-Na sections.

21. Copper-Rhenium

21.1. General Comments

Diffusion studies involving copper and rhenium are few. The only report uncovered dealt with an interdiffusion investigation of the processes which occur during the brazing of rhenium-coated titanium with copper [1]. The study yielded only qualitative results. Reported were the widths of the diffusion zones, microhardness readings, and photomicrographs of these areas. The materials used were poorly characterized, and the experimental control was very lax. The results and their usefulness are very questionable.

21.2. Cu-Re Reference

[1] Bondarev, V. V., and Shinyayev, A. Ya., "Investigation of Diffusion Processes in Brazing Rhenium-Coated Titanium," (in Russian) Tr. Inst. Met. Akad. Nauk SSSR, No. 14, 86–89 (1963) [translation available from NTIS as JPRS 24,761].

22. Copper-Tantalum

22.1. General Comments

The very limited mutual solubility of this system and the disparity in melting points has discouraged diffusion experiments, although the joining of tantalum to copper has been the subject of several attempts to fabricate composite materials for nose-cone applications [1].

22.2. Cu-Ta Reference

[1] Bertossa, R. C., and Rau, S., Stanford Research Inst., Menlo Park, California, *Development of Procedures and Techniques for Preparing Bonded Double Layer Tantalum-Copper Composite Plates*, WADC Tech. Report 58-396, AF 33(616)-5215 (1959), 29 pp.

23. Copper-Terbium

23.1. Tb* → Cu

The tracer diffusion coefficient of the isotope ^{160}Tb in polycrystalline copper has been measured in the temperature interval 770 to 980 °C [1]. The experimental measurements and calculation of the ^{160}Tb diffusion coefficients were obtained in the same fashion as described in a previous section for the rare earth metal isotopes ^{141}Ce and $^{152+154}Eu$ in pure copper. All measurements were made using a residual activity technique. The results are summarized in table 37 and figure 26.

TABLE 37. Terbium-160 tracer diffusion coefficients in copper. Data taken from [1].

T(°C)	D*(cm²/s)
980	1.78×10^{-13}
980	1.63×10^{-13}
906	6.67×10^{-14}
906	6.51×10^{-14}
850	4.27×10^{-14}
850	3.99×10^{-14}
770	1.98×10^{-14}
770	1.85×10^{-14}

The temperature dependence of the terbium tracer diffusivity can be expressed by the following Arrhenius equation:

$$D^*_{Tb} = 5 \times 10^{-9} \exp(-26 \text{ kcal} \cdot \text{mol}^{-1}/RT) \text{ cm}^2/\text{s}.$$

Since the terbium diffusivity was measured concurrently with the europium diffusivity, the comments made about the results in the Cu-Eu section above are also applicable here. The D_0 and Q quoted by the author are rounded-off here. These rounded values are a very reasonable Arrhenius line, shown in figure 26. In view of the scatter and scarcity of the data, use of additional significant figures does not seem justified.

23.2. Cu-Tb Reference

[1] Badrinarayanan, S., and Mathur, H. B., "Impurity Diffusion of Rare Earth Metals in Copper," Indian J. Pure Appl. Phys. **8**, 324–330 (1970).

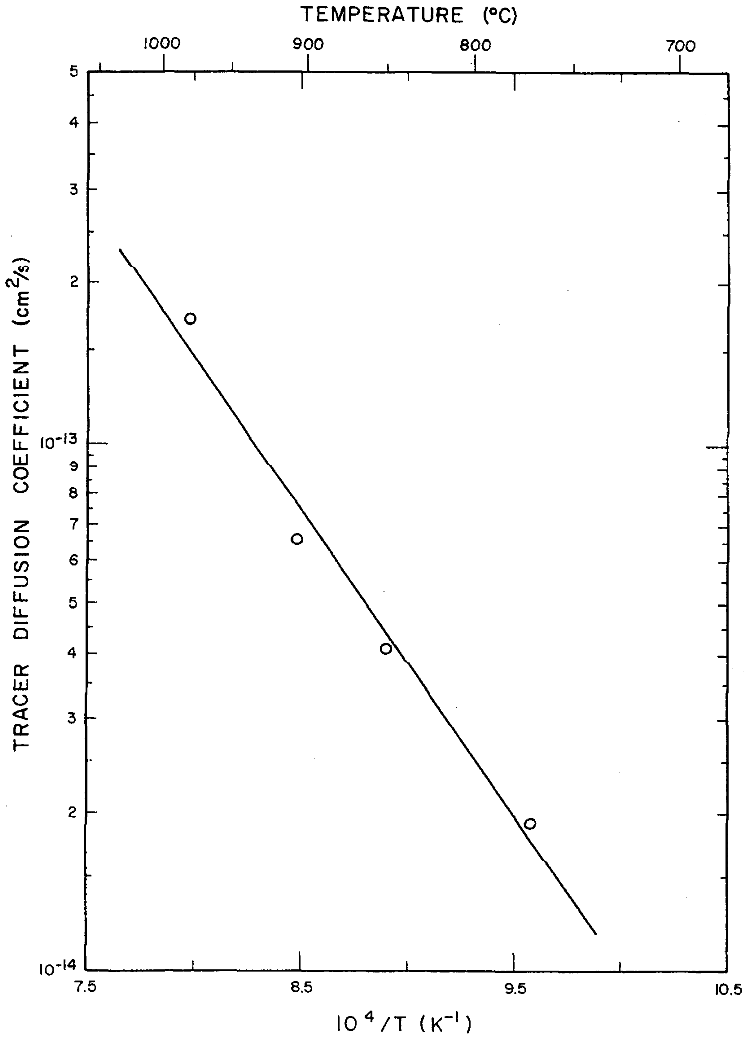

FIGURE 26. The tracer diffusion coefficient of ^{160}Tb in polycrystalline copper as a function of reciprocal absolute temperature.

Data taken from [1].

24. Copper-Titanium

24.1. Cu→ β-Ti

The diffusion rates of copper in the beta-titanium-copper system have been studied in the temperature range 960 to 1460 °C [1]. The impurities contained in the iodide-grade titanium used in the investigation had the following concentrations in ppm: 50 aluminum, 200 iron, 50 silicon, 50 chromium, 45 magnesium, 50 zinc, 50 copper, 30 nickel, 20 tungsten, 40 nitrogen, 90 hydrogen. The titanium specimens were heat treated to minimize hydrogen content, and the final martensitic structure was of approximately 2.5 mm grain size. High purity copper (99.99%) was vacuum deposited to a depth of 1 μm on the titanium specimens, and then diffused in silica chambers containing either a dynamic (10^{-5} torr) or static (10^{-6} torr) vacuum.

An electron microprobe analyzer was used to determine the copper concentration-penetration profiles. It was possible to detect a concentration of less than 0.05 percent. Copper concentrations were assumed to be proportional to the X-ray intensity ratios. Diffusion coefficients were calculated directly from the slope of the straight lines obtained from plotting the log of the X-ray intensity ratios versus the square of the distance measured from the specimen surface. There was no indication of grain boundary diffusion or other structure-sensitive effects. The penetration plots yielded fine straight lines, and the diffusion coefficients calculated from them are listed in table 38. The resulting Arrhenius plot is shown in figure 27. A pronounced curvature is clearly evident in the smooth solid line drawn through the data; the apparent activation energies and frequency factors increasing with temperature.

