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Diffusion in Copper and Copper Alloys
Part II. Copper-Silver and Copper-Gold Systems

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A survey, comparison, and critical analysis is presented of data compiled from the scientific literature concerning diffusion in copper-silver and copper-gold systems. 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, strain enhanced 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; copper; diffusion; electromigration; gold; grain boundary diffusion; impurity diffusion; liquid metal diffusion; silver; surface diffusion; thermomigration.

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1. Introduction

1.1. Organization of Review According to Alloy System

The present review is the second in a series designed to provide data on diffusion in copper and copper alloys. The first paper [1] in this series covered copper self-diffusion. The present paper begins the coverage of diffusion in copper alloys with the copper-silver and copper-gold systems. Succeeding papers in this series will cover the remaining copper alloy systems.

The term "copper alloy system" is interpreted in the broadest sense here. For example, the review of diffusion in the copper-silver system includes all diffusion situations which involve both copper and silver. This same format will be followed for all copper alloy systems. According to this format, the copper-silver review treats:

(1) Diffusion of silver in pure copper.
(2) Diffusion of copper in pure silver.
(3) Diffusion of copper or silver in copper-silver binary alloys.
(4) Diffusion of other elements in copper-silver binary alloys.
(5) Diffusion of any species in any ternary alloy containing both copper and silver (or in any multi-component alloy containing both copper and silver).
(6) Diffusion of copper in any alloy containing silver.
(7) Diffusion of silver in any alloy containing copper.

To present the data in as systematic a form as possible, diffusion situations which involve only copper and silver (items 1, 2, and 3 in the above list) are discussed first and are presented in separate subsections under the Cu-Ag system. Then situations involving a third element in addition to copper and silver are presented, with a separate subsection being provided 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-Ag-M, then this system is simply not listed. Diffusion measurements in quaternary and other higher order multicomponent alloys are not common in copper alloy systems. General discussions of diffusion in these multicomponent alloys are presented in a single subsection, entitled for example in the copper-silver case, Cu-Ag-X, where X indicates that at least two other elements in addition to Cu and Ag are present. A final set of subsections is devoted to special diffusion effects such as grain boundary diffusion, surface diffusion, electromigration, thermomigration, and diffusion in molten metals. By contrast, the earlier subsections treat mainly volume diffusion in solids in the absence of external driving forces. For easy reference, a list of subsections is provided in the table of contents for each alloy system.

The organization of the data by alloy systems is intended to aid the reader in finding specific items of data. To avoid unnecessary fragmentation, all diffusion data for systems which include copper, silver and a given third element, M, are listed under the single ternary system, Cu-Ag-M. This procedure effectively combines items 4, 5, 6, and 7 of the above listing in a single set of subsections. Thus, diffusion of M into CuAg alloys, diffusion in CuAgM alloys, diffusion of Cu into AgM alloys and diffusion of Ag into CuM alloys all would be included in the Cu-Ag-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-Ag-M alloys together, regardless of the concentrations of species Cu, Ag, 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 ($1.987\,\mathrm{cal}\cdot\mathrm{K}^{-1}\cdot\mathrm{mol}^{-1}=8.314\,\mathrm{J}\cdot\mathrm{K}^{-1}\cdot\mathrm{mol}^{-1}$).

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

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 vs 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 to expedite comparisons between differing measurements. Even for the temperature dependence of D, however, the most useful means of presenting and comparing data probably is by means of graphs, showing the diffusion coefficients themselves, in this case with log D plotted versus T^{-1}. A number of these graphs are shown in the present review.

The textual 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.

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 $D_{gb}\cdot\delta$ is then 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 6]. In addition, specific references and comments are provided at points in the textual commentary where results from some of the less standard types of measurements are discussed.

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 assumed to provide a good indication of the precision 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 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

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

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, which tends to shift the lattice plane at 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 [7].

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 [8] 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

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

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

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

where

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

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

$$x_k = 2\tau(D^1_A - D^1_B)(\partial N_A/\partial x)_\tau. \tag{8}$$

From this equation, it is apparent that there is no Kirkendall shift when the intrinsic diffusion coefficient D^1_A of species A equals the intrinsic diffusion coefficient D^1_B of species B. Also, in parabolic diffusion $\partial N_A/\partial x$ 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

$$\tilde{D} = N_A D^1_B + N_B D^1_A. \tag{9}$$

If $\tilde{D}$ and x_k are measured at a binary alloy interface of known composition and concentration gradient, D^1_A and D^1_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 reason to expect D^*_i to depend exponentially on reciprocal absolute temperature, as in eq (2). By contrast, the temperature dependence of D^1 or $\tilde{D}$ may be more complex. Nevertheless, eq (2) is commonly used in the literature to express the temperature dependence of these other diffusion coefficients as well.

Since tracer measurements 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^1 or $\tilde{D}$ may more directly provide the information needed. Nevertheless, as discussed above, these other diffusion coefficients, D^1 and $\tilde{D}$, can often be related to the more fundamental quantities D^*.

The intrinsic diffusion coefficients, D^1, 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^1_i. The D^1 thus determine 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 interdiffusion coefficients are related to fluxes measured relative to the undiffused ends of specimens.

2. Copper-Silver

2.1. Ag*→Cu

Values for the volume diffusion rate of radioactive silver in copper have been reported in a number of papers [9–26], which were not always in agreement with each other. Figures 1 (high temperature region) and 2 (low temperatures) are a comparison of the Arrhenius plots for lattice diffusion from a number of these sources.

The first systematic measurements of the lattice diffusion of radioactive silver in pure copper were reported in the thesis of Mercer [11]. In the temperature region 850 to 1070 °C, he obtained the following Arrhenius expression for the tracer diffusion coefficient:

$$D^*_{\mathrm{Ag}\to\mathrm{Cu}} = (0.846 \pm 7\%) \exp(-47{,}290\ \mathrm{cal \cdot mol^{-1}} \pm 0.4\%/RT)\ \mathrm{cm^2/s}.$$

The temperature dependence of these coefficients are shown in figure 1 in comparison with the results of other investigators. Tomizuka similarly performed tracer diffusion experiments, and his initial analysis of his data yielded the Arrhenius expression:

$$D^*_{\mathrm{Ag}\to\mathrm{Cu}} = 0.23 \exp(-44{,}000\ \mathrm{cal \cdot mol^{-1}}/RT)\ \mathrm{cm^2/s},$$

as being valid for an unspecified high temperature range [13]. A later revision by Tomizuka [14] changed the above expression to:

$$D^*_{\mathrm{Ag}\to\mathrm{Cu}} = 0.63 \exp(-46{,}500\ \mathrm{cal \cdot mol^{-1}}/RT)\ \mathrm{cm^2/s}.$$

The publication of this revised expression in several review papers by Lazarus [10, 28] resulted in it being widely quoted for a number of years although Morrison reports that Tomizuka [27] has since re-calculated the values of the pre-exponential factor, D_0, and the activation energy, Q, to be:

$$D_0 = (0.27 \pm 15\%)\ \mathrm{cm^2/s},$$

$$Q = (44{,}700 \pm 500)\ \mathrm{cal \cdot mol^{-1}}.$$

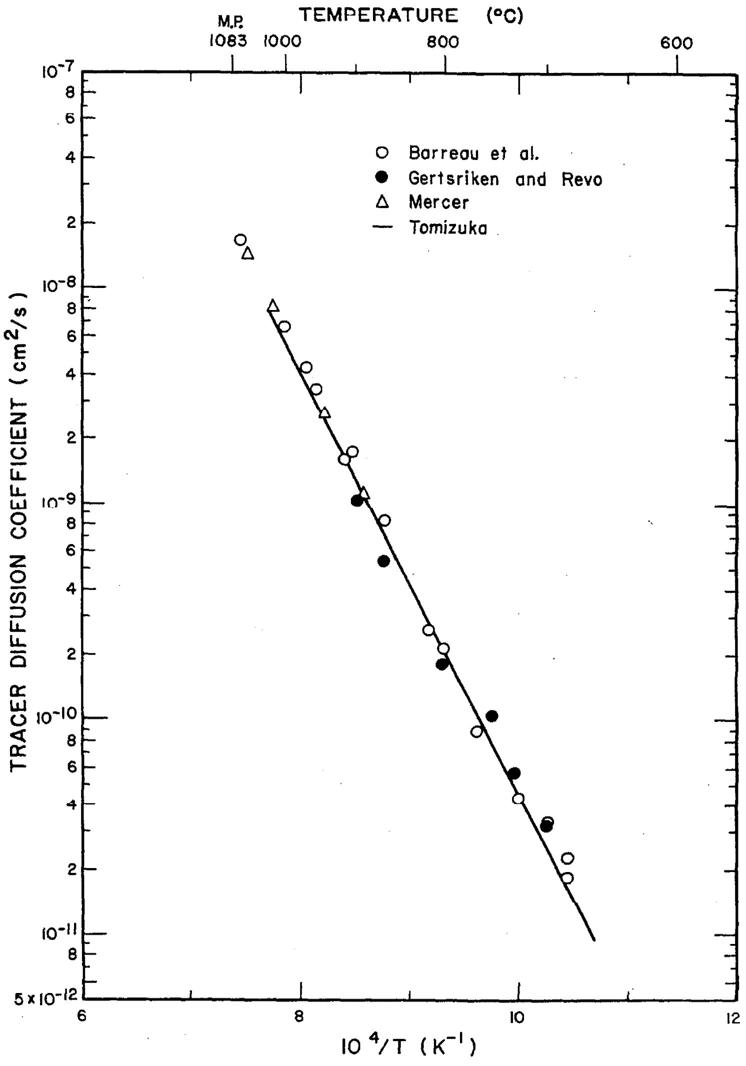

FIGURE 1. Tracer diffusion coefficients of silver in pure copper as a function of the reciprocal absolute temperature.

The data shown are the high-temperature results extracted from the data of Barreau et al. [16], Gertsriken and Revo [20], Mercer [11], and Tomizuka [27].

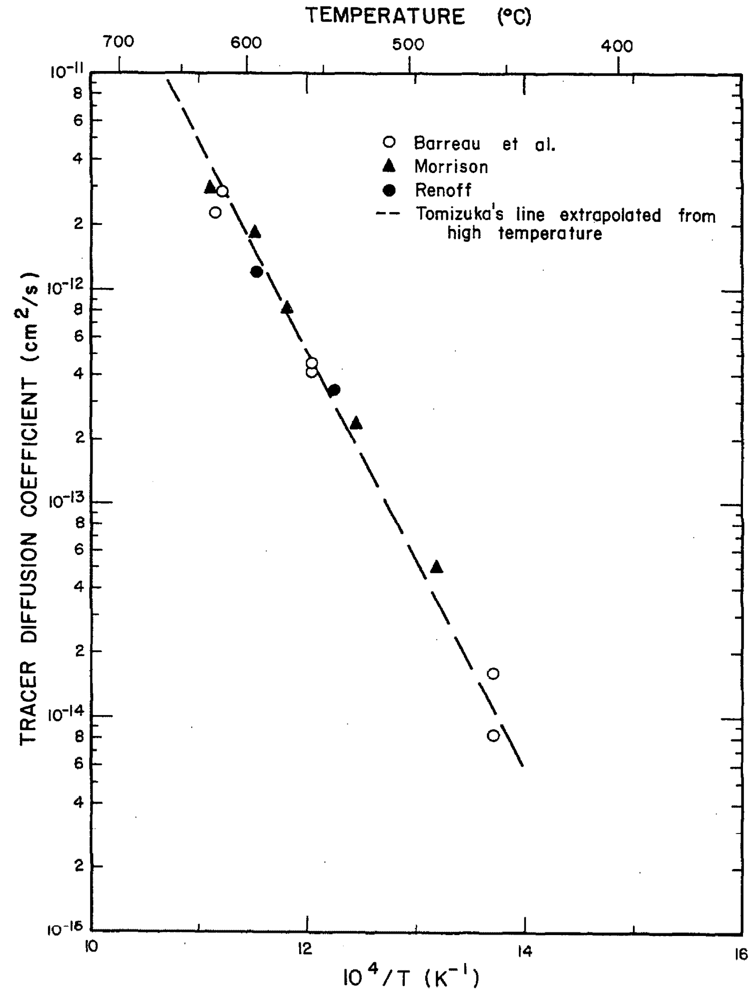

FIGURE 2. Tracer diffusion coefficients of silver in pure copper as a function of the reciprocal absolute temperature.

The data shown are the low-temperature results extracted from the data of Barreau et al. [16], Morrison [26], Renoff [19], and the high-temperature data of Tomizuka [27] extrapolated to low temperature.

TABLE 1. Silver-110 tracer diffusion coefficients in OFHC copper and dilute copper alloys [16]

T(°C)	D^*(cm^2/s)				
	OFHC Cu	Cu-Cr (0.8 wt %)	Cu-Te (0.6 wt %)	Cu-Ti (0.1 wt %)	Cu-Zr (0.12 wt %)
1064	1.69×10^{-8}			2.07×10^{-8}	
1000	6.62×10^{-9}		7.45×10^{-9}	3.93×10^{-9}	
967	4.35×10^{-9}				
960		4.67×10^{-9}			4.37×10^{-9}
954	3.48×10^{-9}		4.25×10^{-9}	2.97×10^{-9}	
916	1.60×10^{-9}	1.65×10^{-9}			1.56×10^{-9}
906	1.76×10^{-9}		2.27×10^{-9}	1.79×10^{-9}	
866	8.35×10^{-10}				
816	2.6×10^{-10}				
800	2.18×10^{-10}				
793		1.80×10^{-10}			1.4×10^{-10}
765	8.9×10^{-11}				
751		1.07×10^{-10}			6.95×10^{-11}
726	4.37×10^{-11}	1.18×10^{-10}			5.17×10^{-11}
700	3.3×10^{-11}		5.80×10^{-11}	3.05×10^{-11}	
697		2.44×10^{-11}			1.3×10^{-11}
684	2.25×10^{-11} 1.85×10^{-11}	7.85×10^{-11}			2.06×10^{-11}
623	[a] 2.3×10^{-12}				
618	2.83×10^{-12}				5.15×10^{-12}
557	4.50×10^{-13} [a] 4.15×10^{-13}				
455	[a] 1.62×10^{-14} 8.4×10^{-15}				

[a] Obtained from single crystal specimens.

TABLE 2. Silver-110 tracer diffusion coefficients in copper [26]

T(°C)	
625	$(2.91\pm0.08)\times10^{-12}$
595	$(1.8\pm0.2)\times10^{-12}$
574	$(8.2\pm0.6)\times10^{-13}$
529	$(2.39\pm0.05)\times10^{-13}$
485	$(4.9\pm0.1)\times10^{-14}$

Barreau et al. [15, 16], more recently, have measured the rate of lattice diffusion of radioactive silver-110 into oxygen-free high-conductivity copper (99.99% purity) over a wide range of temperature (455 to 1064 °C). The values they obtained for the silver tracer diffusion coefficients are listed in table 1 and plotted as a function of reciprocal absolute temperature in figure 3. A straight line can be fitted to the data and the resulting temperature dependence expressed as:

$$D^*_{\mathrm{Ag}\to\mathrm{Cu}}=0.61 \exp\left(-46{,}600 \text{ cal}\cdot\text{mol}^{-1}/RT\right) \text{ cm}^2/\text{s}.$$

Morrison [26] confined his tracer measurements to relatively low temperatures (485 to 625 °C) and observed a somewhat lower activation energy for diffusion (40,000 $\pm$5,000 cal$\cdot$mol^{-1}) than that found by some of the other investigators. The tracer diffusion coefficients he observed (see table 2 and figure 2) were close to the extrapolation of the high temperature data (except for the two lowest temperature determinations, where there is probably an enhancement due to dislocations providing easy paths for silver diffusion in the copper single crystals).

Renouf [19] in his autoradiographic study of the grain boundary diffusion of Ag-110 in copper bicrystals, made several low temperature determinations of the lattice diffusion coefficient. These are plotted in figure 2 and are in reasonable agreement with those of Morrison [26].

Arkharov et al. [9] made a single determination at 650 °C, finding the tracer diffusion coefficient of silver in copper to be 6.4×10^{-12} cm^2/s.

All of the above mentioned results are in good agreement with each other except for Morrison's two determinations where he was probably measuring the diffusion of silver atoms along dislocations rather than pure lattice diffusion. The small descrepancies between the results of Tomizuka, Mercer, and Barreau et al. can probably be attributed to the method of sectioning specimens and the counting of the activity. Tomizuka sectioned his samples on a precision lathe and measured the amount of radioactivity contained in the removed chips. This method can usually be expected to provide the most accurate results. Barreau et al. used a modified Gruzin technique [29–31] of measuring the residual activity in the bulk specimen. Arkharov et al. employed the pure Gruzin method [29, 30] of measuring the silver-110 penetration. The details of Mercer's experiments were never published (although Morrison in his paper [26] gives many of Mercer's results). Morrison, because of the small silver-110 penetration rates, utilized an unconventional sectioning technique (anodic removal of layers from the specimen surface and then counting the amount of activity in the removed material) and interpreted his silver concentration profiles using the analysis of Hart [32] as modified by Mortlock [33].

Other investigations have yielded results which led to unexplicably high [17, 20] or unexplicably low [24] rates of diffusion for the silver tracer.

The effect of dilute alloying additions (0.8 wt. % chromium, 0.6 wt. % tellurium, 0.1 wt. % titanium, or 0.12 wt. % zirconium) on the silver tracer diffusion coefficient were determined over the temperature range 618 to 1064 °C by Barreau and coworkers [15, 16]. The results were obtained in the same manner as the tracer studies performed with pure copper and are found in table 1 and figure 3.

Schreiner et al. [25] diffused radioactive silver into pressed-powder compacts of copper, measuring penetration depths obtained after diffusion anneals at 500 °C.

Grain boundary diffusion, surface diffusion, electromigration, thermomigration, strain-enhanced diffusion and diffusion in molten metals for silver diffusing in copper are discussed in subsequent sections covering these topics for the copper-silver alloy systems.

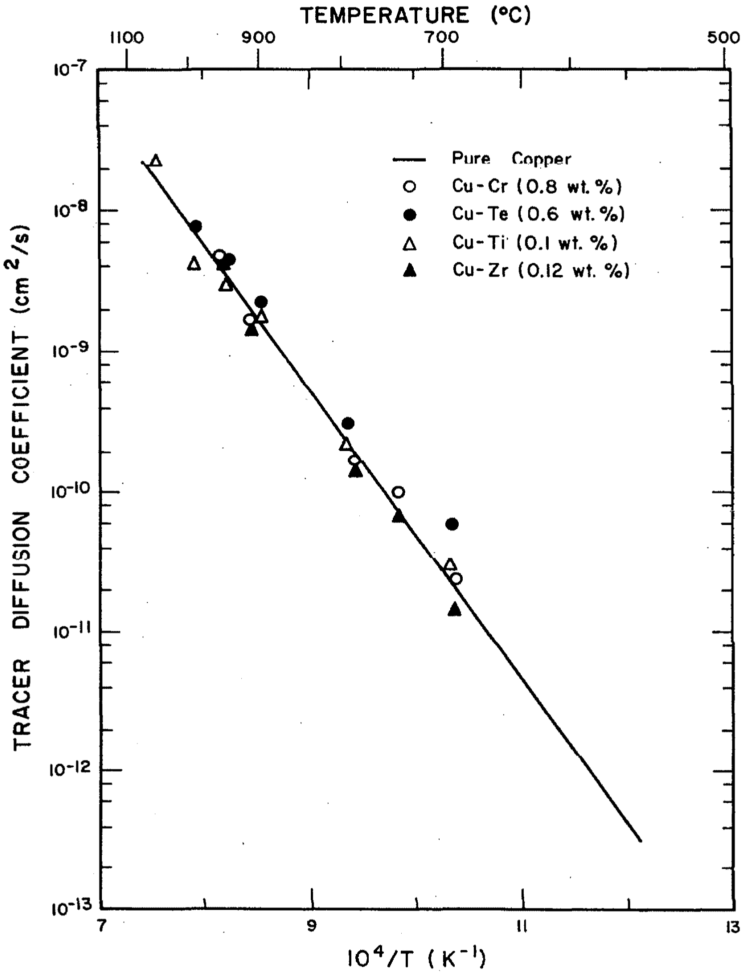

FIGURE 3. Tracer diffusion coefficients of silver in pure copper as a function of reciprocal absolute temperature.