TABLE 38. Copper impurity diffusion coefficients in β-titanium. Data extracted from [1].

T(°C)	Time(s)	D_{Cu}(cm²/s)
1460	6.00×10^2	6.19×10^{-7}
1405	6.00×10^2	4.09×10^{-7}
1355	6.00×10^2	3.31×10^{-7}
1310	6.00×10^2	2.72×10^{-7}
1260	1.80×10^3	1.44×10^{-7}
1210	1.80×10^3	8.72×10^{-8}
1160	3.60×10^3	7.20×10^{-8}
1110	7.20×10^3	5.44×10^{-8}
1060	7.20×10^3	2.77×10^{-8}
1010	1.62×10^4	1.99×10^{-8}
960	2.52×10^4	1.38×10^{-8}

A number of authors have attempted to explain the reasons for this anomalous curvature [2–9]. Caloni et al. treated their data as suggested by Kidson [4, 8], who postulated that, with two volume diffusion mechanisms in competition, the total diffusion process is described by the sum of two exponential terms. The first exponential term in principle can be obtained graphically from the geometrical tangent of the low temperature experimental curve (figure 27, dashed line). Extrapolating this low temperature experimental curve to high temperatures, and then subtracting these new extrapolated values from the high temperature experimental data, yields the second exponential term (figure 27, dotted line). For copper impurity diffusion in β-titanium, this procedure, as quoted by Caloni et al., yielded $D_0 = 2.1 \times 10^{-3}$ cm²/s and $Q = 29.2$ kcal/mol for the low temperature process and $D_0 = 11.3$ cm²/s and $Q = 60.2$ kcal/mol for the high temperature process.

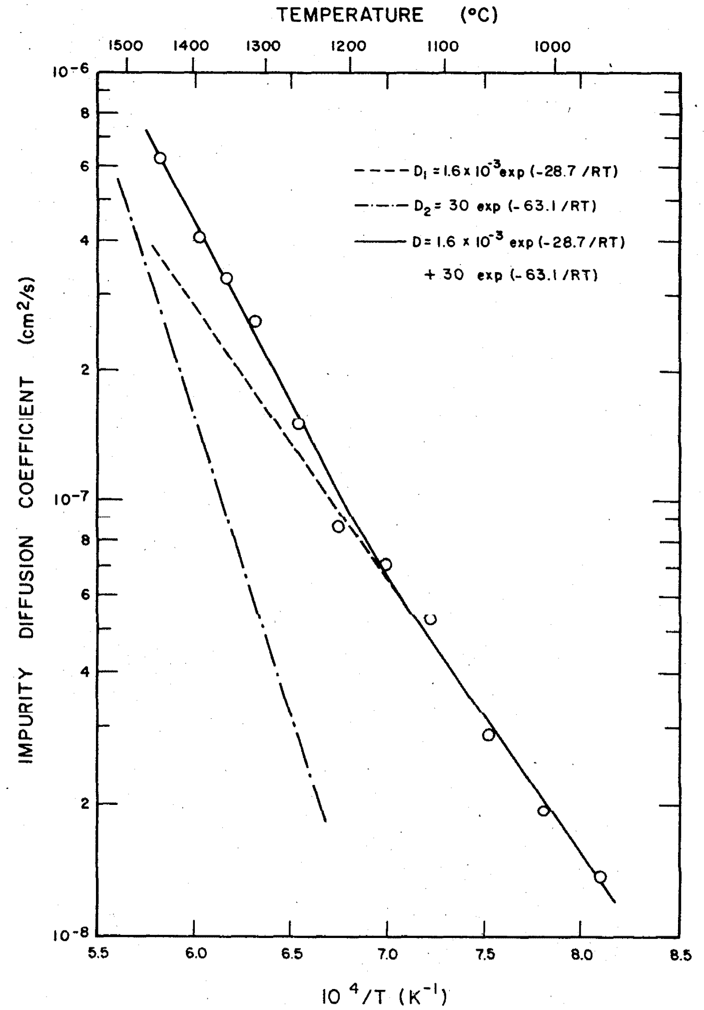

FIGURE 27. The diffusion coefficient of a copper impurity atom in β-titanium as a function of reciprocal absolute temperature.

Data taken from [1]. See discussion in text.

Since there is moderate scatter in the data points, this procedure cannot be expected to yield very accurate values of Q or D_0, especially for the high process, whose magnitude is found by subtraction. Also, the published lines of Caloni et al., which are reproduced in figure 27 do not agree with the quoted D_0 and Q values. Our analysis indicates that the solid line in figure 27, whose value equals the sum of the values of the two dashed lines, is given by:

$$D_{\mathrm{Cu}\to\mathrm{Ti}} = [1.6\times10^{-3}\exp(-28.7\ \mathrm{kcal\cdot mol^{-1}}/RT) + 30\exp(-63.1\ \mathrm{kcal\cdot mol^{-1}}/RT)]\ \mathrm{cm^2/s}.$$

Here the first exponential term is dominant at low temperatures and the second exponential is dominant at high temperatures. Here the D_0 and Q values are lower than those published by Caloni et al. for the first term and higher for the second term.

24.2. Cu-Ti Interdiffusion

Guy [10] has interdiffused pure titanium and copper at 700, 775, 790, 850, and 868 °C and then metallographically examined the multiphase diffusion structures created in the diffusion zone. Widths of the phases were measured in selected cases. The experiments were plagued with difficulties owing to the brittle nature of the intermediate phases as well as their chemical reactivity.

The interdiffusion of copper and titanium has been studied extensively by Shinyayev and coworkers at the Baikov Institute in Moscow [11–16]. Their motivation for this work was the study of the service life of soldered joints at elevated temperatures. This being the case, their investigations were somewhat qualitative in nature. Thick coatings of copper were electrodeposited on titanium (of unspecified purity). Prior to copper electrodeposition, a nickel layer of 5 to 10 micrometer thickness was electrolytically deposited (to "ensure wettability of the copper coating"), and molybdenum wire markers (20 to 50 μm in diameter) were soldered to the titanium surface. After annealing for 2 hours in evacuated quartz ampoules, Kirkendall shifts were measured; all in the direction of the pure titanium side of the diffusion couple. These shifts are listed in table 39.

The only other quantitative data mentioned in their papers was a penetration plot obtained from a couple interdiffused in an atmosphere of flowing argon at 743 to 747 °C for 1 to 2 hours. The chemical concentrations in the diffusion zone were determined from a not-often-used radiation-attenuation technique [14, 17] which is of questionable precision and accuracy. Using these data, the interdiffusion coefficient was found to be approximately 2×10^{-8} cm²/s in the composition range 1 to 2 wt% titanium.

TABLE 39. Kirkendall shifts after two hours for the interdiffusion of copper and titanium. Data extracted from [16].

T(°C)	Kirkendall Shift (microns)
800	170
700	135
600	80
500	38

24.3. Cu-Ti-Ag

The effect of dilute (0.1 wt%) alloying additions of titanium to copper had little or no measurable effect on the lattice diffusion of radioactive silver in the copper [18, 19]. However, this is not the case for the grain boundary diffusion of the ^{110}Ag. Barreau et al. [19] found the temperature dependence of silver grain boundary diffusion to be altered by the addition of 0.1 wt% titanium to pure copper. In their experiments, electrolytically-deposited radioactive ^{110}Ag was diffused into OFHC copper that had been alloyed with the titanium (final grain size was 250 μm). The temperature range of the study extended from 465 to 611 °C. The ^{110}Ag penetration was determined through the use of Gruzin's technique of measuring residual activity [20, 21] as modified by Seibel [22–25]. Grain boundary diffusion coefficients were calculated with the aid of Suzuoka's [26] analysis and are listed in table 40. When the coefficients are plotted as a function of reciprocal absolute temperature (see fig. 28), a straight line can be fitted to the results. Also shown in the figure for comparison are the results obtained by the same authors for unalloyed OFHC copper. The temperature dependence of silver grain boundary

TABLE 40. Value of the product ($D_{gb}\cdot\delta$) from ^{110}Ag grain boundary in a Cu-Ti(0.1 wt%) alloy using Suzuoka's analysis. Data taken from [18, 19]

T(°C)	$D_{gb}^{Ag}\cdot\delta$ (cm³/s)
611	5.60×10^{-14}
578	2.95×10^{-14}
517	7.20×10^{-15}
465	1.80×10^{-15}

δ = mean grain boundary thickness.

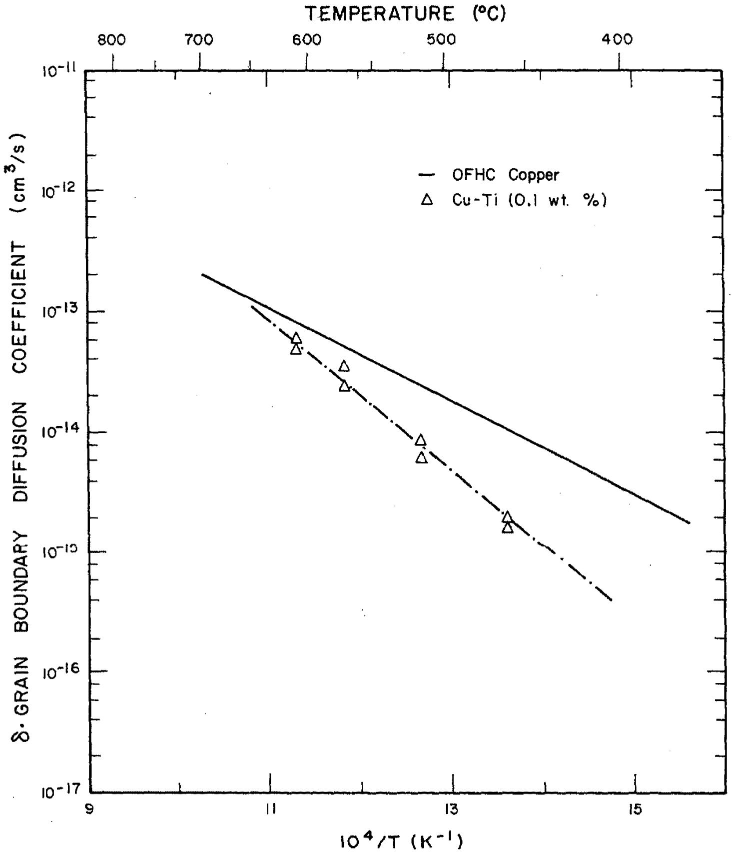

FIGURE 28. The product of the grain boundary diffusion coefficient of silver (D^{gb}_{Ag}) and the mean grain boundary thickness (δ) as a function of reciprocal absolute temperature.

Silver-110 diffusing into OFHC copper and a Cu-Ti alloy. Data extracted from the papers [18, 19].

diffusion in the alloy can be expressed by the following relation:

$$\delta \cdot D^{gb}_{Ag \to CuTi} = 1.3 \times 10^{-6} \exp(-29\ \mathrm{kcal \cdot mol^{-1}}/RT)\ \mathrm{cm^3/s},$$

where δ is the mean grain boundary thickness. The presence of titanium raises the activation energy approximately 11 kcal/mol when compared to grain boundary diffusion in the unalloyed copper (the pre-exponential decreases from 1.3×10^{-6} to 7.1×10^{-10} cm^3/s).

24.4. Cu-Ti-B

Boriding studies of Cu-Ti alloys (solid solutions containing 1.1, 2.9, and 4.1 at.% Ti) have yielded diffusion coefficients for titanium and boron in copper [27]. The titanium diffusion coefficients were determined from concentration changes (measured with an electron microprobe analyzer) occurring ahead of the reaction front. Boron diffusion coefficients were calculated from reaction constant data. The results are listed in table 41.

TABLE 41. Diffusion coefficients of titanium and boron in Cu-Ti solid solutions obtained during the boriding of these alloys. Data after [27]

Cu-Ti Alloy Composition (at.% Ti)	T(°C)	D_{Ti} (cm^2/s)	D_B (cm^2/s)
1.1	800	2.2×10^{-10}	6.1×10^{-9}
1.1	900	5.9×10^{-9}	6.8×10^{-8}
4.1	800	1.9×10^{-10}	
4.1	900	1.2×10^{-9}	

The titanium content was found to have an important effect on the kinetics of the layer growth. With titanium concentrations of less than 2.9 at.%, internal boriding occurred where finely dispersed TiB_2 precipitates formed and which became more coarse with increasing distance from the surface. External boriding occurred in alloys containing more than 2.9 at.% titanium; the external layer being compact TiB_2.

24.5. Cu-Ti-H

The interdiffusion of thin films of titanium (charged by deuteron bombardment) and a copper substrate has been followed with an electron microprobe [28]. The role of diffusion in degassing the specimens was explored.

24.6. Cu-Ti-Ni

Helfmeier [29, 30] and Helfmeier and Feller-Kniepmeier [31], studied the influence of titanium impurities on the diffusion coefficient of copper in nickel in the temperature range 1050 to 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. No apparent effect of the low titanium concentration was noted on the copper mobility over the temperature range investigated.

24.7. Cu-Ti-O

The oxidation kinetics of copper alloys containing titanium (0.5 and 0.1 at.%) has been studied over the temperature range of 900 to 600 °C [32]. Oxidation was linear in the early stages, becoming parabolic in later stages. The parabolic oxidation behavior was found to be controlled by the diffusion of Cu^+ ions through the scale.

24.8. Cu-Ti-Re

There has been an interdiffusion investigation of the processes which occur during the brazing of rhenium-coated titanium with copper [33]. The study yielded only qualitative results. Reported were the widths of the diffusion zones, micro-hardness readings, and photomicrographs of these areas. The materials used were poorly characterized, and the experimental control was very lax. The results and their usefulness are very questionable.