The effect of minor alloying additions of Cr, Te, Ti, and Zr to the copper is also depicted. Data taken from Barreau et al. [15, 16].

2.2. Cu* → Ag

The diffusion of radioactive copper-64 in silver has been measured in the temperature range 700 to 950 °C [34, 35]. Using careful experimental technique [36, 37], single crystals of pure silver (nominally 99.99%), were plated with the copper isotope and given diffusion anneals ranging from 5 to 45 hours. After diffusion, uniform sections were then removed from the specimens with a precision lathe and the activity of each section measured. When the logarithm of the activity was plotted versus the square of the penetration distance, linear curves were obtained. A "least-squares fit" of these concentration-depth curves allowed the tracer diffusion coefficients in table 3 to be calculated directly. Figure 4 is a plot of the tracer diffusion coefficients as a function of the reciprocal of the absolute temperature. A straight line can be fitted to the experimental data points with the aid of a least squares analysis, and an activation energy, Q, and the frequency factor, D_0, determined. The resulting Arrhenius expression for the tracer diffusion coefficient in the temperature range 700 to 950 °C is:

$$D^*_{\mathrm{Cu}\rightarrow\mathrm{Ag}} = 1.23 \exp\left(-46{,}100 \text{ cal}\cdot\text{mol}^{-1}/RT\right) \text{ cm}^2/\text{s}.$$

The estimated probable error in D^* is ±4 percent, in Q is ±2 percent and as much as ±20 percent in D_0. The short half-life of the copper isotope contributed to the loss in accuracy of these data. The average difference between values of the tracer diffusion coefficient measured at a given temperature is a little less than 2 percent, with 6.3 percent scatter present in the highest temperature data. The mean deviations from the values given by Arrhenius expressions are less than 2 percent, with a maximum deviation of about 4 percent.

Surface diffusion measurements of copper on silver are reported in the section on surface diffusion in the copper-silver systems.

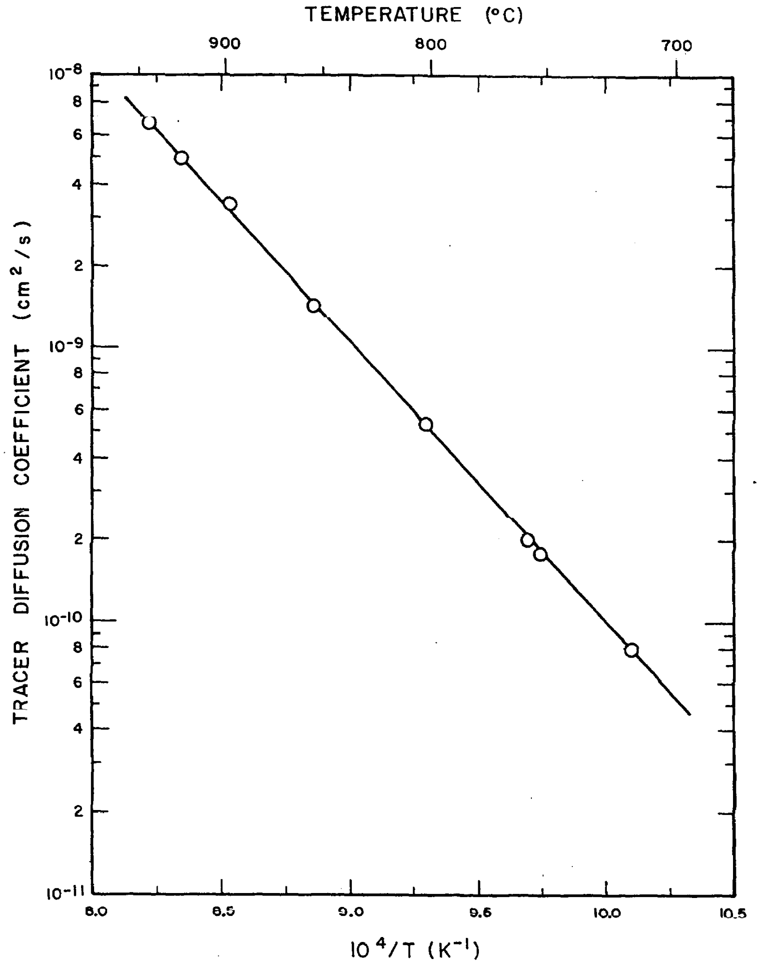

FIGURE 4. Copper tracer diffusion coefficients in silver as a function of reciprocal absolute temperature.

Data taken from Sawatzky [34], and Sawatzky and Jaumot [35].

TABLE 3. Copper-64 tracer diffusion coefficients in silver [35]

T(°C)	D^*(cm²/s)	Average D^*
944.5	6.740×10^{-9} 6.334×10^{-9}	6.54×10^{-9}
925	4.922×10^{-9} 4.710×10^{-9}	4.82×10^{-9}
899	3.371×10^{-9} 3.327×10^{-9}	3.35×10^{-9}
854.5	1.435×10^{-9} 1.395×10^{-9}	1.42×10^{-9}
804	5.429×10^{-10} 5.386×10^{-10}	5.41×10^{-10}
758	2.039×10^{-10} 2.016×10^{-10}	2.03×10^{-10}
752	1.860×10^{-10} 1.838×10^{-10}	1.85×10^{-10}
716.5	8.354×10^{-11} 8.253×10^{-11}	8.30×10^{-11}

2.3. Ag* → Cu-Ag

The self-diffusion of silver-110 in silver-copper alloys has been measured in a number of experiments [17, 20–23, 38–43, 55]. The results, for the most part, are in agreement with each other and the most reliable of the measurements are listed in tables 4, 5, 6, and 7 for a number of alloy compositions. Figures 5, 6, 7, and 8 are plots of the same data, illustrating the temperature and concentration dependence of the silver tracer diffusion coefficients.

The results of Gertsriken and Revo [20] have to be considered erroneous in light of the other errors found in their paper (see the discussion above dealing with the tracer diffusion of silver in pure copper where their values for the actication energy were found to be significantly lower than some of the more reliable determinations). The activation energies obtained by Spasov and Ivanov [17] for silver tracers diffusing in copper rich alloys of Cu-Ag are so much lower than the values obtained by other investigators as to be suspect. (In fact, the activation energy they obtain for silver-110 diffusing in pure copper is less than one-half of the more reliable values).

TABLE 4. Diffusion parameters for silver-110 tracer diffusion in silver-copper alloys in the temperature range 700 to 900 °C (after R. E. Hoffman et al. [38])

Ag-Cu Alloy (at.% Cu)	D_0(cm²/s)	Q(kcal·mol⁻¹)
1.75	0.66	44.8
4.16	1.84	46.6
6.56	0.51	43.5

TABLE 5. Silver-110 tracer diffusion coefficients in silver-copper alloys (after K. Sato [39])

Ag-Cu Alloy (at .% Cu)	T(°C)	D^*(cm²/s)	D_0(cm²/s)	Q(kcal·mol⁻¹)
0.0			0.40	44.1
0.85	850	1.08×10^{-9}	0.39	44.0
	820	6.18×10^{-10}		
	795	3.81×10^{-10}		
	690	4.44×10^{-11}		
2.55	850	1.44×10^{-9}	0.30	43.1
	820	8.45×10^{-10}		
	795	5.21×10^{-10}		
	690	5.99×10^{-10}		
3.36	850	1.60×10^{-9}	0.26	42.2
	820	9.23×10^{-10}		
	795	5.56×10^{-10}		
	690	7.00×10^{-11}		

TABLE 6. Diffusion parameters for silver-110 tracer diffusion in silver-copper alloys (after M. E. Yanitskaya et al. [41])

Ag-Cu Alloy (at .% Cu)	D_0(cm²/s)	Q(kcal·mol⁻¹)	Temperature range (°C)
0.00	0.62	45.2	690–906
0.17	0.65	45.2	780–906
0.17	1.06	41.0	690–780
0.84	0.68	45.2	780–906
0.84	0.08	39.0	690–906
1.68	0.07	40.6	725–906
5.00	0.06	39.9	725–880
8.15	0.04	38.3	725–830

TABLE 7. Silver-110 tracer diffusion coefficients in silver-copper alloys. After Patil and Sharma [43].

Ag-Cu Alloy (at.% Cu)	T (°C)	D^* (cm²/s)	D_0 (cm²/s)	Q (kcal·mol⁻¹)
1.38	840	10.23×10^{-10}	1.04	45.13
	800	6.46×10^{-10}		
	690	5.47×10^{-11}		
	638	1.82×10^{-11}		
	610	7.23×10^{-12}		
2.52	818	1.12×10^{-9}	0.63	43.76
	818	1.03×10^{-9}		
	780	5.39×10^{-10}		
	780	4.78×10^{-10}		
	748	2.39×10^{-10}		
	748	2.36×10^{-10}		
	653	2.81×10^{-11}		
	653	2.56×10^{-11}		
4.43	818	1.10×10^{-9}	0.57	43.31
	780	5.72×10^{-10}		
	780	5.52×10^{-10}		
	748	2.91×10^{-10}		
	748	3.16×10^{-10}		
	653	3.15×10^{-11}		
	653	2.80×10^{-11}		

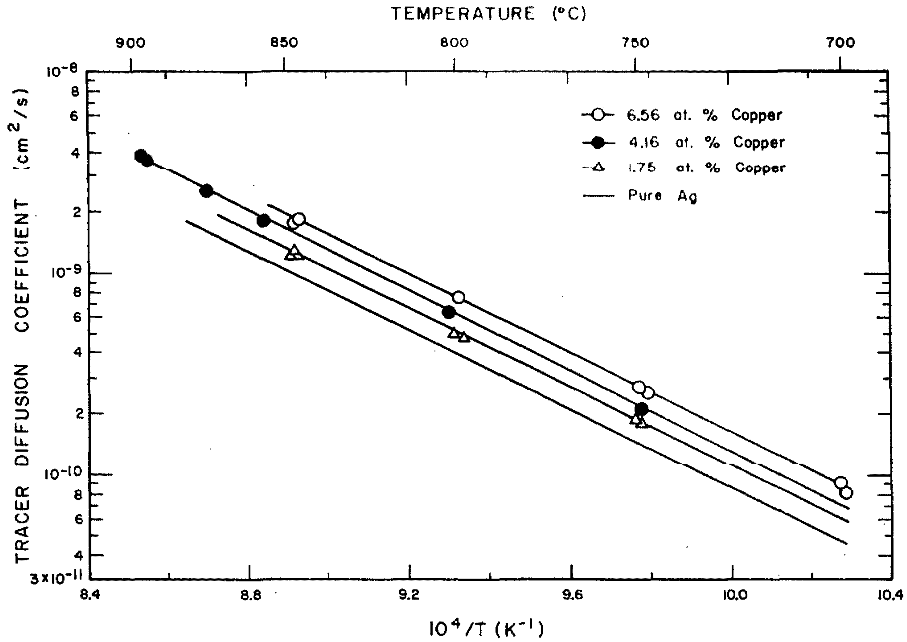

FIGURE 5. Silver tracer diffusion coefficients in several silver-copper alloys (1.75, 4.16, and 6.56 at. % Cu) as a function of reciprocal absolute temperature.

Data of R. E. Hoffman et al. [38].

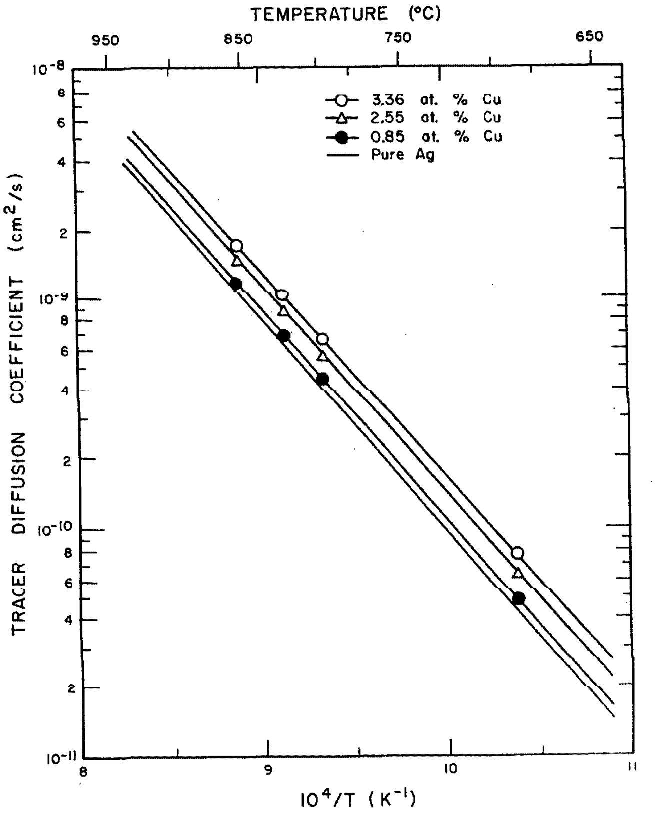

FIGURE 6. Silver tracer diffusion coefficients in several silver-copper alloys (0.85, 2.55, and 3.36 at. % Cu) as a function of reciprocal absolute temperature.

Data taken from K. Sato [39].

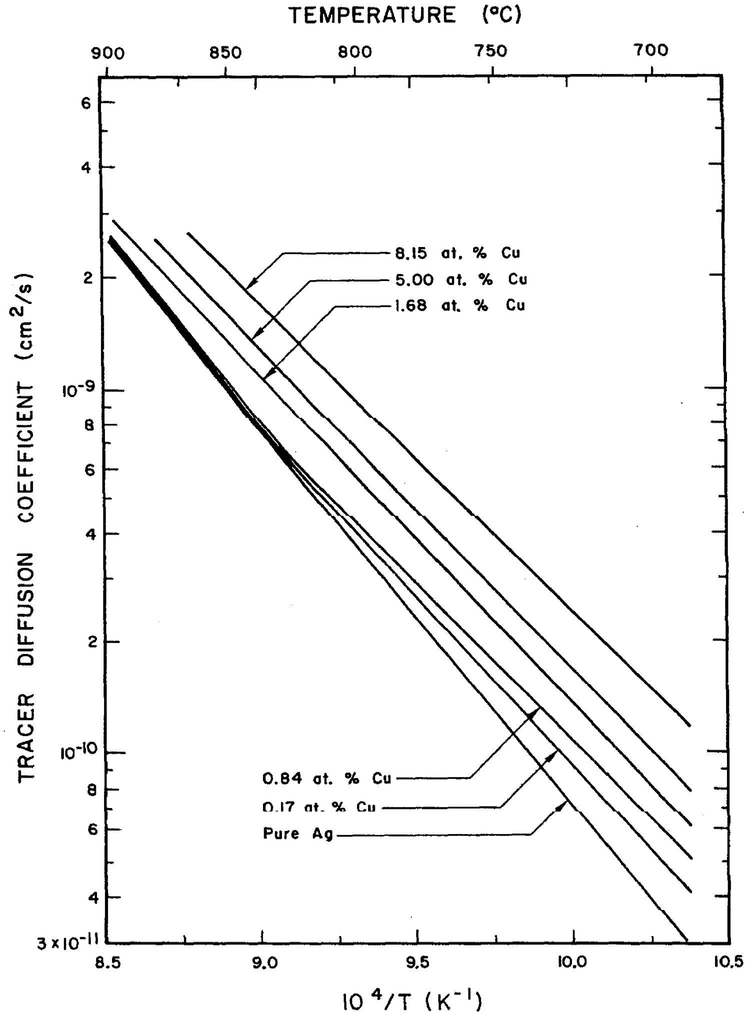

FIGURE 7. Silver tracer diffusion coefficients in silver-copper alloys (0.17, 0.84, 1.68, 5.00, 8.15 at. % Cu) as a function of reciprocal absolute temperature.

The self-diffusion coefficients in pure silver were determined concurrently by the same authors. Yanitskaya et al. [41].

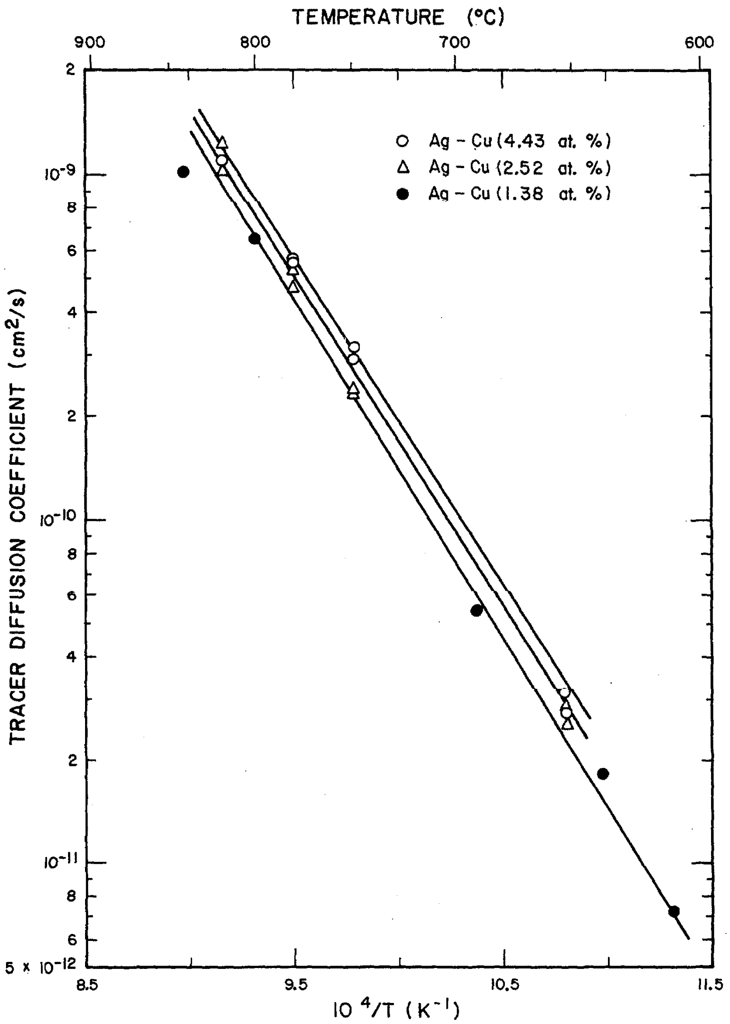

FIGURE 8. Silver tracer diffusion coefficients in several silver-copper alloys (1.38, 2.52, 4.43 at. % Cu) as a function of reciprocal absolute temperature.

Data taken from Patil and Sharma [43].

Zhukhovitskii and co-workers, in an early publication [42], arrived at some incorrect diffusion coefficients. A re-evaluation of their data led to new values for the coefficients [41].

In all of the more carefully performed experiments, it was found that dilute alloying additions of copper enhanced the silver self-diffusion rates.

Grain boundary diffusion and molten metal diffusion measurements for silver in Cu-Ag can be found in the pertinent section covering these topics for the copper silver alloy systems.

2.4. Cu-Ag Interdiffusion

There have been a number of investigations of interdiffusion in the Cu-Ag binary system [16, 21, 23, 44–62, 70]. Not all of the measurements are good, nor are all of the more reliable measurements in agreement with each other. Some of the earliest determinations were either too qualitative in nature [44, 49] or incorrect [47, 48, 50].

Measurements of the rate of interdiffusion of copper in silver [60] and silver (rich)-copper alloys [16, 45] differ in the amount of curvature present in the Arrhenius plots of the data. Cahoon and Youdelis [45], who employed polycrystalline diffusion couples and measured the interdiffusion coefficient over the range 0 to 2 at. percent copper, observed a discontinuity in the Arrhenius plot at ~700 °C. The higher-valued interdiffusion coefficients they observed can be attributed to grain boundary diffusion contributions. Hall and Haworth [60] also observed a marked curvature in the Arrhenius plot of the data they obtained from the interdiffusion occurring between an electroplated copper layer on single crystals of silver in the temperature range 498 to 701 °C. The behavior in this case is attributed to dislocation pipe diffusion. Barreau et al. [16] made the only measurements for which no curvature was found in the Arrhenius plots (see figure 9) even though they performed experiments at temperatures as low as 550 °C. The resulting pre-exponential factors and activation energies for the various compositions of these silver-rich alloys are listed in table 8. These experiments were performed concurrently with experiments in copper-rich alloys, the Arrhenius plots of which are displayed in figure 10. Compiled in table 9 are the values of D_0 and Q obtained from the above Arrhenius plots. All of the interdiffusion coefficients were calculated by the use of the Matano analysis [63] or Hall's method [64]. Shown in figures 11 and 12 are the calculated interdiffusion coefficients as a function of composition. The values of the interdiffusion coefficient near infinite dilution are near the appropriate tracer diffusion coefficient values (mentioned in references [16], [26], and [35]). The effect of dilute alloying additions (0.8 wt. % chromium or 0.12 wt. % zirconium) on the interdiffusion coefficients was also measured and the results are shown in figures 9, 10, 11, and 12.

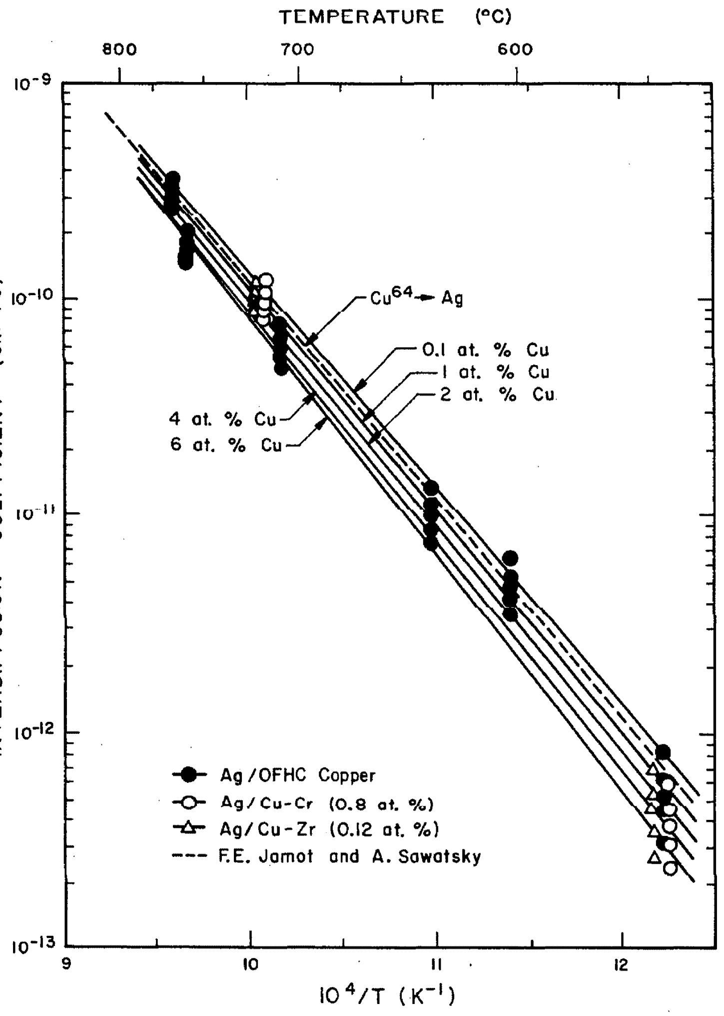

FIGURE 9. Interdiffusion coefficients as a function of reciprocal absolute temperature.

The interdiffusion coefficient in silver-rich alloys as determined by Barreau et al. [16], is compared to the tracer diffusion coefficient of Cu^{64} in pure silver as determined by Jaumot and Sawatsky [35].

TABLE 8. Diffusion parameters for interdiffusion in silver-copper alloys [16]

Ag-Cu Alloy (at.% Cu)	D_0(cm^2/s)	Q(kcal·mol^{-1})
0.1	1.2	45.9
1	1.7	46.9
2	2.5	47.8
4	3.1	48.4
6	6.8	50.2

TABLE 9. Diffusion parameters for interdiffusion in copper-silver alloys [16]

Cu-Ag Alloy (at.% Cu)	D_0(cm^2/s)	Q(kcal·mol^{-1})
99.9	0.88	46.5
99.5	1.6	48.1
99	3.1	49.7
98.5	6.8	51.5

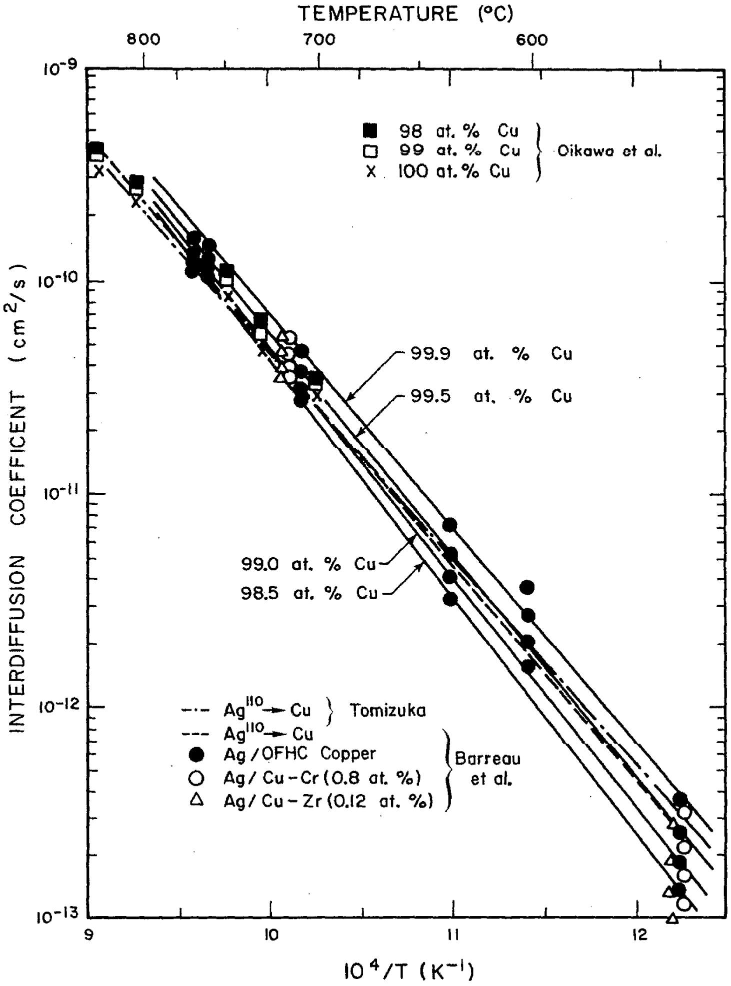

FIGURE 10. Interdiffusion coefficients as a function of reciprocal absolute temperature.

The interdiffusion coefficients between silver and some copper-rich alloys (as determined by Barreau et al. [16] and copper-rich solid solutions by Oikawa et al. [58]) are compared to the silver tracer diffusion coefficient in pure copper (as determined by Barreau et al. [15, 16], and by Tomizuka [27]).

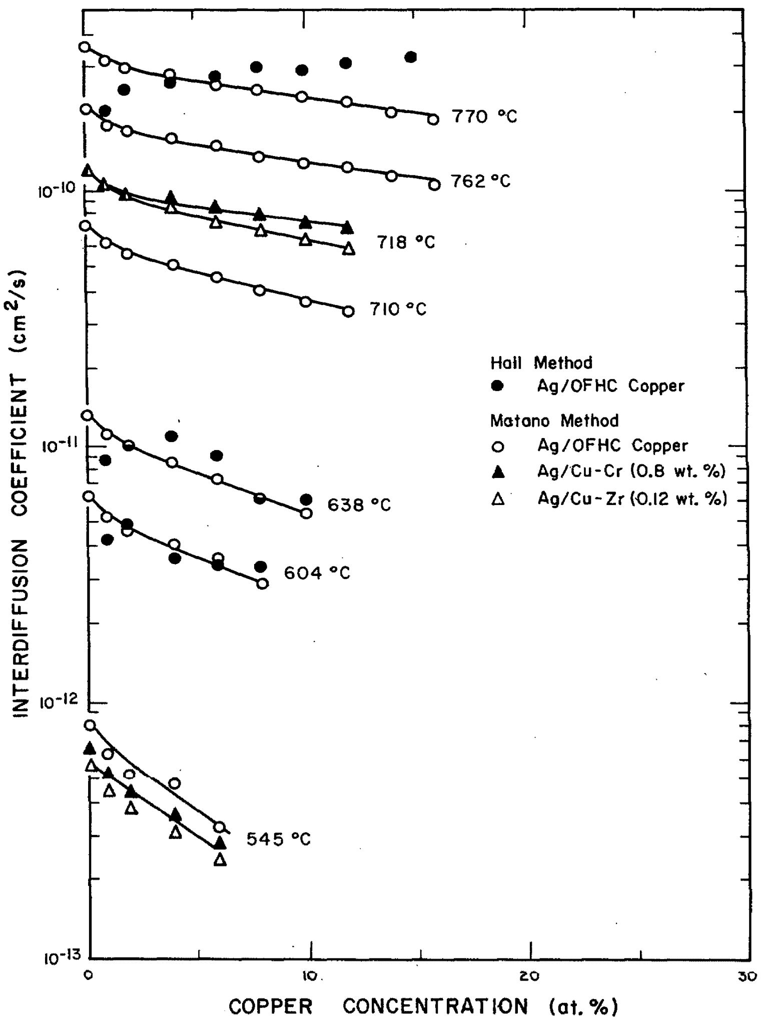

FIGURE 11. Interdiffusion coefficients as a function of composition. Pure silver was bonded to OFHC copper and copper containing chromium or zirconium.

Data taken from Barreau et al. [16].

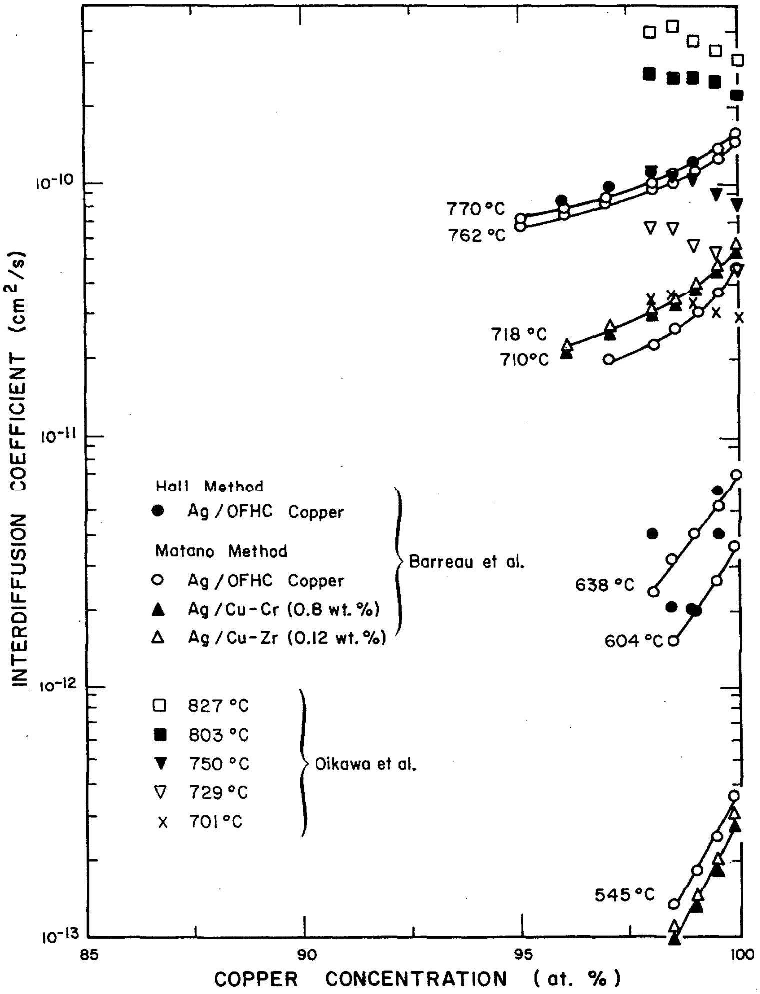

FIGURE 12. Interdiffusion coefficients as a function of copper concentration.

Copper or copper-rich alloys (Cu-Ag, Cu-Cu, Cu-Zr) were bonded to pure silver. Compared are the data of Barreau et al. [16] and the results of Oikawa et al. [58] in solid solutions.

Guy [61] interdiffused pure, polycrystalline copper and silver bars at 755 °C for as long as 46 hours and found a great deal of porosity at the interface of his couples. He was able to reduce pore formation in subsequent experiments by use of pressure (1000 psi). Experiments performed at 610 °C revealed preferential grain boundary diffusion (and precipitation of a silver-rich phase along the boundaries) in the pure metal sandwich couples.

Alexander and Balluffi plated silver on pure copper wire (and vice versa) and interdiffused same at 750 °C [62]. From the relative void content in the couples, they concluded that copper was the faster diffusing species.

It should be pointed out here that in much of the above-mentioned work, pure copper-pure silver configurations were employed in the design of the diffusion couple. This disregard for the large two-phase field existing between the two terminal solid solutions (e.g., see Hansen [65]) and its rôle in the interdiffusion process can, in part, be responsible for the disagreement in results obtained by the different researchers.

Interdiffusion in copper-rich Cu-Ag solid solutions has been investigated by Oikawa and co-workers [58]. They employed sandwich-type diffusion couples, constructed of pure copper and a copper-silver (21. at. %) alloy, which were interdiffused in the temperature range 974 to 1273 K. The silver concentration gradients were determined with an electron microprobe and interdiffusion coefficients were calculated with the aid of the Hall method [64] or the Matano analysis [63]. The diffusion parameters are listed in table 10. These same results are plotted in figure 12 as a function of composition and in figure 10 as a function of reciprocal absolute temperature. As can be seen in each of these figures, there is poor agreement with the results of Barreau and co-workers [16], quite possibly because of the formation of an inteface in the interdiffusion zone of the couples of Barreau et al. In the experiments of Oikawa and co-workers [58], the values of the interdiffusion coefficient, near infinite dilution, are in good agreement with the appropriate tracer diffusion coefficient values.

TABLE 10. The diffusion parameters (with probable errors) for interdiffusion in copper-rich Cu-Ag solid solutions. Data taken from Oikawa et al. [58]

Silver concentration (at.%)	D_0(cm^2/s)	Q(kcal·mol^{-1})
0	$0.206^{+0.092}_{-0.063}$	43.97 ± .74
0.5	$0.251^{+0.089}_{-0.065}$	44.16 ± .57
1.0	$0.177^{+0.067}_{-0.049}$	43.37 ± .55
1.5	$0.187^{+0.069}_{-0.050}$	43.28 ± .60
2.0	$0.224^{+0.088}_{-0.064}$	43.66 ± .64

Kirkendall shift measurements were also made by Oikawa et al. [58] at the single temperature of 1174 K. Marker movement was always toward the silver-rich side of the diffusion couple.

Kuczynski and Alexander [51, 52] made a metallographic study of the copper-silver interface in the interdiffusion zone of sintered wires, though no quantitative information was reported. Carpenter and Houska [53, 54], made an X-ray investigation of the interdiffusion zone between planar deposits of silver on single crystals of copper. Interdiffusion occurring between vacuum-deposited thin films of copper and silver has been followed with electron diffraction techniques [56]. Tanzilli and Heckel [57] undertook research in the Cu-Ag system to compare experimental data with mathematical models of interdiffusion occurring in finite-geometry, two-phase diffusion couples. Ziebold and Ogilvie [59, 70], in their experimental analysis of interdiffusion in the ternary system Cu-Ag-Au, made measurements in the Cu-Ag binary. These measurements are discussed in the context of ternary diffusion in the section dealing with multicomponent alloys. Zhukhovitsky and co-workers [21, 55] performed marker motion studies in couples composed of Ag or Cu and an alloy of Cu-Ag and found that motion was always away from the copper or silver.

2.5. Cu-Ag-Al

The tracer diffusion of silver impurities in single crystals of dilute copper-aluminum alloys has been studied by conventional tracer-sectioning techniques by Alexander and Slifkin [66]. Also reported in the same paper are results for the tracer diffusion of copper impurities in dilute aluminum-silver alloys. The amount of solute (silver or copper) added to the aluminum was one at. percent. Considerable care was exercised in the experiment so as to allow the tracer to diffuse into the bulk, unimpeded by any oxide film. The temperatures of the diffusion anneals, the tracer diffusion coefficients of silver-110 and copper-64 (along with the corresponding values in pure aluminum) are given in table 11 and plotted in figure 13.

From the results, it appears that the copper tracer diffusion coefficient in the aluminum-silver (1 at. %) alloy is enhanced by approximately 13 percent (relative to that for diffusion in pure aluminum).

In the aluminum-copper (1 at. %) alloys, the silver tracer diffusion coefficient is approximately 10 percent larger than in pure aluminum.

Alexander and Slifkin give a semiquantiative interpretation (in terms of the oscillating nature of the electrostatic screening potential) for the enhanced solute diffusion they observed.