24.9. Cu-Ti-X

Most diffusion studies in ternary and higher order systems were of an interdiffusion character and undertaken with the aim of making an effective bond between copper and titanium alloys [34–41]. The success of the joining process is often a function of the diffusion-zone thickness and/or the mechanical properties of the diffusion layer. Joining copper to titanium alloys has been accomplished by both fusion and nonfusion techniques. All of these studies look at the interdiffusion processes from this biased view, and thus are somewhat qualitative in yielding diffusion data. The studies may or may not have been performed in a vacuum; filler metals may or may not have been used as diffusion aids; commercially pure materials are often used in the study; pressure may or may not have been employed to promote bonding, etc.; all complicating the investigations, and thus making interpretations of the interdiffusion process very questionable.

24.10. Molten Metals

Shurygin and Shantarin, in several different papers [42, 43], have reported a diffusion coefficient for titanium in liquid copper. The expression,

$$D_{\mathrm{Ti}\to\mathrm{Cu}} = 1.7\times10^{-2}\exp[-69\ \mathrm{kjoule}\cdot\mathrm{mol}^{-1}/RT]\ \mathrm{cm}^2/\mathrm{s},$$

was arrived at from dissolution measurements in the temperature range 1373 to 1673 K. The experimental technique (designed to overcome convective transfer) involved the measurement of the rate of dissolution of a rotating titanium specimen and calculating diffusion coefficients with assistance of the hydrodynamic expressions, the Levich equations [44].

24.11. Cu-Ti References

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25. Copper-Thulium

25.1. Tm* → Cu

The tracer diffusion coefficient of the isotope ^{170}Tm in polycrystalline copper has been measured in the temperature interval 705 to 953 °C [1]. The experimental measurements and calculation of the ^{170}Tm diffusion coefficients were obtained in the same manner as was that of the other rare earth metal isotopes, ^{141}Ce and $^{152+154}$Eu (see the above section dealing with Cu-Eu alloys), except that the residual activity method was relied on wholly here, and a correction was made for absorption by the sample of the ^{170}Tm beta particle (0.97 MeV). Listed in table 42 are the thulium tracer diffusion coefficients. In figure 29 are plotted the data. The temperature dependence of the thulium diffusivity can be expressed by the following Arrhenius equation:

$$D^*_{\mathrm{Tm}} = 3.5\times10^{-9}\exp(-23\ \mathrm{kcal\cdot mol^{-1}}/RT)\ \mathrm{cm^2/s}.$$

There is considerable scatter in the data and also disagreement was found in the third significant figure between the authors' published Q value and that obtained from our least squares analysis of the data. Consequently, D_0 and Q in the above expression are quoted

TABLE 42. Thulium-170 tracer diffusion coefficients in copper [1].

T(°C)	D*(cm^2/s)
953	3.54×10^{-13}
905	1.71×10^{-13}
905	1.41×10^{-13}
855	9.86×10^{-14}
855	9.66×10^{-14}
795	6.87×10^{-14}
795	6.70×10^{-14}
763	5.03×10^{-14}
705	2.74×10^{-14}
705	2.45×10^{-14}

to only two significant figures, yielding the line shown in figure 29, rather than to the three or four significant figures given in reference 1.

The reader is referred to the section dealing with Cu-Eu alloys for comments regarding the results for that system, since the same may be justifiably offered here also. For example, the D_0 and D^* values are very small.

25.2. Cu-Tm Reference

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26. Copper-Uranium

26.1. Cu* → U

The diffusion of copper tracer in γ(b.c.c.) uranium has been measured from 780 to 1080 °C by Peterson

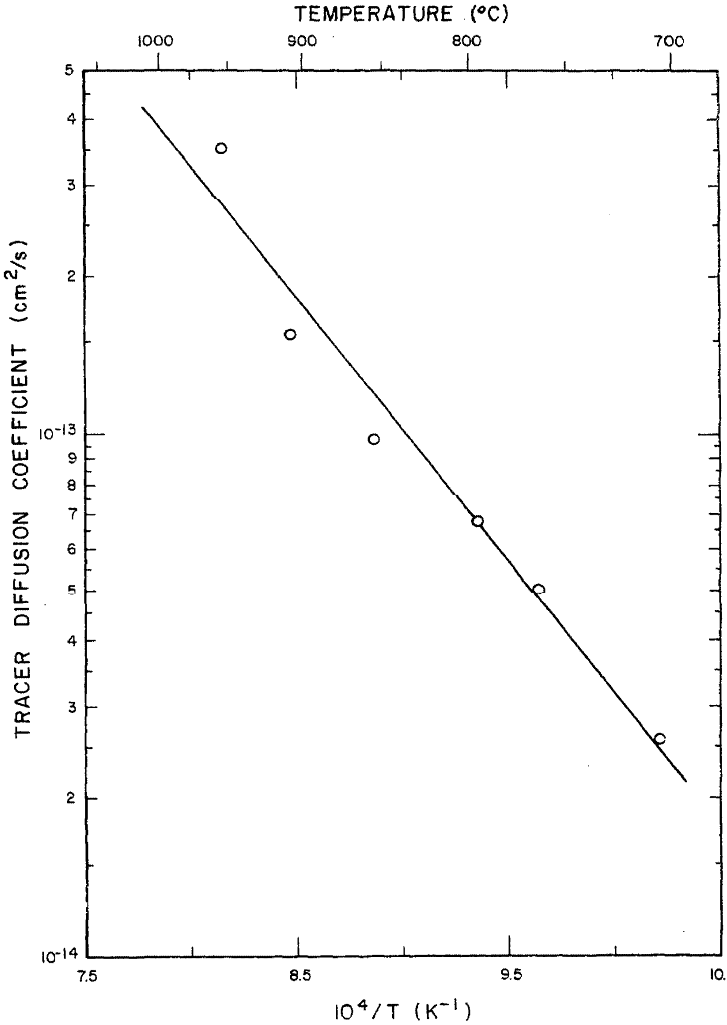

FIGURE 29. The tracer diffusion coefficient of ^{170}Tm in polycrystalline copper as a function of reciprocal absolute temperature.

Data extracted from [1].

and Rothman [1, 2]. A layer of ^{64}Cu was deposited on high purity uranium (containing less than 100 ppm by weight of total impurities) and the specimens were annealed, sectioned, and then counted. The penetration plots obtained were linear to the lowest annealing temperatures, indicating that the initial and boundary conditions for the experiments were fulfilled and that no grain-boundary diffusion was present. The diffusion coefficients obtained from a least-squares analysis of their data are given in table 43. The Arrhenius plot for the data is shown in figure 30. The errors in D due to sectioning and counting were estimated by the authors to be 3%, with 1 to 2% error due to a ±1 °C uncertainty in the temperature. Calculating from the linear portion of the Arrhenius plot, one arrives at an activation energy of 24.06±0.40 kcal/mol and a frequency factor of $1.96^{+0.35}_{-0.30} \times 10^{-3}$ cm^2/s.