The tracer diffusion of silver-110 in copper-rich copper-aluminum alloys has been studied by Spasov and Ivanov [67]. The composition of their alloys varied from 1 to 5 weight percent aluminum and the temperature range of their investigation was 750 to 950 °C. Their

TABLE 11. Silver-110 and copper-64 tracer diffusion coefficients in aluminum and dilute aluminum alloys [66]

Tracer	T(°C)	D^*(cm^2/s)		
		Aluminum	Al-Ag(1 at.%)	Al-Cu(1 at.%)
Ag	634.0	2.2×10^{-8}		3.64×10^{-8}
Ag	613.2	1.5×10^{-8}		1.88×10^{-8}
Cu	608.0	5.4×10^{-9}	6.17×10^{-9}	
Ag	581.2	8.76×10^{-9}		9.52×10^{-9}
Ag	558.0	5.4×10^{-9}		
Cu	489.0	3.44×10^{-10}	3.88×10^{-10}	
Ag	469.8	7.6×10^{-10}		7.87×10^{-10}
Ag	411.3	1.6×10^{-10}		1.76×10^{-10}
Ag	342.0	1.44×10^{-11}		1.55×10^{-11}

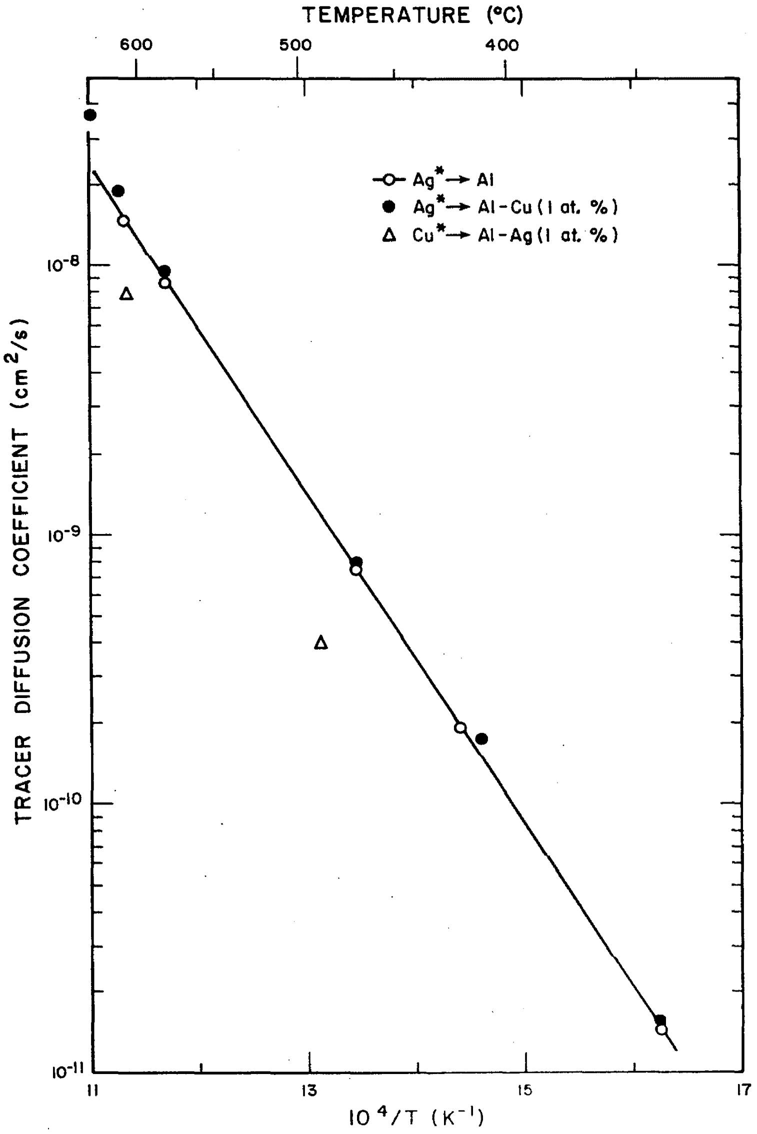

FIGURE 13. Tracer diffusion coefficients of Ag-110 and Cu-64 in aluminum and dilute aluminum alloys as a function of reciprocal absolute temperature.

Data taken from Alexander and Slifkin [66] results were very peculiar (activation energies ranging from 17 to 62 kcal · mol^{-1}) and will need some verification.

Aaron and Weinberg [68], with the aid of autoradiography, studied the diffusion of silver-110 along interphase boundaries of a two phase alloy, copper-aluminum (14.3 at. %). After diffusion anneals at 600 °C, the results seemed to indicate that interphase boundaries provide short-circuit paths for the silver-110 diffusion, similar to grain boundaries. Also, the results suggest that the enhanced interphase boundary diffusion of silver-110 is a function of the coherency of the boundary, the incoherent interphase boundaries being more effective short circuit paths for silver diffusion than semicoherent interphase boundaries.

2.6. Cu-Ag-Au

Braune [69], while studying interdiffusion in couples constructed of pure copper and silver-gold alloys, found copper to diffuse more rapidly in the silver-rich alloys than the gold-rich alloys in the temperature range 1040 to 1189 K.

Ziebold [70] and Ziebold and Ogilvie [59] have reported on a series of interdiffusion experiments in this ternary system at a temperature of approximately 725 °C. Some 17 sandwich diffusion couples were employed in their investigation (see table 12 for the terminal compositions of the couples). After interdiffusion, the specimens were subjected to electron microprobe analysis. The method [71–73] employed in converting X-ray intensities to chemical compositions yielded an overall reproducibility of composition measurements within 1 at. percent. From the penetration curves, composition-dependent interdiffusion coefficients were calculated with the aid of Kirkaldy's extension of the Boltzmann-Matano analysis [74]. Coefficients were computed at 28 points in the ternary system (see table 13). The authors also present in their paper a number of diagrams graphically illustrating trends in the partial interdiffusion coefficients D^3_{ij}:

The direct coefficient for copper (D^3_{11}) appears to be nearly independent of silver concentration for low-silver alloys. Because the authors were able to correlate the silver cross coefficient with thermodynamic data in these dilute (< 20 at. % silver) silver alloys, they were led to conclude that the mobilities of copper and gold are nearly equal. Interdiffusion occurring near the critical point of the two-phase field in the isothermal section of 725 °C causes the copper and silver composition gradients to approach infinity while the direct and cross coefficients become equal. Kirkaldy and Purdy [75] have analyzed this data near the ternary critical state more recently from the thermodynamic point of view. Guy and Philibert [76] feel that the Matano-type analysis applied to the data obtained from these experiments in the copper-silver-gold system does not yield completely satisfactory final results. DeHoff and coworkers [77] have calculated composition paths and Kirkendall shift patterns in this ternary alloy system.

TABLE 12. Diffusion couple compositions in experiments by Ziebold et al. [59, 70]

Couple number	Cu-Au Alloy		Ag-Au Alloy	
	Cu(at.%)	Au(at.%)	Ag(at.%)	Au(at.%)
1	100.0	0.0	0.0	100.0
2	100.0	0.0	8.65	91.35
3	100.0	0.0	30.9	69.1
4	100.0	0.0	55.4	44.6
5	100.0	0.0	72.8	27.2
6	100.0	0.0	100.0	0.0
7	82.3	17.7	100.0	0.0
8	67.4	32.6	100.0	0.0
9	44.0	56.0	100.0	0.0
10	12.6	87.4	100.0	0.0
11	0.0	100.0	100.0	0.0
12	92.3	7.7	88.0	12.0
13	67.4	32.6	55.4	44.6
14	44.0	56.0	30.9	69.1
15	92.3	7.7	55.4	44.6
16	44.0	56.0	55.4	44.6
17	44.0	56.0	8.65	91.35

TABLE 13. Interdiffusion coefficients in the copper-silver-gold system at 725 °C [59]

Composition		Interdiffusion coefficient [a] (cm^2/s × 10^{-10})			
Cu(at.%)	Ag(at.%)	D^3_{11}	D^3_{22}	D^3_{12}	D^3_{21}
2.1	86.9	1.2	0.42	0.07	−0.60
5.9	84.5	1.7	1.4	0.04	0.19
13.8	78.1	0.74	1.6	−0.28	0.81
3.6	72.7	2.3	0.63	0.70	0.00
11.2	71.9	2.1	1.3	0.50	0.21
7.3	59.3	1.2	0.76	0.28	0.83
7.5	58.6	1.00	0.91	0.22	0.96
14.0	45.7	1.9	2.4	1.1	2.1
13.1	34.0	0.99	1.3	0.09	1.7
35.1	18.0	2.5	4.0	1.6	2.8
35.1	4.2	3.0	2.8	1.7	0.57
41.8	3.0	3.1	2.0	0.75	0.29
44.6	2.5	3.2	3.3	0.73	0.81
58.5	4.8	2.3	3.0	0.53	0.81
60.3	12.9	2.3	3.1	1.11	1.8
62.9	9.5	2.4	3.6	1.04	1.9
66.6	2.7	1.8	1.5	0.20	0.18
66.3	0.7	2.1	1.8	2.4	0.04
79.8	5.9	1.11	1.5	0.28	0.42
81.0	3.9	0.93	1.4	0.20	0.17
81.6	2.4	0.73	1.3	−0.01	0.11
88.6	3.0	0.61	0.93	−0.03	0.08
90.1	2.1	0.43	0.85	−0.21	0.04
6.0	59.5	1.1	indeterminate		0.77
6.2	59.3	0.86	indeterminate		0.57
1.2	56.2	0.53	indeterminate		0.39
6.3	36.6	0.89	indeterminate		0.86
6.1	11.8	1.3	indeterminate		0.73

[a] Subscripts: 1 refers to copper.
2 refers to silver.
3 refers to gold.

2.7. Cu-Ag-Be

Arkharov and co-workers investigated [49, 78–82] the effect of dilute alloying additions of beryllium on the diffusion of silver in polycrystalline copper. In the studies made on the effect of beryllium alloying additions on the grain boundary diffusion of silver in polycrystalline copper [78, 81], the results conflict. The earlier results [49, 81] (which claim 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 [78] utilized a radioactive tracer (silver–110) which was vacuum sputtered onto the copper-beryllium alloy specimens. After the diffusion anneals, the specimens were analyzed using Gruzin's method [30]. Grain boundary diffusion coefficients were calculated using Fisher's analysis [83]. The calculations assumed a grain boundary width of approximately 10^{-6} cm and a volume diffusion coefficient of silver–110 in the copper-beryllium alloys of approximately 10^{-12} cm^2/s at 590 °C. The volume diffusion coefficient assumption was based on similar work in copper-antimony alloys [12]. All the diffusion studies were performed at 590 °C for 100 hours, although pre-diffusion heat treatments were different for each specimen. The results are given in table 14 and seem to indicate that a minor alloying addition of beryllium (of the order of 0.1 wt%) accelerates the grain boundary diffusion of silver in copper. Special note should be taken that results are based upon a "less-than rigorous" calculation.

TABLE 14. Silver grain boundary diffusion coefficients in a Cu-Be (0.1%)[a] alloy at 590 °C [78]

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}

[a] Author did not specify atomic or weight percent.

2.8. Cu-Ag-Cd

The effects of small amounts of cadmium on the aging process in copper-silver solid solutions in the temperature range 300–700 °C has been studied [119]. Although the significance of diffusion in the aging process is made apparent, no diffusion data is measured.

2.9. Cu-Ag-Cr

Measurements [15, 16] of the tracer, grain boundary and interdiffusion of silver in a dilute copper-chromium (0.8 wt%) alloy are reported in the sections on Ag* → Cu, chemical interdiffusion in Cu-Ag, and grain boundary diffusion in the copper-silver system, respectively.

2.10. Cu-Ag-Fe

Arkharov et al. [79] qualitatively followed the interdiffusion processes occurring between silver and polycrystalline copper-iron alloys (0.001 to 0.04 wt% iron) at 500 °C. The silver penetration was primarily through the grain boundaries rather than through the lattice. Varying iron concentrations caused no substantial changes in the rate of interdiffusion of the silver. The addition of antimony and/or beryllium to the copper-iron alloys and their effects or the interdiffusion process were also observed.

Arkharov and co-workers [80] also examined the interdiffusion occurring between silver and copper-bearing steels at 900 °C. Metallographic examination revealed little or no preferential diffusion of silver in the grain boundaries of the steels.

2.11. Cu-Ag-O

The diffusion of silver impurities in cuprous oxide (Cu_2O) has been the subject of several studies by Andrievskii and co-workers [84–87]. Their most recent study [84] was an experimental investigation into the diffusion of radioactive silver-110 in cuprous oxide in the temperature range 700 to 1050 °C. The cuprous oxide was prepared by the oxidation of metallic copper in air at a temperature of 1030 °C, the technique yielding single crystals of Cu_2O [87]. After the electrolytically-deposited silver-110 was diffused into the Cu_2O, the amount of penetration was determined by grinding and counting the radioactivity in the bulk specimen. The results are plotted in figure 14 as function of the reciprocal absolute temperature.

The temperature dependence of the lattice diffusion of radioactive silver-110 in single crystals of Cu_2O can be expressed as:

$$D^*_{Ag\rightarrow Cu_2O} = 0.6\times10^{-2}\exp\left(-27{,}630\ \mathrm{cal\cdot mol^{-1}}/RT\right)\ \mathrm{cm^2}/s.$$

The tracer diffusion coefficient of silver-110 impurities into large-grained polycrystals of cuprous oxide did not possess the same simple temperature dependence (see figure 15). The temperature dependence of the tracer diffusion coefficient in the polycrystalline oxide can be written as the sum of two exponential functions,

$$D^*_{Ag\rightarrow Cu_2O} = (0.56\times10^{-2})\exp(-28{,}270\ \mathrm{cal\cdot mol^{-1}}/RT)\ \mathrm{cm^2/s} + (0.24\times10^{-4})\exp(-14{,}080\ \mathrm{cal\cdot mol^{-1}}/RT)\ \mathrm{cm^2/s},$$

the first term referring to the high-temperature region, the second term to the low-temperature region.

The authors also studied the diffusion of the silver-110 tracer in copper oxide during the growth of the latter at temperatures of 950, 1000, and 1050 °C. The oxidation

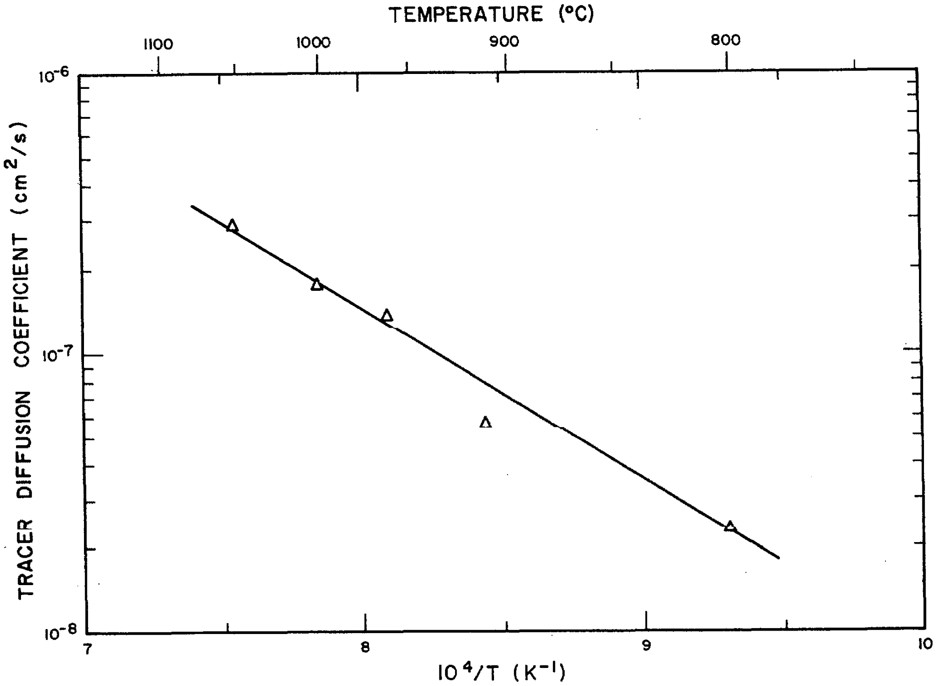

FIGURE 14. The tracer diffusion coefficients of silver-110 into single crystals of Cu_2O as a function of reciprocal absolute temperature.

Data from Andrievskii et al. [84].

process resulted in the formation of Cu_2O and the silver tracer diffusion coefficients ranged in value from 0.808×10^{-8} cm²/s at 950 °C to 1.60×10^{-8} cm²/s at 1050 °C. The activation energy determined for the process was 41,600 cal·mol⁻¹. The penetration curves revealed that the silver-110 diffused from the surface of the copper through the oxide layer with the maximum silver concentration near the outer surface of the Cu_2O layer.

It is hard to assess the reliability of these measurements in view of the difficulty in producing a single-phase homogeneous layer of Cu_2O on the copper metal. There is a strong possibility that the layer of scale produced consisted of several oxide phases with the lowest oxidation state located next to the metal and the highest oxidation state in equilibrium with the oxidizing atmosphere. The oxide layer on the copper probably does consist primarily of Cu_2O with only a very thin exterior layer of CuO. What effect all this (plus the other usual problems which plague diffusion studies in oxides) has on the silver-110 diffusion rate was not made apparent by the authors.

The internal oxidation of copper-silver alloys has been studied by both Combe-Brun et al. [88] and Podgurski and Davis [89], the investigations directed towards determining the atom ratio of oxygen to copper.

The process of oxygen absorption in the liquid copper-silver alloy system was found to be controlled by the diffusion of oxygen in the bulk of the metal [90]. Relative to pure molten copper, the alloying addition of 5 at. percent silver increased the oxygen diffusion rate by a factor of three.

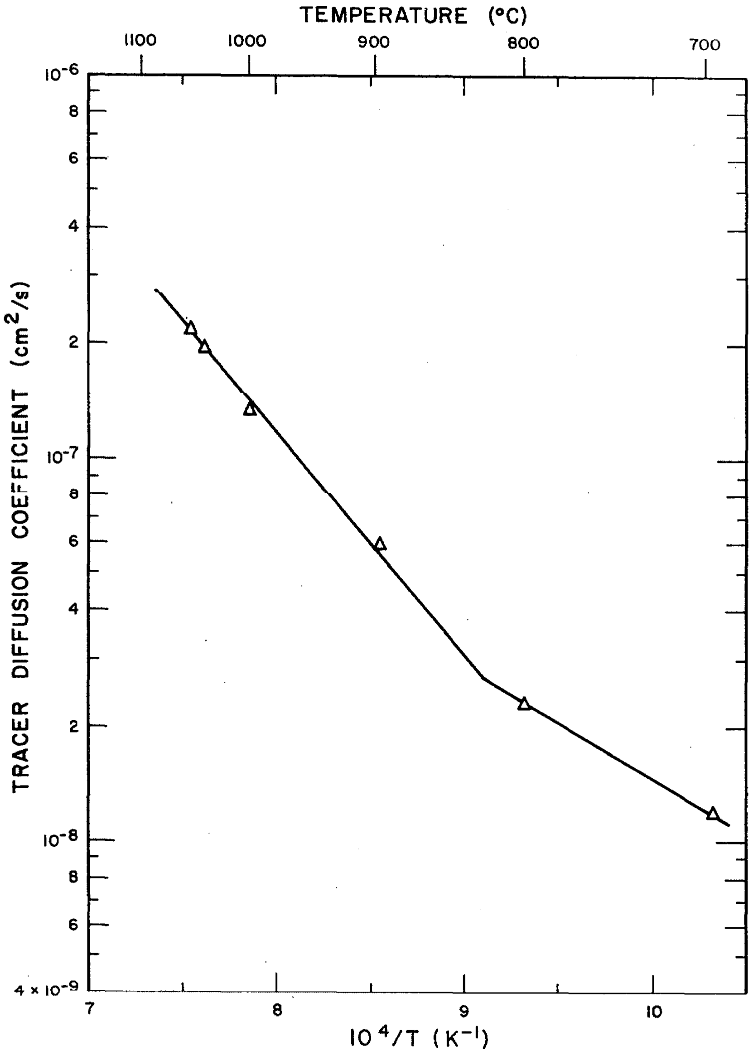

FIGURE 15. The tracer diffusion coefficient of silver-110 into polycrystalline Cu_2O as a function of reciprocal absolute temperature.

Data from Andrievskii et al. [84].

2.12. Cu-Ag-S

The interdiffusion of copper in silver sulfide (Ag_2S) has been studied by Braune and Kahn [91] and Tubandt and co-workers [92, 93]. Their results are listed in table 15 and plotted in figure 16. Braune and Kahn [91] arrived at the following expression for an average interdiffusion coefficient for copper in Ag_2S:

$$\tilde{D}^{\text{avg.}}_{\text{Cu}} = (1.2\times10^{-4}) \exp\,(-3160\ \text{cal}\cdot\text{mol}^{-1}/RT)\ \text{cm}^2/\text{s},$$

where T is expressed in kelvin.

Boltaks [94], using the above data, arrived at the following Arrhenius expression for what he terms a "copper impurity diffusion coefficient" in Ag_2S:

$$D^{\text{impurity}}_{\text{Cu}} = (4.6\times10^{-4}) \exp\,(-3250\ \text{cal}\cdot\text{mol}^{-1}/RT)\ \text{cm}^2/\text{s}.$$

TABLE 15. Average copper interdiffusion coefficients in Ag_2S [91–93]

T(°C)	Average $\tilde{D}_{\text{Cu}}$ (cm²/s)	Reference
713	$^a2.32\times10^{-5}$	Braune et al.
535	$^a1.67\times10^{-5}$	Braune et al.
420	1.64×10^{-5}	Tubandt et al.
330	6.2×10^{-6}	Tubandt et al.
328	$^a7.87\times10^{-6}$	Braune et al.
230	4.1×10^{-6}	Tubandt et al.
220	$^a4.72\times10^{-6}$	Braune et al.
202	$^a4.14\times10^{-6}$	Braune et al.
190	3.2×10^{-6}	Tubandt et al.
170	3.9×10^{-7}	Tubandt et al.
150	1.9×10^{-8}	Tubandt et al.