The Arrhenius plot is curved at the lower temperatures. As described by the authors, the experimental procedure which was used rules out the possibility of the curvature being caused by diffusion along grain boundaries of dislocations, or by defects introduced by the β–γ transformation.

26.2. Cu-U Interdiffusion

The results of studies of the interdiffusion rates of uranium and copper have been reported [3–10] by several authors. Since copper and uranium are not completely mutually soluble, more than one phase is present in the diffusion zone, and the interdiffusion investigations have dealt with which phases form, their rate of growth, the concentration gradients in the different phases, and the compositions at the phase boundaries. All the studies undertaken indicate the existence of one intermetallic compound UCu$_5$ and are in agreement with the phase diagram [11]. A comparison of the results is shown in the Arrhenius plot for the thickness of the intermetallic compound layer formed during the interdiffusion of uranium and copper (fig. 31). The data for equivalent treatments is in good agreement for low temperatures and short times. The poor agreement at the higher temperatures and longer times may be ascribed to the fact that Bear and LeClaire measured average thickness and experienced some oxidation problems, while Weil used maximum thickness measurements. Weil calculated an activation energy of 23.5 kcal/mol, while Bear and LeClaire calculated 21.6 kcal/mol.

TABLE 43. Copper-64 tracer diffusion coefficients in b.c.c. γ-uranium. Data taken from [1, 2].

T(°C)	D*(cm^2/s)
1039.2	1.97×10^{-7} 1.94×10^{-7}
989.8	1.38×10^{-7} 1.31×10^{-7}
935.6	8.53×10^{-8} 8.22×10^{-8}
891.2	5.93×10^{-8} 5.88×10^{-8}
838.1	3.78×10^{-8} 3.63×10^{-8}
812.2	3.01×10^{-8} 2.98×10^{-8}
786.6	2.50×10^{-8} 2.44×10^{-8}

Bear and LeClaire found the ratio:

$$\frac{\text{Phase Boundary Movement into Copper}}{\text{Total Width of Diffusion Zone}} \simeq 0.62,$$

thus indicating that uranium diffuses faster in the compound than does copper.

Adda [4–7] and coworkers not only studied the interdiffusion of uranium and copper at zero pressures, but also the influence of uniaxial and hydrostatic pressure. All their results are in agreement with the equilibrium diagram and show the existence of a single phase of the composition UCu$_5$. The size of the diffusion zone increased as a function of the square root of the diffusion time (fig. 32). The effect of pressure (both uniaxial and hydrostatic) on the growth kinetics of the diffusion zones is shown by plotting log x_i^2/t vs applied pressure, where x is the width of the zone (measured in the microscope) after a time t of diffusion.

Microprobe measurements of diffusion couples annealed at 650 and 700 °C without external pressure reveal that the composition of UCu$_5$ varies almost linearly across the compound from 55.4 to 58.4 wt% (82.3 to 84 at.%) of copper. This indicates a stoichiometric error and permits a continuous transformation from UCu$_{4.70}$ to UCu$_{5.25}$. If diffusion occurs at 700 °C under uniaxial or hydrostatic pressure greater than or equal to 500 kg/cm^2, the homogeneity range of the compound is reduced. The growth rate of the UCu$_5$ layer was found to slightly increase with the application of pressure, contrary to the qualitative predictions of Seith [12]. It has been speculated [13] that one of the reasons for the increased growth rate of the UCu$_5$ layer under pressure might be that diffusion in the intermetallic compound takes place by an interstitialcy mechanism since the volume of a crystal will decrease when an interstitial is formed. Other variables may also have to be considered (e.g. creep of the diffusion zones).

There are no strong indications of a second phase existing in any of the interdiffusion studies reviewed.

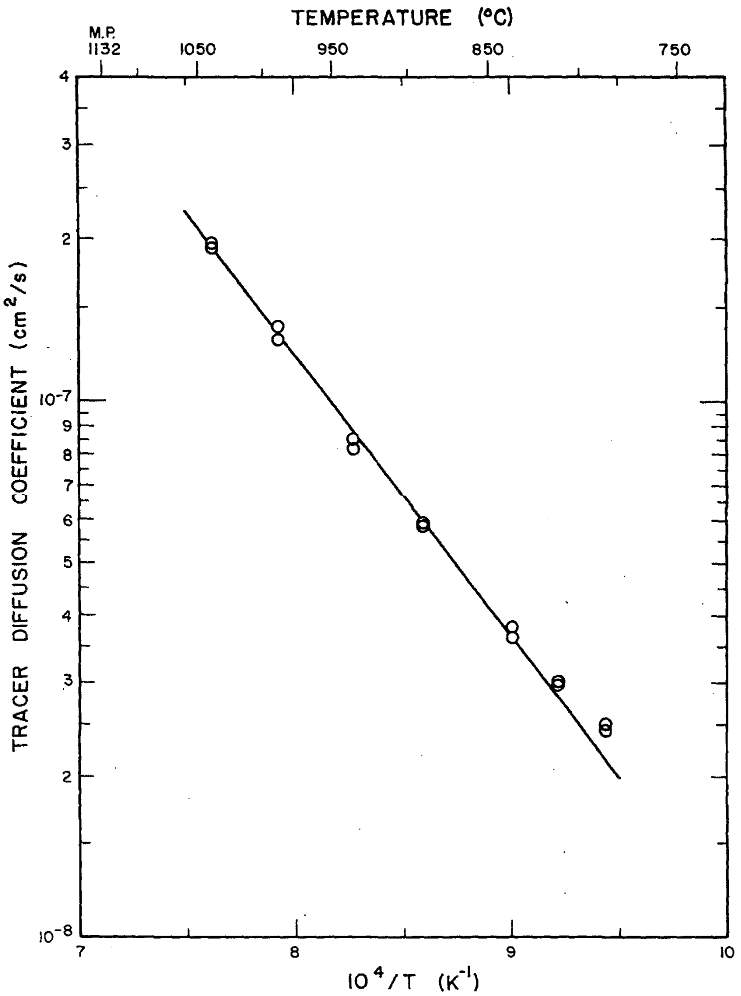

FIGURE 30. The diffusion coefficient of ^{64}Cu in bcc γ-uranium as a function of reciprocal absolute temperature.

Data extracted from [1, 2].

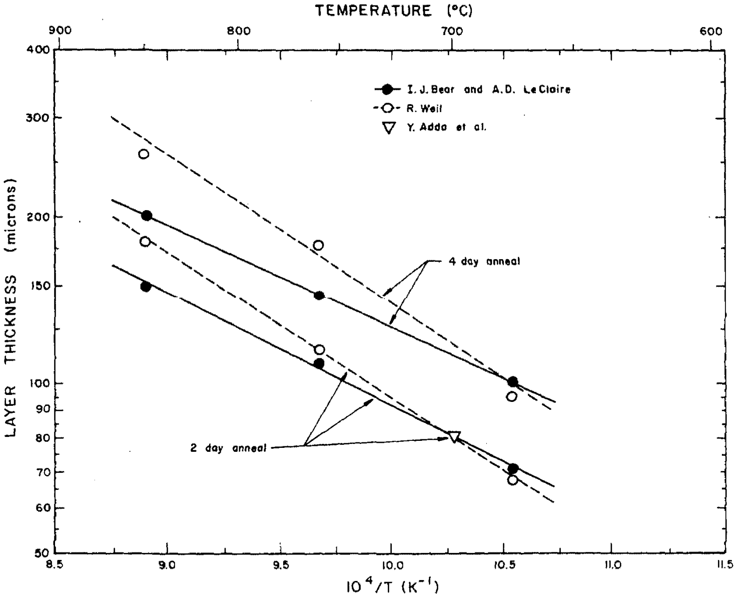

FIGURE 31. Thickness of the layer of UCu_5 formed during interdiffusion of U and Cu as a function of reciprocal absolute temperature.

Data taken from [3, 5, 9].

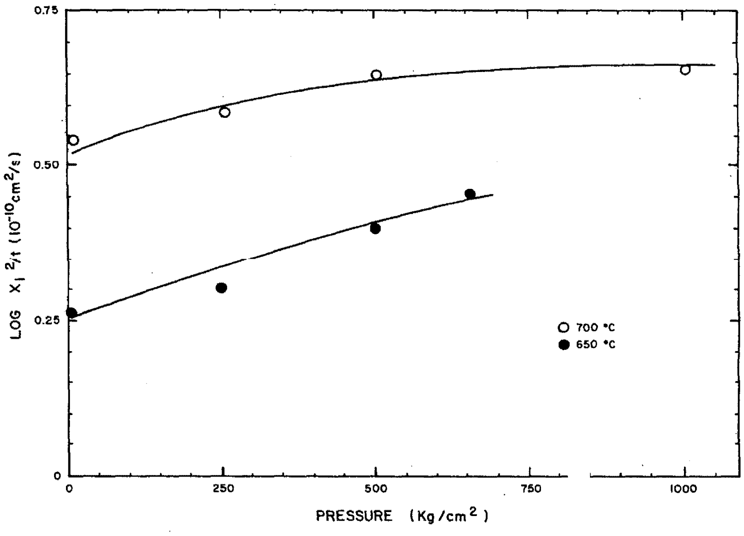

FIGURE 32. Effect of pressure on the interdiffusion of uranium and copper at 650 and 700 °C.

Width of the diffusion zone is x, and t is time of interdiffusion. Data extracted from [4, 6, 7].

26.3. Cu-U-O

The oxidation kinetics of the intermetallic compound UCu_5 in carbon dioxide has been investigated in the temperature range 850 to 350 °C [14]. At all temperatures, a mixture of copper and UO_2 was formed on the surface of the specimens, followed by the migration of copper to the outer surface to form a layer. With the continued thickening of the copper layer, oxygen diffused inward through copper to form a subscale. The subscale thickened by the continued oxygen diffusion and reaction at the subscale-alloy interface. Eventually the outer copper layer remained a constant thickness. It appears that above 690 °C the rate-determining step is initially the self-diffusion of copper, and then oxygen diffusion through copper. At lower temperatures, it was not possible to reach the same conclusion.

Other limited studies [15, 16] have been made into the oxidation behavior of U-Cu alloys with the result that attack proceeds via internal oxidation.

26.4. Cu-U-Zr-X

To prevent interdiffusion between Zr-Cu alloys and UO_2 (and thus make them compatible in reactor piles), copper, chromium, and carbon have been utilized as diffusion barriers [17].

26.5. Electromigration (Cu → U)

The solid-state electromigration of copper impurities in γ-uranium has been studied in a very qualitative way [18, 19]. The studies were performed at 900 ± 10 °C for 50 and 162 hours using a current of 126 ± 1 ampere and a voltage of 1.68 V. Unfortunately, the results were inconclusive because of the very low copper concentrations ($\leqq 10$ ppm Cu) and the imprecise spectrographic method of analysis. The most that can be said was that the copper impurity showed evidence of anode-directed electromigration.

26.6. Pressure Effects

Measurements by Adda and coworkers concerning pressure effects are noted at the end of the section on Cu-U interdiffusion.

26.7. Cu-U References

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27. Copper-Vanadium

27.1. Cu-V-Ga

The interdiffusion between VGa_2 and a vanadium substrate at 700 °C is significantly affected by the presence of copper impurities [1]. During a diffusion anneal, the amount of grain boundary diffusion occurring is reduced by the presence of copper.

27.2. Cu-V-X

Širca [2, 3] investigated the volume and grain boundary diffusion of copper in vanadium steels (containing 6.6 wt% vanadium) in the termperature range 1000 to 1100 °C. The results of these studies in ferritic steels were quite qualitative, no numerical data on penetration rates being taken.

27.3. Cu-V References

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28. Copper-Tungsten

28.1. Cu-W Interdiffusion

Composite sheets of copper and tungsten have been formed through diffusion welding techniques [1]. Copper has been employed as a solder in joining tungsten [2], the liquid copper penetrating the tungsten grain boundaries at temperatures above 1100 °C.

28.2. Cu-W-Ni

The diffusion of radioactive ^{63}Ni into tungsten-reinforced copper specimens has been reported in the literature [3]. As the concentration (volume percent) of the tungsten fibres was increased, significant changes in the activation energy and pre-exponential factors were noted, although at the melting point the tracer diffusion coefficients were comparable to those in pure copper.

28.3. Surface Diffusion

The surface diffusion of copper on tungsten has been well determined as a result of field-emission microscope studies of the copper-tungsten adsorption system [4–7]. The most recent studies are in good agreement [4, 7]. Only the results of Melmed [4] will be given here since he has given most attention to the energetics of surface diffusion. Sufficiently low temperatures were used to minimize evaporation and volume diffusion. The surface diffusion of copper on tungsten was found to be anisotropic. The copper diffused rapidly over the (011) type regions of the surface, more slowly near and on (111) regions, and most slowly in the (001) regions.

Surface diffusion was found to obey an Arrhenius-type equation,

$$\frac{1}{t} = A \exp(-B/T),$$

where A and B are constants, t is the time required for the edge of a copper deposit to move some fixed distance, and T is absolute temperature. The results are shown in table 44.

From the table, one notes that the activation energy for surface diffusion of copper drops sharply after one layer of copper is placed on the tungsten surface, and then slowly decreases for subsequent layers.