[a] Braune's original values divided by four as suggested by Jost.

The same groups of investigators (and in the same published papers) [91–93] also measured the rate of

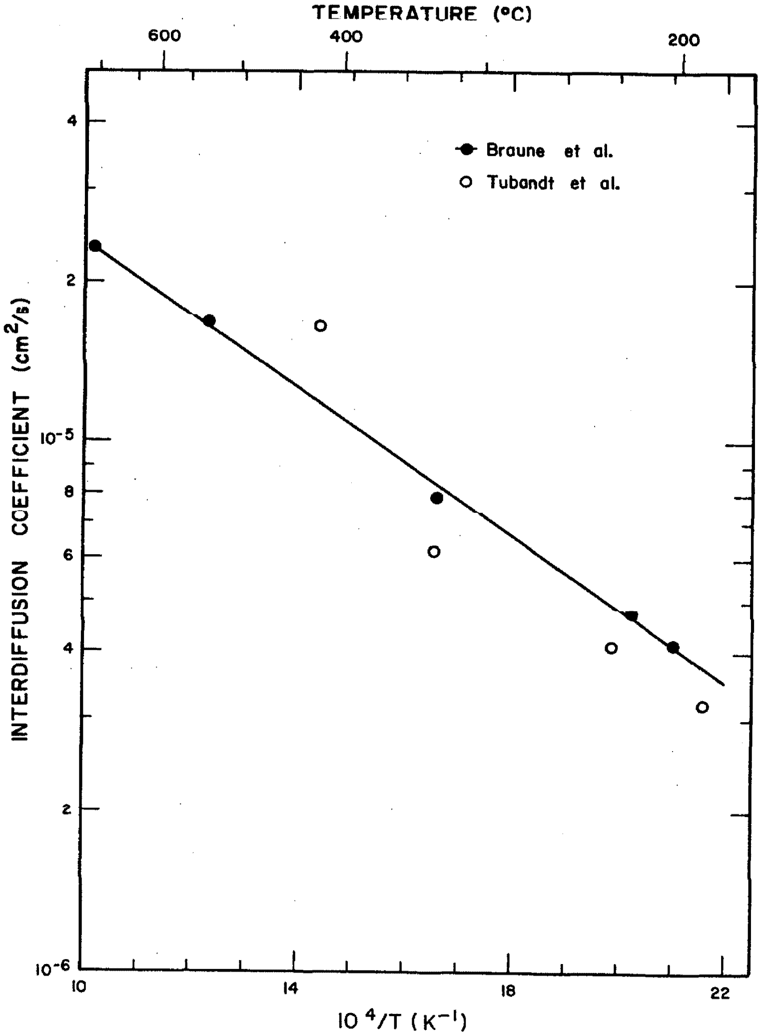

FIGURE 16. Average interdiffusion coefficients for the interdiffusion of copper in silver sulfide (Ag_2S) as a function of reciprocal absolute temperature.

Data taken from Braune and Kahn [91] and Tubandt et al. [92, 93].

interdiffusion of silver in Cu_2S (see table 16 and figure 17). From their data, Braune and Kahn [91] arrive at an expression for the average interdiffusion coefficient of silver in Cu_2S,

$$\tilde{D}_{Ag}^{avg.} = (3\times10^{-6})\ .\exp\ (-4550\,\mathrm{cal}\cdot\mathrm{mol}^{-1}/RT)\ \mathrm{cm}^2/\mathrm{s}.$$

Boltaks, [94] using the above data, obtains the following Arrhenius expression for the average interdiffusion coefficient:

$$\tilde{D}_{Ag}^{avg.} = (3\times10^{-6})\quad \exp\ (-4610\,\mathrm{cal}\cdot\mathrm{mol}^{-1}/RT)\ \mathrm{cm}^2/\mathrm{s}.$$

Wagner [95] has derived the equations needed for the calculation of the cation distribution in Cu_2S-Ag_2S solid solutions formed on copper-silver alloys.

TABLE 16. Average silver interdiffusion coefficients in Cu_2S [91–93]

T(°C)	Average $\tilde{D}_{Ag}$ (cm²/s)	Reference
919	$^a4.65\times10^{-5}$	Braune et al.
713	$^a3.25\times10^{-5}$	Braune et al.
550	$^a2.3\ \times10^{-5}$	Braune et al.
420	9.43×10^{-6}	Tubandt et al.
330	4.65×10^{-6}	Tubandt et al.
315	$^a7.10\times10^{-6}$	Braune et al.
230	1.86×10^{-6}	Tubandt et al.
223	$^a3.15\times10^{-6}$	Braune et al.

[a] Braune's original values divided by four as suggested by Jost.

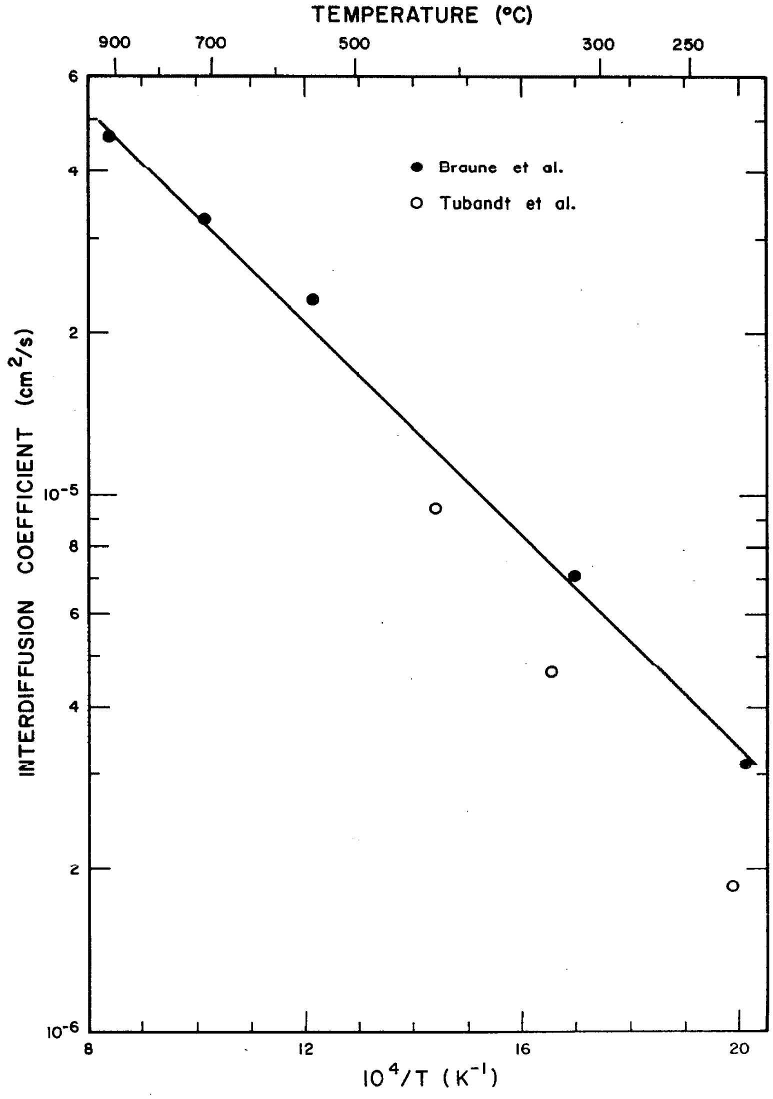

FIGURE 17. Average interdiffusion coefficients for the interdiffusion of silver in copper sulfide (Cu_2S) as a function of reciprocal absolute temperature.

Data from Braune and Kahn [91] and Tubandt et al. [92, 93].

2.13. Cu-Ag-Sb

In early interdiffusion studies [49, 120], both the volume and grain boundary diffusion of silver in copper-antimony alloys was enhanced with increasing antimony content in the alloy. In these experiments, polycrystalline silver wires were inserted into the core of the copper-antimony specimens to form the interdiffusion couples. The copper-antimony alloys contained from 0.003 to 4.72 wt percent antimony and were of varying grain size. The diffusion anneals took place at 630 to 700 °C, ranging in time from 69 to 101 hours. After quenching, the microstructure and width of the interdiffusion zones were examined micrometallographically. From their observations the authors concluded that the mobility of silver within the copper-antimony alloys increased with increasing percentage of antimony as well as with decreasing grain size. Interdiffusion zone widths were found to increase correspondingly. In those experiments utilizing high antimony contents ($\sim$4.7 wt %), it was found that the grain boundary diffusion contributions of silver dropped off due to increased volume diffusion.

2.14. Cu-Ag-Se

Diffusion studies in this ternary system have been limited to the compounds Ag_2Se, Cu_2Se.

Reinhold and Seidel [96] made e.m.f. measurements on cells constructed of $Cu_xAgSe|Cu_xSe$ and thus were able to study the diffusion of silver ions in these cells. The silver content was kept constant while the copper and selenium compositions were varied. Jost [97] summarizes their results in table 17.

TABLE 17. Silver interdiffusion coefficients in copper-selenium alloys [96]

Couple configuration	$\tilde{D}(10^{-6}\ cm^2/s)$		
	165 °C	198 °C	272 °C
$Cu_{1.77}Ag_{0.05}Se/Cu_{1.77}Se$	0.4	0.7	1.6
$Cu_{1.89}Ag_{0.05}Se/Cu_{1.89}Se$	1.6	2	3.6
$Cu_{1.95}Ag_{0.05}Se/Cu_{1.95}Se$	1.1	1.3	4.4

Barrer [98] summarized the data from a number of sources [99–101] before 1940 and concluded that the diffusion of copper in the α-modification of Ag_2Se could be expressed as:

$$D = D_0 \exp(-Q/RT)$$
$$= 15.5\times 10^{-5} \exp(-2940\ \mathrm{cal\cdot mol^{-1}}/RT)\ \mathrm{cm^2/s}.$$

A recent estimate [103] of the impurity diffusion coefficient of copper in polycrystalline Ag_2Se placed the room temperature value at 4.7×10^{-8} cm^2/s. The experiments were restricted to room temperatures. The source of the copper was a $Cu|Ag_2Se$ soldered junction. The primary purpose of the investigation was to study contact resistance but sufficient data were obtained from the measurement of the rate of change of the resistivity profile of a partially copper-plated ingot of the semiconductor material to permit the calculation of a diffusion coefficient. The method used for the measurement is the same method widely used to study contact resistances of metal-semiconductor junctions [104, 105]. In relating the measured potential profile to the copper concentration, it is necessary to assume that the diffusion coefficient and electron mobility are constant over the concentration range in question. This may not always be true although the diffusion coefficient arrived at is not an unreasonable value.

The diffusion of silver into thin films of $Cu_{1.8}Se$ was observed in an electron microscope, the silver diffusing as a positive ion [102].

2.15. Cu-Ag-Te

The tracer diffusion coefficient of silver-110 in copper-tellurium (0.6 wt.% tellurium) alloys has been reported [15]. The radioactive tracer was electrodeposited onto oxygen-free, high conductivity copper and then diffused at temperatures from approximately 700 to 1000 °C. After annealing, the silver penetration was determined by using Gruzin's residual activity method of analysis [29]. The diffusion coefficients obtained from the data are shown in figure 18. Also plotted in the same figure are the silver tracer diffusion coefficients in unalloyed OFHC copper. According to the authors, the tellurium additions resulted in a smaller grain size in the specimens, thus increasing the amount of grain-boundary diffusion taking place. Because of this increased grain boundary contribution, the "apparent" volume diffusion coefficient is somewhat larger than the "true" value.

In the same paper [15], the grain-boundary diffusion of the silver-110 tracer is determined for the same copper-tellurium alloy. Using Suzuoka's method [106], the grain-boundary diffusion coefficients can be expressed by the relation:

$$D_{gb}\cdot\delta\ (\mathrm{cm^3/s}) = 1.10\times 10^{-6}$$
$$\exp(-27{,}000\ \mathrm{cal\cdot mol^{-1}}/RT)\ \mathrm{cm^3/s}.$$

where δ is the thickness of the grain boundary. The specimen grain size was of the order of 100 μm, but not over 250 μm. To compare the results to those determinations in unalloyed copper, the grain-boundary diffusion coefficients are plotted as a function of $1/T$ for both cases in figure 19. It is obvious that tellurium additions result in not only a larger activation energy but also a larger pre-exponential for the grain-boundary diffusion of silver in copper.

Barrer [98] collects the data of several publications [99–101] and gives the following expressions for the impurity diffusion of copper and silver in the compounds Ag_2Te and Cu_2Te respectively:

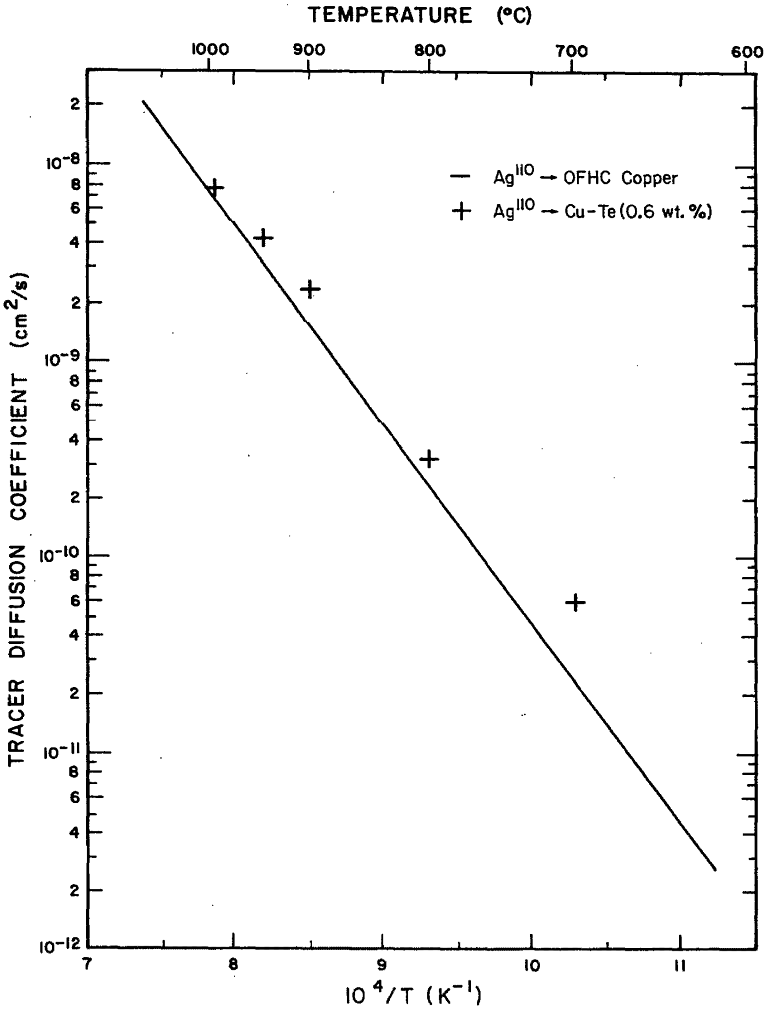

FIGURE 18. Tracer diffusion coefficients of silver-110 in copper (OFHC) and a copper-tellurium alloy (0.6 wt % Te) as a function of reciprocal absolute temperature.

Data taken from Barreau et al. [15].

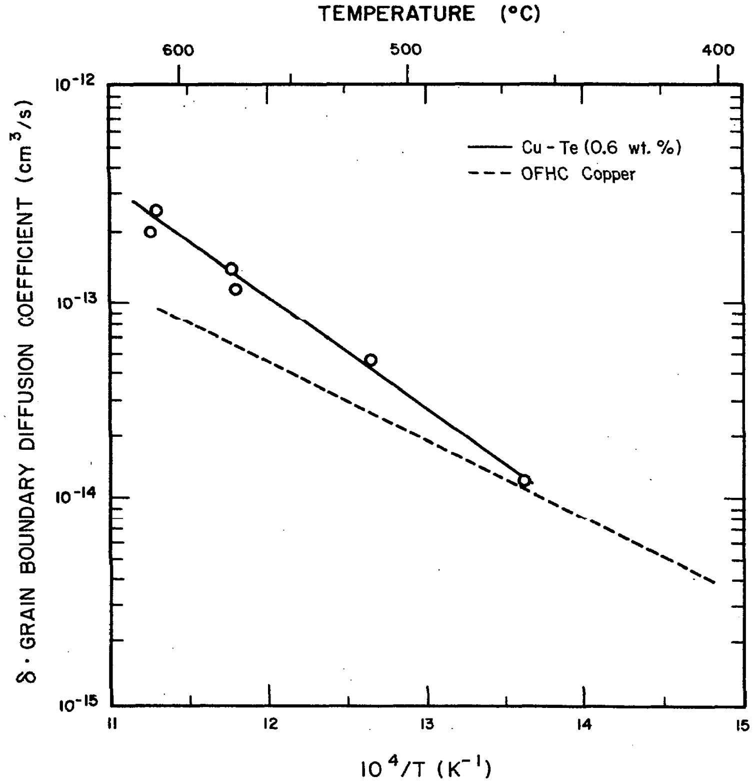

FIGURE 19. The product of the grain boundary diffusion coefficient of silver-110 in a copper-tellurium alloy times the grain boundary thickness as a function of reciprocal absolute temperature.

The copper-tellurium alloy contains 0.6 wt % Te and had a grain size of ~ 100 μm (but not more than 250 μm). For comparison, the same determinations made in unalloyed copper are also shown. Data taken from Barreau et al. [15].

$$D_{\mathrm{Cu}\rightarrow \mathrm{Ag_2Te}}=3.85\times 10^{-5}\exp(-2{,}660\ \mathrm{cal\cdot mol^{-1}}/RT)\ \mathrm{cm^2/s},$$

$$D_{\mathrm{Ag}\rightarrow \mathrm{Cu_2Te}}=2.4\exp(20{,}860\ \mathrm{cal\cdot mol^{-1}}/RT)\ \mathrm{cm^2/s}.$$

2.16. Cu-Ag-Ti

The effect of titanium impurities on the tracer and grain boundary diffusion of silver in copper (see Barreau et al. [15, 16]) is discussed in the sections on Ag* → Cu and grain boundary diffusion.

2.17. Cu-Ag-Zn

The tracer diffusion coefficient of silver in the disordered as well as the ordered phase CuZn has been reported by Camagni and co-workers [108, 109]. Radioactive silver–110 was electrolytically deposited onto the polycrystalline β-brass (47.2 at. % zinc) specimens, diffused at temperatures in the range 320 to 700 °C, and the silver penetration determined by sectioning. The calculated values of the tracer diffusion coefficients are plotted as a function of the reciprocal absolute temperature in figure 20.

In the disordered region (above the transition temperature ≈ 468 °C) a straight line can be drawn through the data points and an Arrhenius relationship established. From a least-squares fit of the data in the disordered region, the following expression is obtained for the silver tracer diffusion coefficient:

$$D^*_{\mathrm{Ag}}=0.014\exp(-21.90\ \mathrm{kcal\cdot mol^{-1}}/RT)\ \mathrm{cm^2/s}.$$

At the transition temperature and below, in the ordered region, the plot has a finite curvature although at lower temperatures a straight line could be fitted to the data.

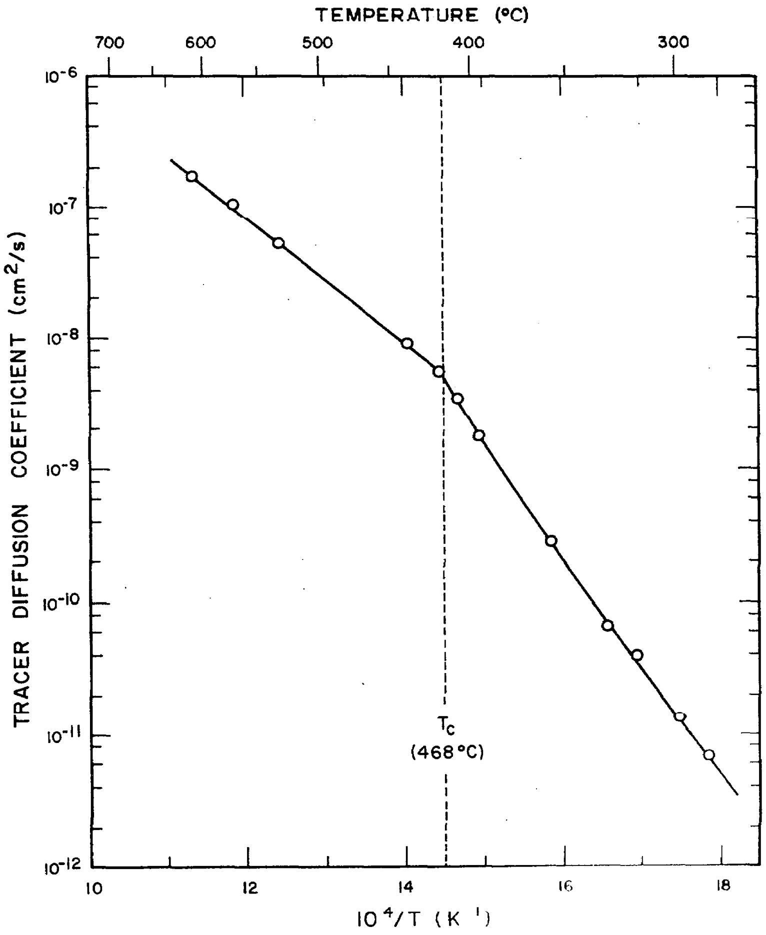

FIGURE 20. Tracer diffusion coefficients of silver-110 in ordered and disordered polycrystalline β-bass (47.2 at. % Zn) as a function of reciprocal absolute temperature.

Data taken from Camagni and co-workers [108, 109].

2.18. Cu-Ag-Zr

Barreau and co-workers [15, 16] have measured the diffusion of silver (tracer, grain boundary, and interdiffusion coefficients) in a dilute copper-zirconium (0.12 wt%) alloy. These results are included in the discussion dealing with Ag*→ Cu, chemical interdiffusion, and grain boundary diffusion in copper-silver alloys.

2.19. Cu-Ag-X

Interdiffusion occurring between electrodeposited coatings of silver, gold, tin, and lead on a copper substrate in the temperature range 23 to 212 °C has been studied by Creydt [110] and Creydt and Fichter [111]. Diffusion anneals of up to 11,500 hours were employed, resulting in the formation of the phases $AuSn_2$, $AuSn_4$, Ag_3Sn, Cu_5AuSn_5, $Cu_3Au_3Sn_5$, $Cu_4Au_2Sn_5$, Cu_3Sn, and Ag_3Sn in the interdiffusion zone.

Interdiffusion processes occurring during the brazing of rhenium-coated titanium with copper-silver braze alloys have been followed by recording the changes in microhardness and microstructure [112]. The interdiffusion zone was found to contain an assortment of phases after brazing in the temperature region 740 to 850 °C for 15 to 30 minutes. No calculations were made with the data.

Modjeska and Kann [113] electroplated a variety of metals onto copper alloys (phosphor bronzes) and diffusion annealed them for short times at 371 and 538 °C, noting in a qualitative manner the interdiffusion which took place.

2.20. Grain Boundary Diffusion

The grain boundary diffusion of silver in copper has been subjected to much investigation [9, 12, 15, 16, 19, 20, 114–125]. Although Berman and Harrington [123] had shown qualitatively for this system that silver diffuses into copper more rapidly in the grain boundaries than in the adjoining grains, it was the studies of Smoluchowski and co-workers [114–118, 126, 127] which resulted in the first direct experimental evidence for such. In fact, it was these pioneering investigations in the copper-silver system which revealed for the first time the variation of grain boundary diffusion rates with relative grain orientation. Achter and Smoluchowski [114–116, 126] and Couling and Smoluchowski [118, 127] in their experiments measured the rate of diffusion of silver between grains of copper having a common cube direction. For small misorientations the silver grain boundary penetration was not distinguishable from lattice diffusion, but at ≃ 20° misorientation it increased rapidly, reaching a maximum value at 45°. For higher angles, the silver grain boundary penetration decreased again to indistinguishable values. Their results reveal not only a dependence of the silver grain boundary coefficient upon the orientation of the copper grains but also, for fixed orientation, upon the direction within the grain boundary, i.e. an anisotropy of silver grain boundary diffusion. Figures 21, 22, and 23 summarize the results of their measurements. Smoluchowski has variously estimated the activation energy for the grain boundary diffusion of silver in copper as being about 23.8 kcal · mol^{-1} [115, 126, 128] (or of the order of one-

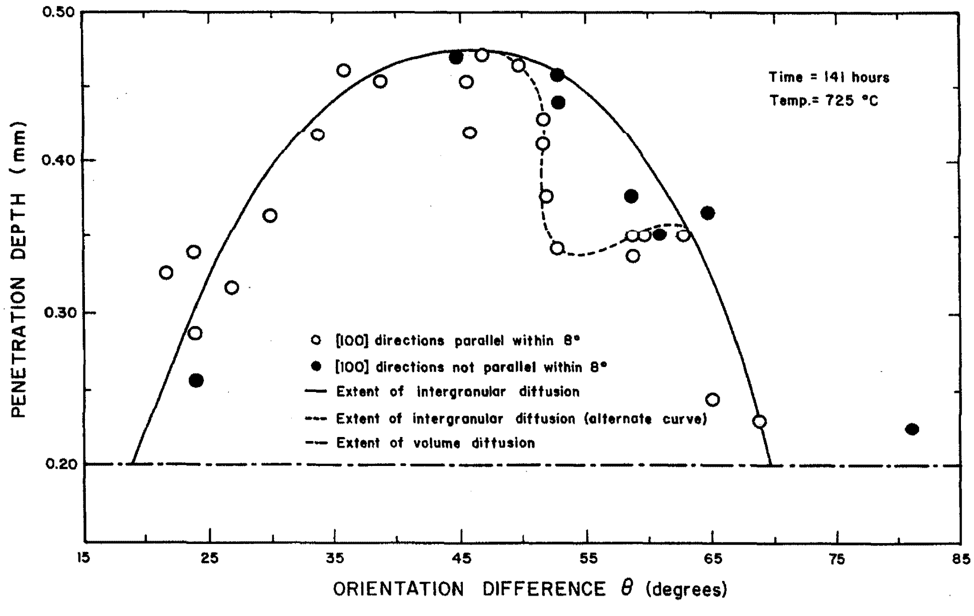

FIGURE 21. Grain boundary penetration of silver as a function of orientation difference (θ) of two columnar grains of copper after 141 hours of diffusion annealing at 725 °C.

The relative orientation of the two grains flanking the boundary is given by the angle θ between a pair of cube axes normal to the columnar direction. From the data of Achter and Smoluchowski [114].

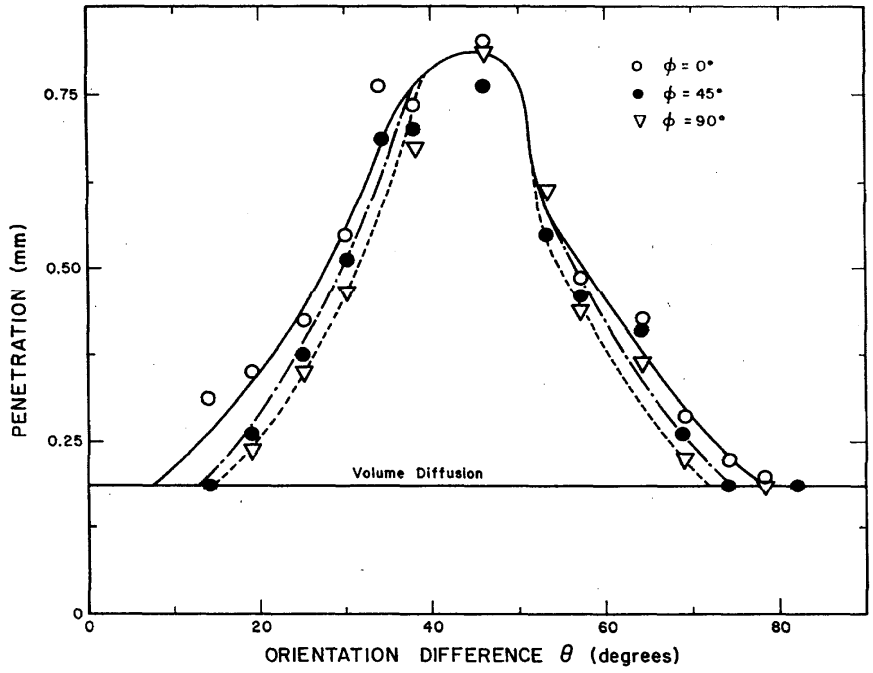

FIGURE 22. Grain boundary penetration of silver in copper as a function of orientation difference (θ) measured for three different values of ϕ (where ϕ is the orientation of specimens with respect to the common [100] direction and the plane of the grain boundary).

ϕ=0° corresponds to diffusion in the columnar direction. From the data of Couling and Smoluchowski [118].

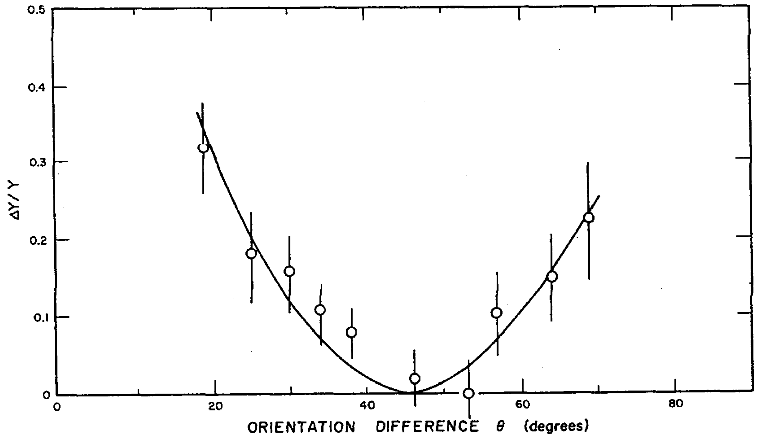

FIGURE 23. Relative grain boundary diffusion anisotropy, defined as $\frac{\Delta\gamma}{\gamma}=\frac{\gamma(0°)-\gamma(90°)}{\gamma(0°)}$ where γ= penetration depth, as a function of orientation difference (θ).

Bicrystals with a common [100] axis but with different θ values were used. For every θ value, the silver penetration was determined parallel, perpendicular, and at 45° to the boundary axis. From the data of Couling and Smoluchowski [118].

half that known for lattice diffusion at the time of his studies). Dawson's [129] criticisms of Smoluchowski's grain boundary investigations are unfounded in view of later results [117, 130].

Arkharov and co-workers [9, 12, 49, 119, 120, 125] investigated the rate of silver diffusion in the grain boundaries of copper, restricting themselves to the single temperature of 650 °C. Using radioactive silver and Gruzin's experimental technique [29, 30], and by applying Fisher's theoretical analysis [83] to the data, silver grain boundary diffusion coefficients of the order of 10^{-8} cm^2/s were obtained.

TABLE 18. Average grain boundary diffusion coefficients of silver in copper and Cu-Ag (0.1 at.%) [20]

T(°C)	D_{gb} (cm^2/s)	
	Copper	Cu-Ag (0.1 at.%)
450	1.7×10^{-11}	1.4×10^{-11}
400	9.0×10^{-12}	4.5×10^{-12}
350	2.7×10^{-12}	1.4×10^{-12}
300	7.1×10^{-13}	5.7×10^{-13}
250	1.6×10^{-13}	1.4×10^{-13}

Gertsriken and Revo [20] measured the rate of penetration of radioactive silver in the grain boundaries of pure copper and a dilute copper-silver alloy making their measurements in the temperature range 250 to 450 °C. Similarly, they employed Gruzin's experimental technique, but applied Gertsriken's analysis [131] in their calculations of the silver grain boundary diffusion coefficients. Their results for pure copper and a copper-silver alloy are listed in table 18. The average values of the coefficients are plotted in figure 24. A straight line, when drawn through these points yields the following temperature dependence in the temperature range 250 to 450 °C:

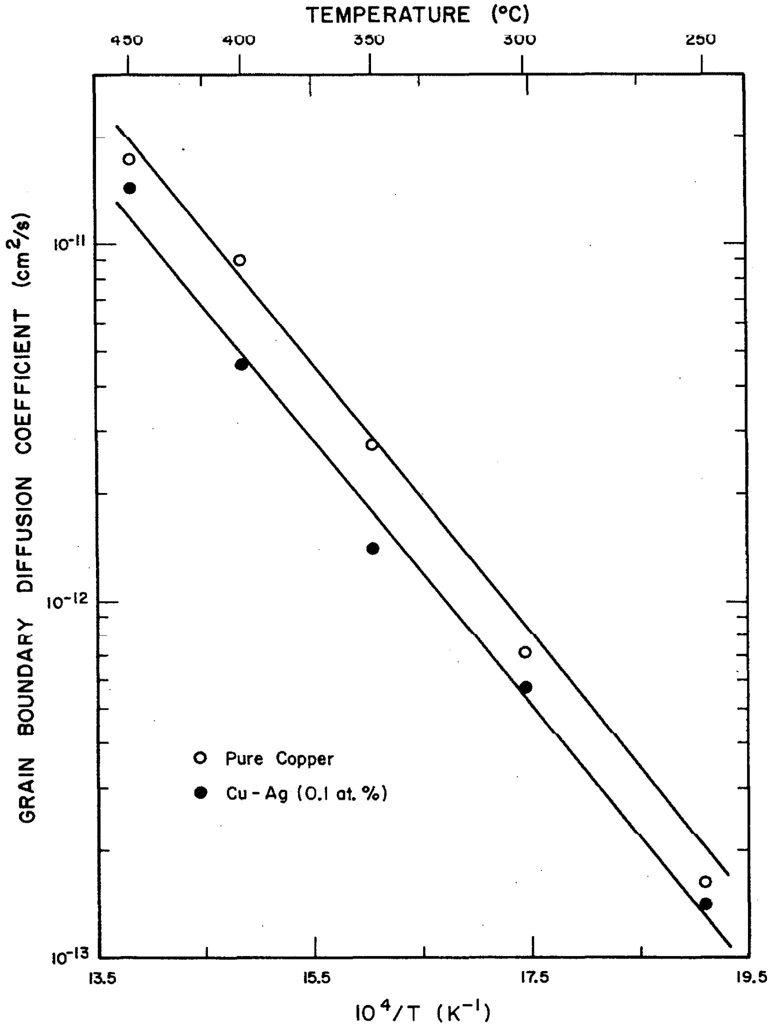

FIGURE 24. Average grain boundary diffusion coefficients of silver in pure copper and a copper-silver alloy (0.1 at. % Ag) as a function of reciprocal absolute temperature.

Data of Gertsriken and Revo [20].

For silver diffusing along grain boundaries in pure copper,

$$D_{gb}^{avg.} = 3.1 \times 10^{-6} \exp\,(-17{,}200 \pm 500 \text{ cal} \cdot \text{mol}^{-1}/RT) \text{ cm}^2/\text{s}.$$

For silver diffusing along the grain boundaries of a copper-silver (0.1 at. %) alloy,

$$D_{gb}^{avg.} = 1.7 \times 10^{-6} \exp\,(-17{,}050 \pm 500 \text{ cal} \cdot \text{mol}^{-1}/RT) \text{ cm}^2/\text{s}.$$

Romashkin and Shestopalov [124] claimed to have measured equivalent activation energies for the grain boundary diffusion of silver in copper.

TABLE 19. Value of the product $D_{gb} \cdot \delta$ from silver-110 grain boundary diffusion in OFHC copper [16]

T(°C)	$D_{gb} \cdot \delta$(cm^3/s)	
	Fisher's analysis	Suzuoka's analysis
618	2.31×10^{-14}	6.63×10^{-14}
573	1.93×10^{-14}	6.36×10^{-14}
560	1.33×10^{-14}	3.89×10^{-14}
525	1.08×10^{-14}	2.94×10^{-14}
475	3.68×10^{-15}	1.19×10^{-14}
456	2.75×10^{-15}	9.29×10^{-15}
398	9.7×10^{-16}	3.02×10^{-15}

δ = mean grain boundary thickness.

Most recently, a detailed investigation of the grain boundary diffusion of silver in copper has been reported by Barreau et al. [15, 16]. Electrolytically-deposited radioactive silver-110 was diffused into pure copper (O.F.H.C., with impurities × 10^{-6}: P < 3, S < 10, Zn < 3, Mg < 1, Pb < 10, Cd < 2, Se < 10, Bi ≦ 10, Te ≦ 10, O ≦ 10) whose grain size was ≧ 250 μm. The temperature range of the study extended from 398 to 618 °C. Silver-110 penetration was determined through use of Gruzin's technique of measuring residual activity [29, 30] as modified by Seibel [31, 132–134]. Grain boundary diffusion coefficients were calculated with the aid of Fisher's [83] and Suzuoka's [106] analysis and are listed in table 19. When the coefficients are plotted as a function of reciprocal absolute temperature (see figure 25), straight lines can be fitted to the results from both

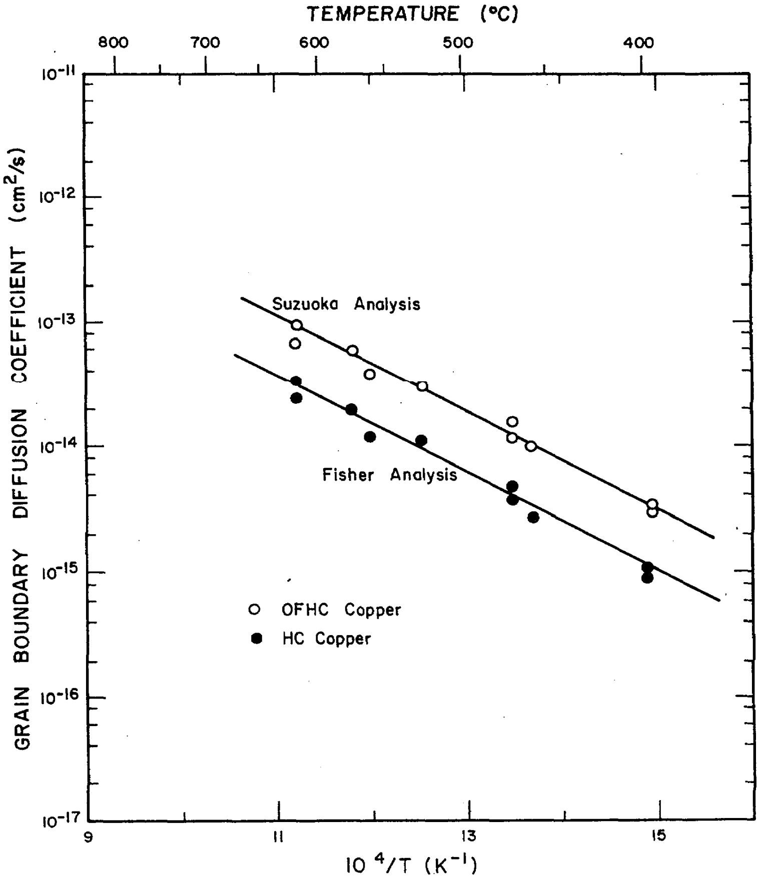

FIGURE 25. Grain boundary diffusion coefficients of silver-110 in relatively pure copper (OFHC and HC) as a function of reciprocal absolute temperature.