28.4. Cu-W References

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TABLE 44. Diffusion parameters for the surface diffusion of copper on tungsten (zero field values). From the data of Melmed [4]

Diffusion Type	Surface Region	T(°C)	D_0 (cm²/s)	Q(kcal/mol)
Single layer	Average	275 - 400	6×10^{-5}	17 ± 2
Double layer	Average	260 - 380	6×10^{-6}	13 ± 1
Triple layer	Average	215 - 380	6×10^{-7}	10 ± 1
Second layer	Average	280 - 400	2×10^{-6}	11 ± 1
Third layer	Average	280 - 400	2×10^{-6}	10 ± 1
Fourth layer	Average	280 - 400	1×10^{-6}	9 ± 1
Thermal desorption of three layers Cu/W		1240 - 1340		88 ± 6

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29. Copper-Zirconium

29.1. Cu* → α-Zr

The diffusion of ^{64}Cu tracer into randomly oriented single crystals of α-zirconium has been reported [1]. Measurements were all made near the α/β transformation temperature (865 °C). The anisotropy of copper diffusion in a single crystal of the α(h.c.p.)-zirconium showed diffusion parallel to the *c*-axis to be twice as fast as diffusion perpendicular to it. The diffusion coefficients were approximately 10^{-8} cm²/s. Hood [1], like Dyson et al. [2], speculates that the rapid diffusion of copper parallel to the *c*-axis is consistent with an interstitial mechanism. A crude calculation based on geometry, lattice spacing, and an assumed ion size for zirconium and copper shows that the α-zirconium lattice can accept an interstitial solute of radius less than 1.5 Å in the octahedral site and 1.2 Å in the tetrahedral site. Hence, a more open interstitial jump path exists parallel to the *c*-axis.

29.2. Cu-Zr Interdiffusion

Interdiffusion studies [3] in the Cu-Zr system have been performed to observe the phase relationships existing at 650, 701, 750, and 801 °C. Pure zirconium (99.99 wt%) and oxygen-free copper (99.99 wt%) were bonded together and annealed for as long as 3000 hours. Metallographic examinations of the microstructures of the diffusion couples were corroborated by microhardness measurements, and concentration determinations were made with an electron microprobe analyzer. The investigations revealed the intermetallic phases $ZrCu_5$, $ZrCu_4$, $ZrCu_3$, $ZrCu_2$, ZrCu, and Zr_2Cu. In all diffusion couples, a pronounced Kirkendall effect was observed but not measured. Also, no diffusion coefficients were measured. There was a contraction in the length of the specimens in the direction parallel to the diffusion. The exponent in the growth rate equation was found to vary from 1.5 to 3.5.

Generally, the displacement of a plane of constant concentration in a diffusing system and the growth of an intermetallic layer are described by the expression:

$$d^2 = kt, \tag{1}$$

where *d* is the displacement during the time, *t*, and *k*, is constant for a given temperature. Its dependence on temperature is frequently described by the Arrhenius equation:

$$k = k_0 \exp(-Q/RT), \tag{2}$$

where k_0 is a constant, *Q* the so-called activation energy, and *R* the gas constant. In many practical cases, the exponent in eq (1) differs somewhat from two. The difference is generally attributed to a deviation from ideal diffusion. In the present case, this deviation occurred probably because of the anisotropy of the intermediate phases.

Later interdiffusion investigations [4–7] confirmed the existence of the above-mentioned phases.

Similar interdiffusion studies have been performed at temperatures between 500 and 600 °C [8]. Rather than using a high purity zirconium, a Zircalloy-2 alloy (tin-1.38%, aluminum-90 ppm, carbon-100 ppm, chromium-970 ppm, iron-1220 ppm, nickel-630 ppm, oxygen-680 ppm) was used as the other half of the diffusion couple. After the copper was electroplated onto the zircalloy, the specimens were diffused for times varying from 10 to 500 hours. The maximum widths of the diffusion zones as revealed by metallographic examination and electron microprobe analysis were then measured.

The thickness of the interdiffusion layer could be expressed as:

$$d^n = k_0 e^{-Q/RT} t, \tag{3}$$

where d, is the width, t the diffusion time, and

$$n = 2.66$$

$$Q = 30{,}466 \text{ cal/mol}$$

$$k_0 = 4.7 \times 10^{-5} \text{ cm}^n\text{s}.$$

A logarithmic plot of the interdiffusion zone width as a function of temperature is shown in figure 33.

Electron microprobe analysis revealed the presence of only three intermetallic compounds: Zr_2Cu, Zr_2Cu_3, and $ZrCu_3$. A Kirkendall shift, if found, was not reported. These findings are not in agreement with Hillman and Hofmann [3] who found some six intermetallic compounds. Brossa et al. [8] did not find the well established compound ZrCu, he "newly observed" phase of Hillman and Hofman, $ZrCu_5$, or $ZrCu_4$.

The discrepancy in results can be attributed to the use of an alloy rather than pure zirconium, lower temperatures (resulting in more grain boundary diffusion), and the shorter diffusion anneals (lack of equilibrium) used by the French authors.

29.3. Cu-Zr-Ag

Diffusion (tracer, grain boundary, and interdiffusion coefficients) of silver in Cu-Zr (0.12 wt%) alloys has been measured by Barreau and coworkers [9, 10]. The effect of the small zirconium additions used in these experiments on diffusion of silver in copper appears to be small except in the case of grain boundary diffusion *when this small addition of zirconium decreases the* silver diffusion rate by as much as a factor of 10. Then results are discussed more thoroughly in a previous monograph in the present series [11] where diffusion in the Cu-Ag system was described.

29.4. Cu-Zr-Fe

The interdiffusion of copper with Zircalloy-2 (a Zr-alloy, whose major alloying constituent is iron; present in this case in a concentration of 1220 ppm) over the temperature range 500 to 600 °C has been studied [8] 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 earlier section on interdiffusion in binary Cu-Zr alloys.

29.5. Cu-Zr-Nb

Pure copper has been interdiffused with Zr-Nb alloys in the neighborhood of the α/β phase transformation temperature, and the phases formed in the diffusion zone examined metallographically [7]. It was found that the interdiffusion zone was essentially the same as that found where pure copper was interdiffused with pure zirconium, except that this same result could be

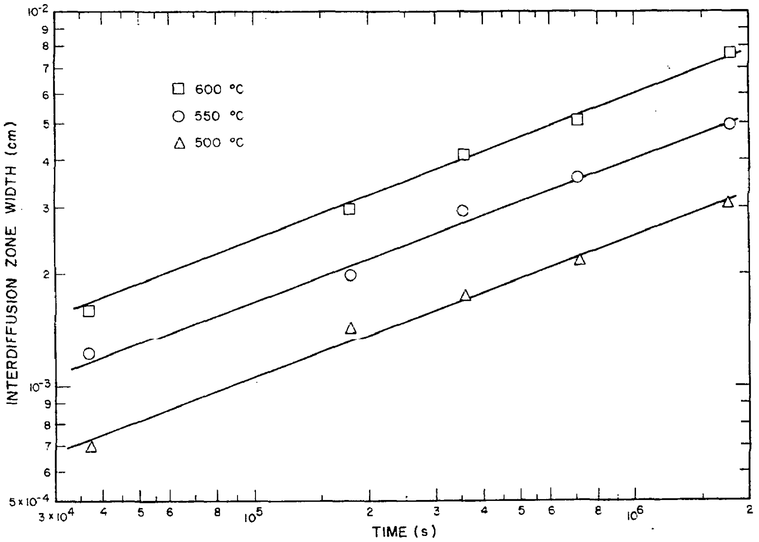

FIGURE 33. Interdiffusion zone width as a function of time for Zircalloy-2 interdiffused with copper.

Data taken from [8].

accomplished with temperatures approximately 100 °C less.