Data of Barreau et al. [15, 16].

analyses. The temperature-dependence of the silver-110 grain boundary diffusion coefficient derived from Suzuoka's analysis can be expressed as:

$$D_{gb} \cdot \delta = 2.3 \times 10^{-9} \exp(-18{,}000 \text{ cal} \cdot \text{mol}^{-1}/RT) \text{ cm}^3/\text{s},$$

and from Fisher's method,

$$D_{gb} \cdot \delta = 7.1 \times 10^{-10} \exp(-18{,}000 \text{ cal} \cdot \text{mol}^{-1}/RT) \text{ cm}^3/\text{s},$$

where δ is the mean grain boundary thickness. Suzuoka's method of calculation yields grain boundary diffusion coefficients which are approximately three times larger than those derived from Fisher's analysis at comparable temperatures.

Barreau et al. [16] found that the addition of metallic impurities (0.8 wt. % chromium, 0.6 wt. % tellurium, 0.1 wt. % titanium, and 0.12 wt. % zirconium) to the pure copper caused a change in the grain boundary behavior of the diffusing silver-110 (see figure 26 and table 20). The temperature dependence of silver grain boundary diffusion in these alloys (as determined from Suzuoka's analysis [106]) can be expressed by the following relations:

$$\delta \cdot D^{gb}_{Ag \to CuTe} = 1.1 \times 10^{-6} \exp(-27 \text{ kcal} \cdot \text{mol}^{-1}/RT) \text{ cm}^3/\text{s},$$

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

$$\delta \cdot D^{gb}_{Ag \to CuZr} = 9.61 \times 10^{-7} \exp(-31 \text{ kcal} \cdot \text{mol}^{-1}/RT) \text{ cm}^3/\text{s}.$$

Because of the scatter in the data, no expression was calculated for the copper-chromium (0.8 wt%) alloy.

In contrast to the above-mentioned investigations in

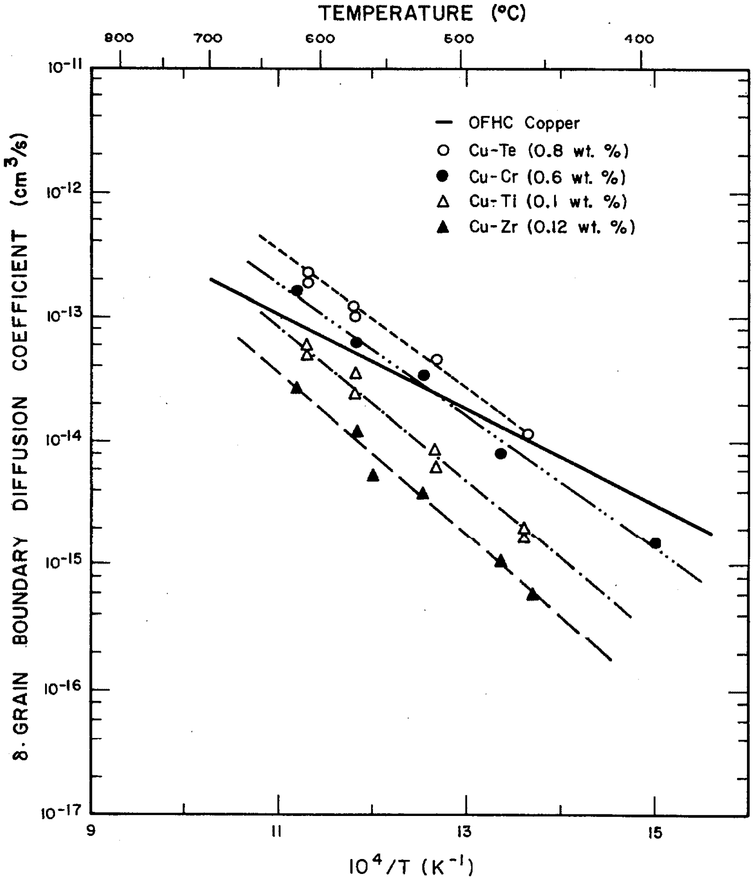

FIGURE 26. The product [$\delta \cdot D_{gb}$] (where δ is the mean grain boundary thickness and D_{gb} is the grain boundary diffusion coefficient of silver) as a function of reciprocal absolute temperature for silver diffusion in the grain boundary of pure (OFHC) copper, and some dilute copper alloys of (Cu-Cr, Cu-Te, Cu-Ti, and Cu-Zr).

Data taken from Barreau et al. [16].

TABLE 20. Value of the product $D_{gb} \cdot \delta$ from silver-110 grain boundary diffusion in copper containing dilute alloy additions using Suzuoka's analysis [106]

T(°C)	$D_{gb} \cdot \delta$(cm³/s)			
	Cu-Cr(0.8 wt %)	Cu-Te(0.6 wt %)	Cu-Ti(0.1 wt %)	Cu-Zr(0.12 wt %)
618	1.61×10^{-13}			2.71×10^{-14}
611		2.10×10^{-13}	5.60×10^{-14}	
578		1.20×10^{-13}	2.95×10^{-14}	
573	6.65×10^{-14}			1.19×10^{-14}
525	3.6×10^{-14}			3.88×10^{-15}
517		4.75×10^{-14}	7.20×10^{-15}	
475	8.16×10^{-15}			1.00×10^{-15}
465		1.04×10^{-14}	1.80×10^{-15}	
456				5.82×10^{-16}

δ = mean grain boundary thickness.

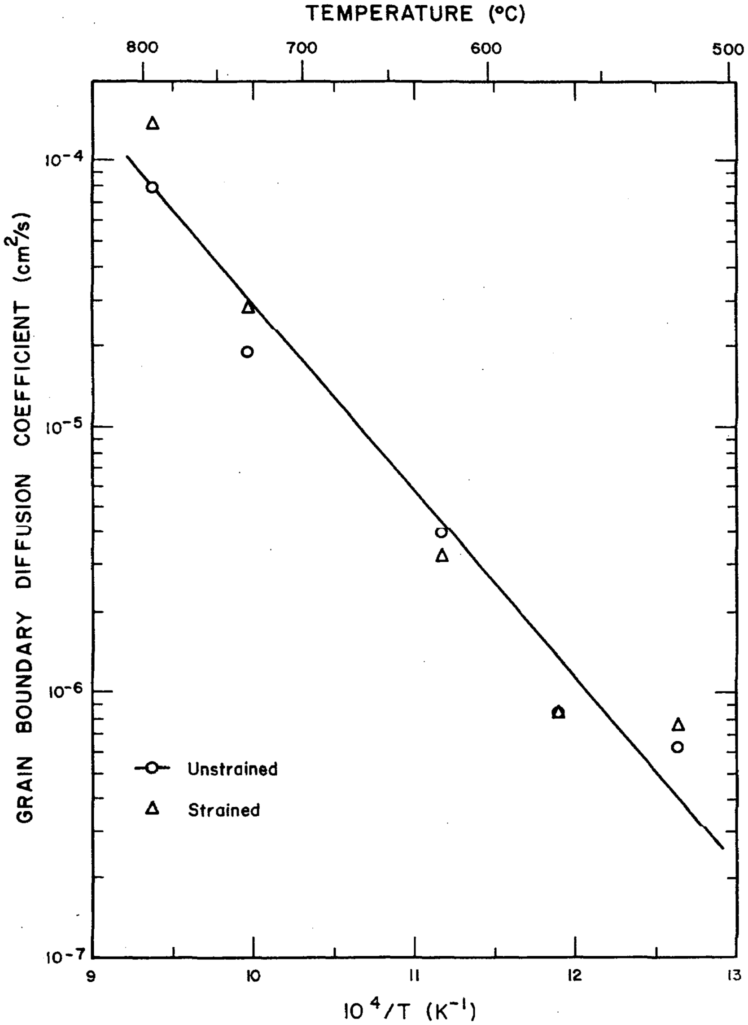

FIGURE 27. Grain boundary diffusion coefficients of silver in static and moving grain boundaries of copper as a function of reciprocal absolute temperature.

Data taken from Blackburn and Brown [122, 135].

TABLE 21. Silver-110 grain boundary diffusion coefficients in static and moving grain boundaries of copper [a] [122]

T(°C)	D_{gb}(cm^2/s)	
	Unstrained	Strained
794 ±0.5	$(7.9\pm2)\times10^{-5}$	$(1.4\pm0.7)\times10^{-4}$
731 ±0.7	$(1.9\pm0.2)\times10^{-5}$	$(2.8\pm0.2)\times10^{-5}$
623 ±1	$(4.0\pm0.6)\times10^{-6}$	$(3.2\pm0.3)\times10^{-6}$
623 ±1		$(1.6\pm0.1)\times10^{-6}$
567.5±0.5	$(8.4\pm0.5)\times10^{-7}$	$(8.4\pm0.7)\times10^{-7}$
517 ±0.5	$(6.4\pm0.3)\times10^{-7}$	$(7.6\pm0.6)\times10^{-7}$

[a] Grain boundary width taken as 7.6×10^{-8} cm.

static grain boundaries of copper are the diffusion studies of Blackburn and Brown [122, 135] in moving grain boundaries. They diffused radioactive silver-110 into single tilt boundaries in spectroscopically pure (~ 6 ppm impurity) copper bicrystals over the temperature range 517 to 794 °C. Penetration of silver-110 into static boundaries and boundaries sliding (being sheared along a common boundary) at rates of 0.05 to 3 μm/h was measured by autoradiography. It was found that the silver grain-boundary diffusion coefficient in sliding boundaries is slightly (30%) higher than in static boundaries of the same orientation. Table 21 and figure 27 summarizes all of their grain boundary diffusion data. No change in activation energy for the process was found, as is indicated in figure 27. The activation energy for the grain boundary diffusion of silver into maximum misorientation grain boundaries of copper was found to be 32,000±3,500 cal · mol^{-1}. This is considerably higher in value than any of the previously-mentioned investigations. The results obtained from low-angle boundaries are in agreement with Achter

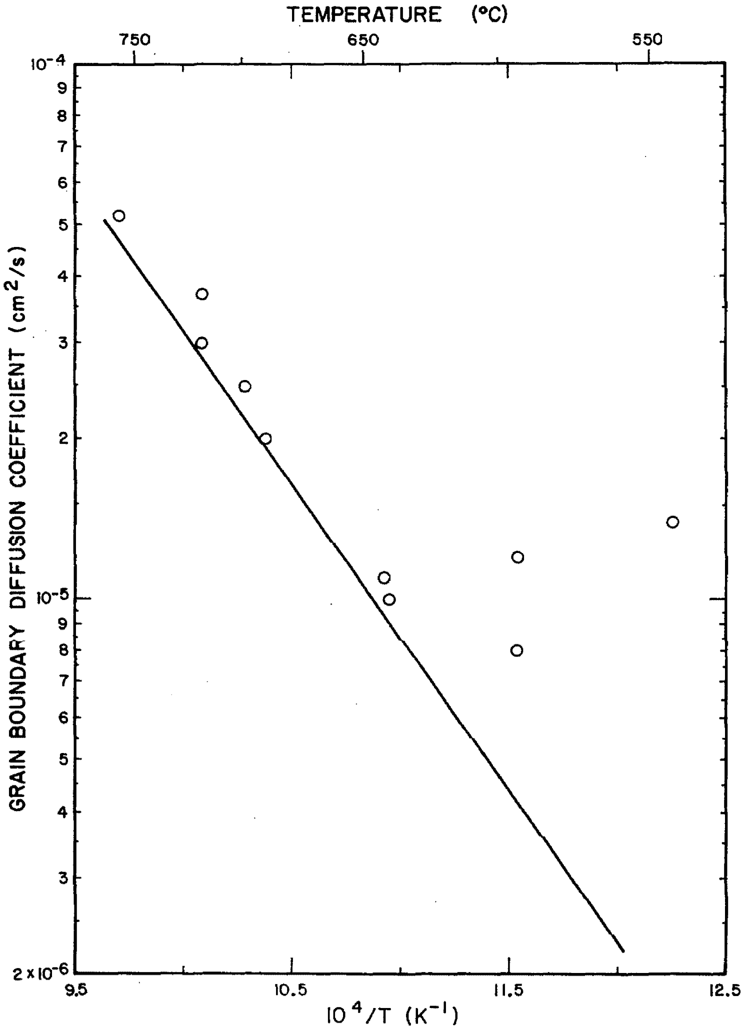

FIGURE 28. Grain boundary diffusion coefficients of silver-110 in the grain boundaries of copper bicrystals (misoriented at 45°) as a function of reciprocal absolute temperature.

Data of Renouf [19].

TABLE 22. Grain boundary diffusion coefficients of Ag-110 in the grain boundaries of copper bicrystals misoriented at 45 °C. After the data of Renouf [19].

T °C	D_{gb} (10^{-6} cm^2/s)
543	14 ±6 6.5±3
593	8 ±2 6.0±2
593	12 ±4 9.6±3
640	10 ±2
642	11 ±2
690	20 ±4
698	25 ±4
718	37 ±7
719	30 ±6
757	52 ±15

and Smoluchowski [114] who also found that the grain-boundary diffusivity of silver in low-angle boundaries was not measureably different in the chosen direction from the lattice diffusivity of the crystal.

Quantitative autoradiographic measurements by Renouf [19] in the temperature range 543 to 757 °C has yielded another set of data. His technique [18], employing copper bicrystals misoriented at 45 °C, was based on matching the experimental density distribution to a distribution that is computed from an assumed theoretical model. The results of the calculation (obtained from penetration depth measurements taking the mean grain boundary width to be 5×10^{-8} cm) are listed in table 22. An Arrhenius plot of the same data is shown in figure 28. An activation energy of 26 ± 2 kcal · mol^{-1} and a pre-exponential factor of 15^{+10}_{-3} cm^2/s is obtained from the straight line fitted to the data. The marked departure from linearity is apparent at the lower temperatures.

Unfortunately, agreement is not good among these investigations into the rate of grain boundary diffusion of silver in copper. The differences may, in part, be attributed to the large amount of scatter contained in the results obtained in the individual investigations. Additionally, exact comparisions are difficult in view of the differences not only in the experimental conditions but in the methods of interpretation. Until additional results are available confirming one or the other of the above mentioned determinations, the presently published values should be used with caution.

Grain boundary diffusion in an electric field is discussed in the subsequent section on electromigration in the copper-silver system. Diffusion along interphase boundaries is discussed in the preceding section on copper-silver-aluminum. Grain boundary diffusion also is mentioned in the section on Cu-Ag-Fe.

2.21. Surface Diffusion

The migration of copper on silver surfaces has been studied by Kehoe et al. [136] and Pines et al. [137]. In the experiments of Kehoe et al., copper was condensed onto a smooth (111) silver surface which had been formed by deposition on heated mica. The silver surface was maintained at a temperature near 270 °C during the copper deposition. After deposition, the copper atoms retained a certain mobility, moving over the silver surface. The authors, in a qualitative fashion, followed the epitaxial growth of the copper crystallites, noting migration distances of the order of 10 μm, with substrate temperatures of 270 °C. Pines and co-workers studied the kinetics of the surface diffusion on thin films ($\sim 10^{-6}$ cm thick) of silver. Using an electron-diffraction technique to make their measurements, they arrive at an "apparent surface diffusion coefficient" for copper flowing on and near the surface of the thin silver film. Because the mechanism involves a lattice component as well as a surface component, the corresponding total flux being measured is an "apparent surface diffusion coefficient" rather than a pure surface diffusion coefficient. The temperature dependence of this coefficient for copper on silver is shown in figure 29. In spite of the scatter, a straight line was fitted to the data, yielding an activation energy of approximately 14 kcal · mol^{-1} for the migration process.

Pines and co-workers [137], in a similar experimental manner, measured the migration of silver over a thin film of copper. The results, although similar (see figure 30), yield a somewhat higher activation energy (~ 20 kcal · mol^{-1}). Shpilevskii [138] and Kunin and Shpilevskii [139], also working with thin films of silver and copper, followed surface diffusion processes occurring in the temperature range 120 to 220 °C.

Roulet and co-workers [140–143] have employed a novel oxidation technique in order to follow small concentration changes of silver on singular and vicinal surfaces of copper. Determining these concentration profiles, silver surface diffusion coefficients were measured in the temperature range 250 to 500 °C on a number of planes. When plotted as a function of the reciprocal absolute temperature, activation energies and pre-exponential factors can be calculated. Table 23 contains a summary of their data.

In an early experiment, Frauenfelder [144] followed the diffusion of radioactive copper-64 on the surface of silver at 750 °C. His measurements yielded diffusion rates of the order of 10^{-5} to 10^{-6} cm^2/s at this temperature.

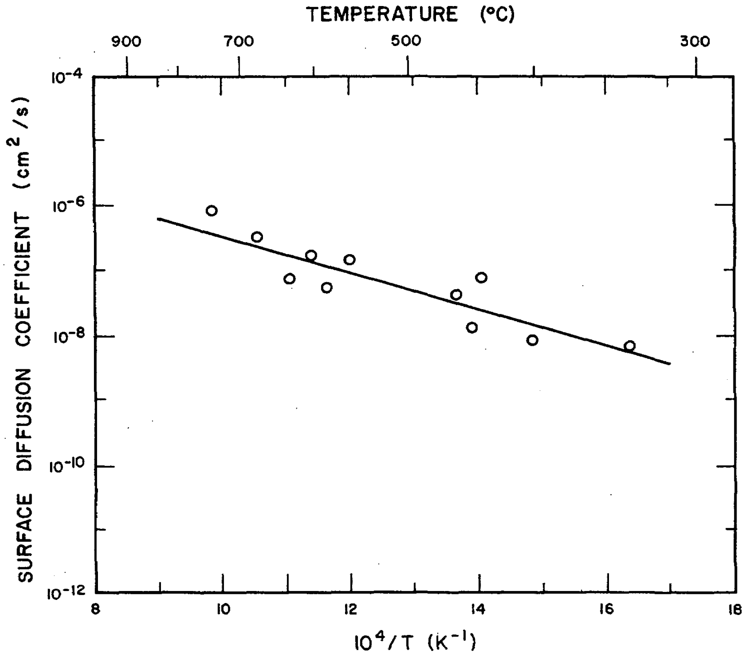

FIGURE 29. The "apparent surface diffusion coefficients" of copper on a silver surface as a function of reciprocal absolute temperature.

Since the measurement contains a lattice diffusion component, as well as a surface component, it is referred to as an "apparent surface diffusion coefficient," rather than a true surface diffusion coefficient. After the data of Pines and co-workers [137].

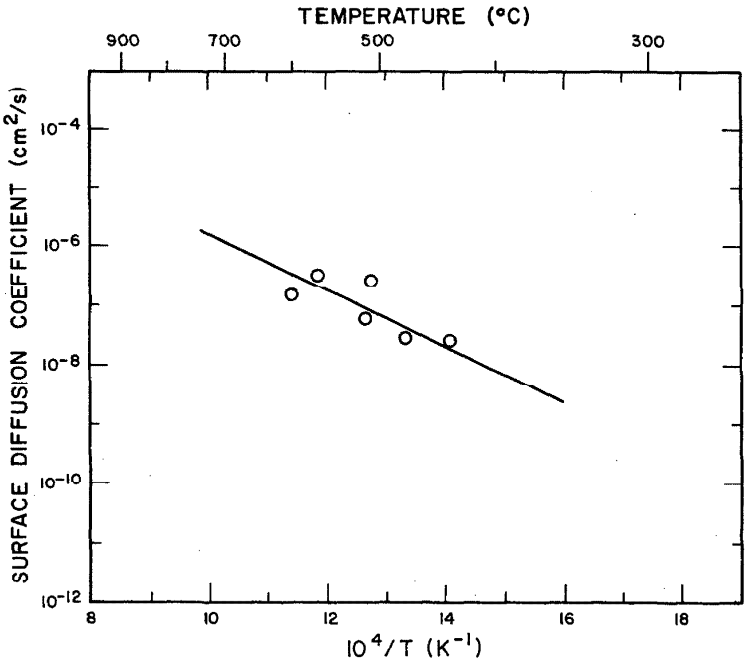

FIGURE 30. The "apparent surface diffusion coefficients" of silver on a copper surface as a function of reciprocal absolute temperature.