29.6. Cu-Zr-O

Binary Cu-Zr alloys have received some attention because of their possible use as canning materials for fuel elements in advanced reactors cooled by carbon dioxide [12–23]. In those studies [16–18] where quantitative data were taken, diffusion coefficients of oxygen were determined for both the oxide layer and the underlying Cu-Zr alloy. The results of both groups are in surprisingly good agreement, being of the same order of magnitude. The diffusion coefficients of oxygen in binary Cu-Zr alloys at 750 °C (using CO_2 at one atmosphere pressure) as obtained by Guerlet and Lehr [17] are listed in table 45. Loriers and coworkers [16, 18] obtained the diffusion coefficient of oxygen in Cu-Zr alloys at 600 to 700 °C for one hour, using CO_2 at 60 atmospheres pressure. Their results are in table 46.

The parabolic oxidation of Cu-Zr (1 wt%) alloys in the temperature range 900–600 °C is believed to be controlled by the diffusion of Cu^+ion [19]. Shmykov [21] has discussed the role of oxygen diffusion during the internal oxidation of these Cu-Zr alloys.

TABLE 45. Oxygen diffusion coefficients in zirconium-copper alloys at 750 °C with carbon dioxide at 1 atm pressure. Data taken from [17].

Zr-Cu alloy (wt% Cu)	D(cm^2/s)
0.5	6.68×10^{-11}
1.0	6.25×10^{-11}
1.0^a	2.2×10^{-11}
1.6	4.30×10^{-11}
2.5	3.26×10^{-11}

^{a}Annealed in the β-region before oxidation.

TABLE 46. Oxygen diffusion coefficients in Zr-Cu alloys with CO_2 at 60 atm pressure. Data taken from [16, 18]

Zr-Cu Alloy (wt% Cu)	D(cm^2/s) 600 °C	700 °C
1.0	1.1×10^{-12}	1.3×10^{-11}
1.6	0.85×10^{-12}	1.4×10^{-11}
2.5	0.85×10^{-12}	0.64×10^{-11}
4.0	1.0×10^{-12}	0.82×10^{-11}

The high-temperature oxidation and wear resistance of copper having a diffusion-coating of zirconium has been examined in scaling-resistance experiments [20]. Increased service life was found in some cases.

An experimental method making use of the nuclear reaction $O^{16}(d, p)O^{17}$ to study oxygen diffusion in Cu-Zr alloys has been reported [22]. The concentration of oxygen dissolved in the Cu-Zr alloy during oxidation in an atmosphere of oxygen was measured directly. A diffusion profile for a Zr-Cu (2.5 wt%) alloy, oxidized for 24 hours at 750 °C in an atmosphere of oxygen, is shown in figure 34 where the measured values of the oxygen content, $(c\text{-}c_0)$, in atoms/cm^3 $\times 10^{-20}$, are plotted versus the various depths x, in microns, from the metal-oxide interface. The authors did not try to interpret their results because of complications arising from the appearance of a new phase near the metal-oxide interface.

The preliminary results of a study to improve the oxidation resistance of copper by a protective coating of zirconium have been published [23]. Copper surfaces were impregnated with zirconium by diffusion, and then exposed to air at 850 °C. The only results reported were the weight gains of the samples, and these are shown in figure 35. Very little improvement in oxidation resistances was experienced over that of uncoated copper using the technique of diffusion impregnation of copper with zirconium. No interdiffusion data were reported for the metals employed, nor were any oxygen diffusion coefficients in the alloy reported in this rather cursory study.

29.7. Cu-Zr-U-X

See discussion in the Cu-U section, under Cu-U-Zr-X.

29.8. Cu-Zr References

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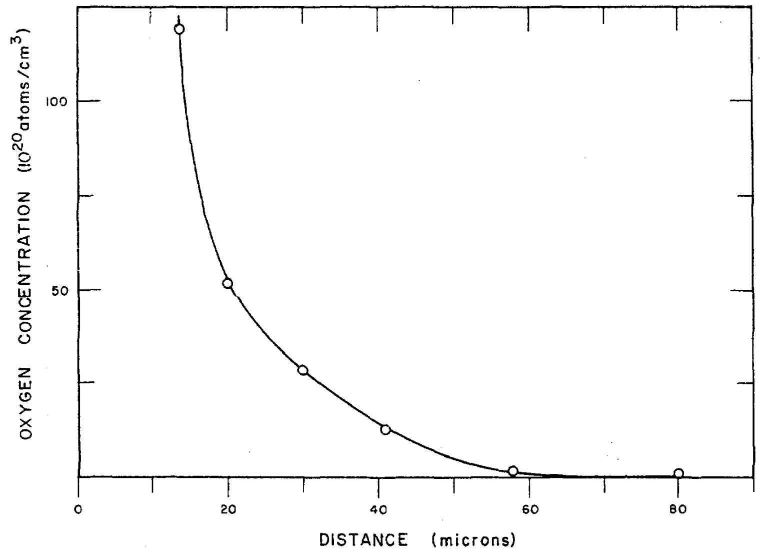

FIGURE 34. Oxygen content as a function of distance from the metal-oxide interface in an oxidized Zr-Cu (2.5 wt%) alloy.

Data extracted from [22].

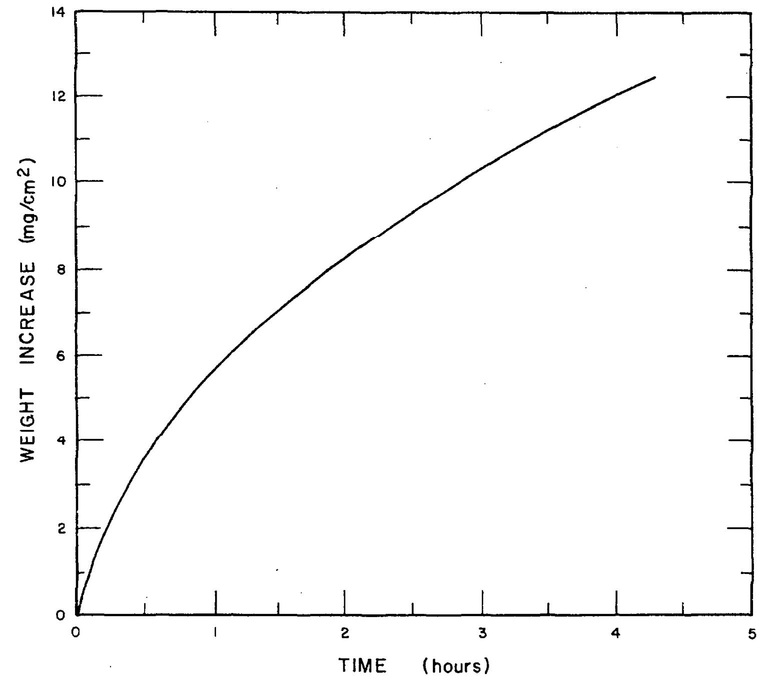

FIGURE 35. Weight gain of copper specimens (whose surfaces were diffused coated with zirconium) exposed to air at 850 °C as a function of time.

Data taken from [23].

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