The measurement contains a lattice diffusion component, as well as a surface component, hence it is referred to as an "apparent surface diffusion coefficient." After the data of Pines and co-workers [137].

TABLE 23. Silver surface diffusion coefficients on the (001), (111), and (110) planes and on some vicinal surfaces of copper. Data from Roulet [143].

Plane	Direction	Temperature range (°C)	D_0 (cm^2/s)	Q (kcal·mol^{-1})
(001)	isotropic	250–500	6.2×10^{-2}	17.5 ± 3.7
(111)	isotropic	250–500	4.6×10^{-1}	17.5 ± 3.7
(110)	$\langle 1\bar{1}0\rangle$	250–450	2.8	17.0 ± 5.8
(110)	$\langle 001\rangle$	250–450	7.3	19.6 ± 6.9
(001)[a]	$\langle 110\rangle$	300–450	2.4×10^{-4}	9.7 ± 2.3
(001)[a]	$\langle 1\bar{1}0\rangle$	300–450	5.8×10^{-4}	10.4 ± 2.8
(111)[a]	$\langle 112\rangle$	250–450	2.3×10^{-2}	14.3 ± 4.1
(111)[a]	$\langle 1\bar{1}0\rangle$	250–450	1.6×10^{-2}	12.9 ± 5.1

[a] Vicinal surfaces, rotation of 6° about the $\langle 1\bar{1}0\rangle$.

2.22. Electromigration

The influence of an electric field on the lattice and grain boundary diffusion of silver in copper has been reported by Klotsman and co-workers [145–147]. The lattice diffusion investigations [146] measured the effect of a direct current (with a density of 100 to 150 A/mm^2) on the migration of radioactive silver-110 in copper of nominal purity (total content of 11 impurities was less than 0.0025%). The silver-110 was vacuum-evaporated onto the polycrystalline specimens. Two specimens with their active faces together were diffusion annealed in an apparatus [148] at each temperature (in the range 790 to 1062 °C). Upon completion of the annealing (7 to 19 h), the specimens were separated and sectioned. The residual activity method of counting was employed [149, 150]. The direction of electromigration was found to be towards the anode in all cases. The effective ion charge was also calculated from the data taken but the calculations not only failed to take into account alterations in the Einstein relation necessary when impurity diffusion is involved but also used incorrect values of silver diffusion coefficients and thus are in error. The silver-110 tracer diffusion coefficients listed for the various temperatures are incorrect since the diffusion annealing temperatures were corrected on the basis of their calculated tracer diffusion coefficient values and the temperature dependence for the lattice diffusion of silver in copper reported by Gertsriken and Revo [20], whose results are incorrect. An attempt [147] to correct this determination of the effective charge by taking into account the correlation factor (though the incorrect temperature was still employed in the calculations) yielded results which were stated to be in agreement with Kuzmenko and Ostrovskii [151]. How the correlation factor was taken into account was not discussed in detail. As a consequence, and because of erroneous temperatures, the calculated magnitudes of effective charge are still of questionable value.

The effect of an electric field on the grain boundary diffusion of radioactive silver-110 in copper has also been studied by Klotsman and co-workers [145, 147]. The experimental technique they used was the same as that used in the lattice diffusion investigations discussed above. The temperature range was 430 to 540 °C. Applying Fisher's analysis [83] with some modification [152], a model was arrived at to describe grain boundary diffusion in an electric field. The Nernst-Einstein relation was used again to determine an effective charge of the diffusing silver ion in the grain boundary. In all their experiments, silver diffusion was found to be directed toward the cathode.

2.23. Thermomigration

The thermomigration of silver in copper has been studied by Jaffee and Shewmon [153] and Schroerschwarz and Heitkamp [154], with the results not in agreement with each other. Although both studies employed similar experimental techniques (a steady-state technique which measured the stationary redistribution of radioactive silver-110 in a linear temperature gradient, similar temperatures, etc.) the redistribution of the silver in the temperature gradient was noticeably less in the experiment of Schroerschwarz and Heitkamp (effective heat of transport $Q^{**}\approx 0$ to -3 kcal·mol^{-1}) than in that of Jaffee and Shewmon ($Q^{**}\approx -5$ kcal·mol^{-1}) at about the same temperature ($\simeq 1000$ °C). Different theoretical models were used to analyze the data. Jaffee and Shewmon applied a rather simple analysis whereas Schroerschwarz and Heitkamp made their calculations with the aid of Heitkamp's model [155], corrected for vacancy-impurity association as suggested by Howard and Manning [156] and the electron interaction contribution as estimated by Gerl [157]. Both investigations do agree that the silver-110 tracer concentration increases towards the hot side of the alloy specimen.

2.24. Strain-Enhanced Diffusion

Strain-enhanced diffusion rates of silver in pure copper have also been reported [124, 158, 159]. Shestopalov and Romashkin [124, 158] diffused radioactive silver-110 into deforming (compression) copper. Their initial results published in [158] were partially in error (see also comments by Ruoff and Balluffi [160]) and so they redid their experiments [124]. Enhanced silver diffusion in coarse-grained copper was found over a range of strains, the amount of enhancement increasing with an increase in strain rate at constant strain, reaching an enhancement factor of 4 at $\epsilon = 200\%/\mathrm{h}$. All the experiments were performed at one temperature (600 °C). Romashkin and Shestopalov claim that their results indicate that plastic deformation causes an acceleration in silver lattice diffusion with increasing distance from the surface of the specimens. They also conclude that their experimental data agree with the phenomenological model of Balluffi and Ruoff [161] as well as the kinetics described in [162, 163].

Fatigue tests conducted on oxygen-free high-conductivity copper specimens (polycrystalline) possessing a surface-alloyed layer of silver have detected enhanced silver diffusion rates [159]. The silver concentration varied from approximately 4 percent at the surface to zero at a depth of 90 μm in the copper specimens. Fatigue tests were performed at room temperature. After failure of the specimens, the radial distribution of the silver was measured by means of electron-probe microanalysis. Comparison was made with specimens prepared under identical conditions, but not fatigue-tested. Differences in silver concentration and penetration revealed that the silver diffusion rate during fatigue was significantly increased. The authors computed that the amount of silver diffusion which took place was equivalent to that which would have occurred had the specimen been diffusion-annealed at 300 °C for 60 hours (the duration of the fatigue test). It was also postulated that the long-range diffusion phenomena found in the fatigue specimens were apparently due to an abnormally high vacancy concentration being produced during fatigue.

2.25. Molten Metals

The tracer diffusion coefficients of silver-110 in molten copper at infinitely high dilution have been studied [164] within the temperature range 1143 to 1290 °C using the capillary-reservoir technique. The temperature dependence of the silver tracer diffusion coefficient can be represented by the expression:

$$D^*_{\mathrm{Ag}\to\mathrm{Cu}} = (1.93 \pm 0.31) \times 10^{-3} \exp(-11{,}210 \pm 440\ \mathrm{cal \cdot mol^{-1}}/RT)\ \mathrm{cm^2/s}.$$

The same authors [164] also showed the concentration dependence of the silver tracer diffusion coefficients on the silver concentration. In the temperature range of 1150 to 1311 °C and for $N_{\mathrm{Ag}} = 0.146$, the results can be represented by:

$$D^*_{\mathrm{Ag}\to\mathrm{Cu-Ag}} = (6.63 \pm 1.43) \times 10^{-4} \exp(-8{,}950 \pm 590\ \mathrm{cal \cdot mol^{-1}}/RT)\ \mathrm{cm^2/s}.$$

3. Copper-Gold

3.1. Au → Cu

The rate of diffusion of gold (from thin layers) into pure copper (massive specimens) has been reported a number of times [165–173]. Although most of the experiments appear to have been carefully performed, there is disagreement among the results (see figures 31 and 32).

Conventional radioactive tracer and sectioning techniques were employed by Martin and co-workers [165, 166] and Tomizuka [167] in their investigations. Tomizuka restricted his experiments to relatively high temperatures (700 to 1030 °C) and single crystal copper specimens and found that he could express his results (see figure 31) most aptly with the following Arrhenius expression:

$$D^*_{\mathrm{Au}} = 0.69 \exp(-49.7\ \mathrm{kcal \cdot mol^{-1}}/RT)\ \mathrm{cm^2/s}.$$

In a later private communication [168], Tomizuka put the following limits on the pre-exponential factor and the activation energy,

$$D_0 = 0.69 \pm 0.07\ \mathrm{cm^2/s},$$

$$Q = 49.7 \pm 0.5\ \mathrm{kcal \cdot mol^{-1}}.$$

These values appear to be quite reliable in spite of the lack of reported experimental detail. This data is shown extrapolated to relatively low temperatures in figure 32.

Martin and co-workers made their measurements over a much broader temperature range, 375 to 1000 °C. In view of the apparently large grain-boundary diffusion contributions occurring at the lower temperatures, only the gold-198 tracer diffusion coefficients in the temperature range from 750 to 1000 °C were fitted to the Arrhenius law by the least squares method in order to determine the frequency factor, D_0, and the activation energy, Q, for the lattice diffusion. The tracer diffusion coefficients, determined by the method of Johnson [174], are compared with others in figure 31. The resulting Arrhenius expression (and probable errors calculated by the least squares method) is given as

$$D^*_{\mathrm{Au}} = (0.10 \pm 0.06) \exp(-44.9 \pm 1.3\ \mathrm{kcal \cdot mol^{-1}}/RT)\ \mathrm{cm^2/s}.$$

Because of the short half-life of the radioactive gold-198, the usual techniques could not be employed in their long-time diffusion anneals (550 to 375 °C). Hence, a thin layer of non-active stable gold was diffused into the copper, after which the specimens were neutron-irradiated in a cooled test hole of a reactor and then sectioned in the manner of their other specimens. The resulting values of the calculated coefficients ($D_{\mathrm{Au}} \cong 2 \times 10^{-12}$ cm²/s at 550 °C and $D_{\mathrm{Au}} \cong 2 \times 10^{-13}$ cm²/s at 375 °C) are appreciably higher than what would be given by the Arrhenius expression quoted above.

Neutron-activation analysis was employed by Archbold and King [171, 172] and Chatterjee and Fabian [173] in determining the lattice diffusion rates of gold impurities in pure copper. These results also are plotted in figure 31. Archbold and King made their measurements on polycrystalline copper (following the experimental procedure of Kirkaldy and co-workers [175, 176]) in the temperature range 700 to 1000 °C. The gold impurity diffusion coefficients calculated from their data exhibited a great deal of non-linearity. The coefficients were fitted to the Arrhenius equation by the

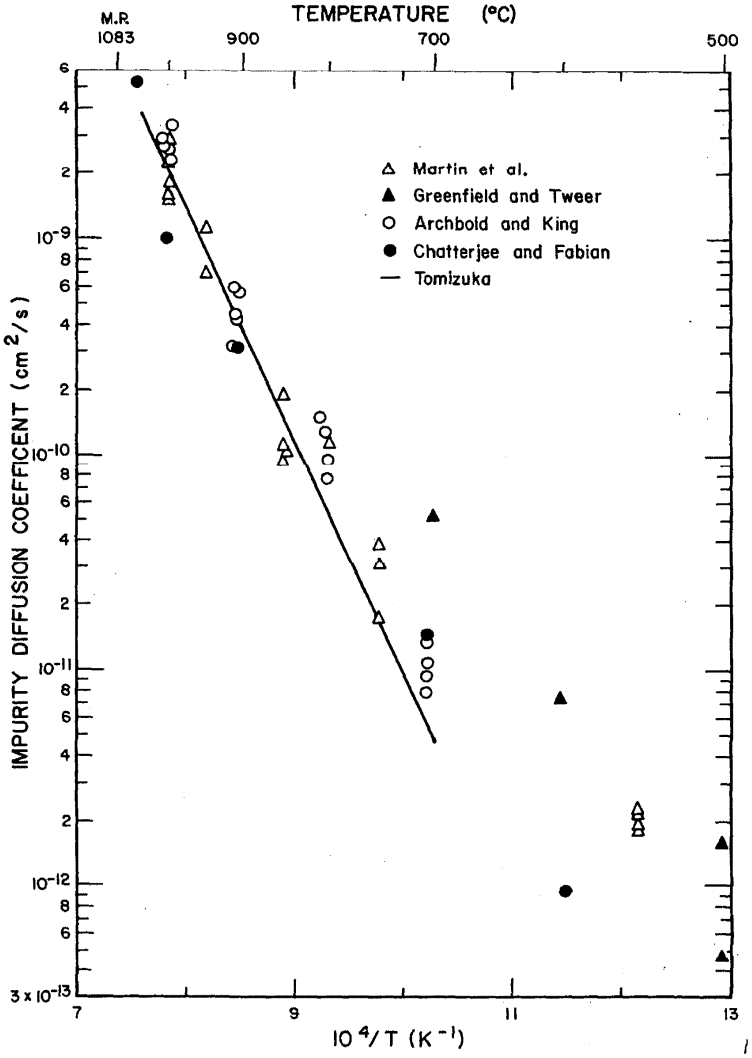

FIGURE 31. Impurity and tracer diffusion coefficients of gold in pure copper in the temperature range 1070 to 500 °C.

Data taken from the research of Archbold and King [171, 172], Chatterjee and Fabian [173], Martin et al. [165, 166], Greenfield and Tweer [178], and Tomizuka [168], Tomizuka reported only the Arrhenius equation and here his data is displayed as a line.

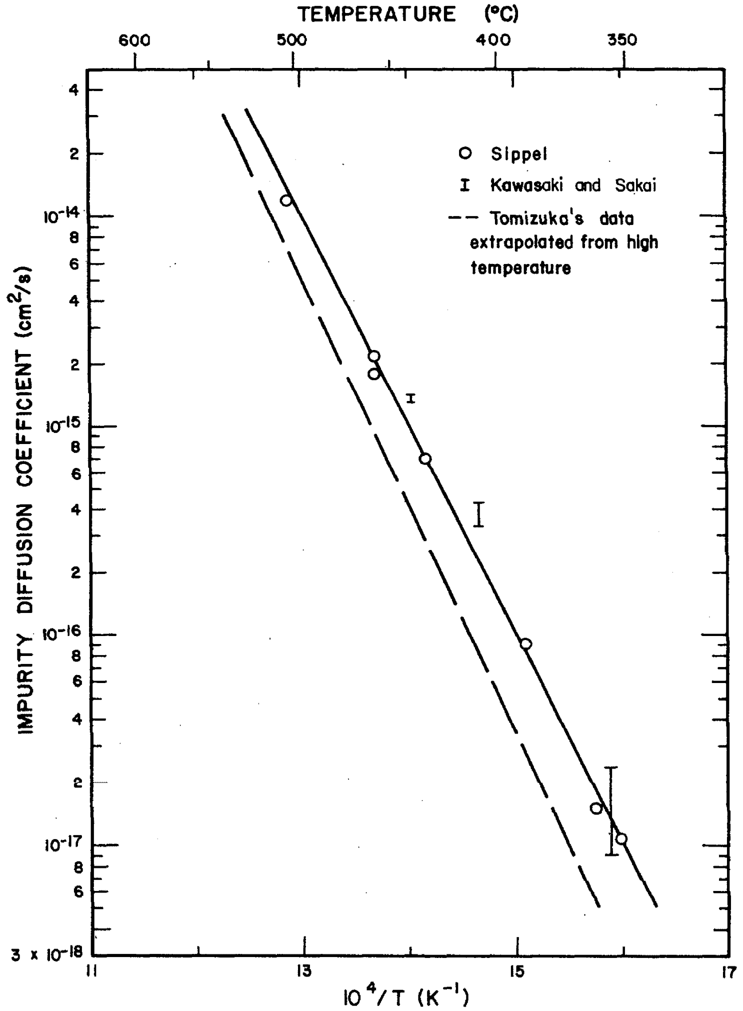

FIGURE 32. Impurity and tracer diffusion coefficients of gold in pure copper (at low temperatures, 500 to 350 °C) as a function of reciprocal absolute temperature.

Data excerpted from the results of Sippel [169], and Kawasaki and Sakai [170]. The dotted line is an extrapolation of Tomizuka's high-temperature tracer results [168]. The low-temperature results of Martin et al. [165, 166] at 375 °C are not shown as these results were far removed from the other data.

least squares method and the resulting expression (and probable errors) is as follows:

$$D^{\text{impurity}}_{\text{Au}\to\text{Cu}} = (0.15 \pm 0.07) \exp\,(-45{,}700 \pm 1400\ \text{cal}\cdot\text{mol}^{-1}/RT)\ \text{cm}^2/\text{s}.$$

Chatterjee and Fabian made their study over a much broader temperature range, 400–1050 °C, using both single-crystal and polycrystalline copper specimens. Their procedures [177] for specimen preparation and neutron activation involved the plating of layers of gold of approximately 100 Å thickness, diffusion-annealing, sectioning, and irradiation. Their measurements (and the errors estimated from the scatter of the coefficient values) for the lattice diffusion of gold in copper were summarized in the expression:

$$D^{\text{impurity}}_{\text{Au}\to\text{Cu}} = (0.03 \pm 0.002) \exp\,(-42.6 \pm 1.0\ \text{kcal}\cdot\text{mol}^{-1}/RT)\ \text{cm}^2/\text{s}.$$

Below 750 °C, significant grain-boundary diffusion contributions to the process were found in polycrystalline copper specimens, and non-linear penetration profiles, resulting in the determination of only "apparent values" of the diffusion coefficient which showed considerable scatter.

Greenfield and Tweer [178] arrived at lattice diffusion constants of gold in copper from the determination of compositional profiles near grain boundaries. Gold (from a thin deposit) was diffused into copper grain boundaries and an electron diffraction technique was employed to obtain the gradients in the vicinity (five microns) of the boundaries. The results (see figure 31) yield a rather low activation energy (~ 30 kcal · mol^{-1}) when compared with some of the more traditional methods of investigation.

In addition to the conventional tracer-sectioning techniques and the neutron-activation method, a third technique, that of elastic scattering of protons and deuterons, has been employed in the making of gold diffusion measurements in copper. Sippel [169] used a broad-range magnetic spectrograph [179] to study the impurity diffusion of gold into copper in the temperature range 360–500 °C. Comparison of the proton (and deuteron) spectra with convoluted solutions of the diffusion equation yielded the gold impurity diffusion coefficients listed in table 24. An Arrhenius plot of the data is shown in figure 32, where a straight line is fitted to the individual data points with a root mean square deviation of 12.6 percent. The absolute accuracy of the data points is estimated by the author to be better than ± 20 percent. The resulting expression used to describe the straight line and the gold diffusion rate is:

$$D^{\text{impurity}}_{\text{Au}\to\text{Cu}} = (0.104 \pm 0.06) \exp\,(-45{,}750 \pm 750\ \text{cal}\cdot\text{mol}^{-1}/RT)\ \text{cm}^2/\text{s}.$$

TABLE 24. Gold impurity diffusion coefficients in copper (after Sippel [169])

T(°C)	Time(s)	D (cm^2/s)
503	3.60×10^{2}	1.2×10^{-14}
457	7.20×10^{2}	1.8×10^{-15}
457	7.20×10^{2}	2.2×10^{-15}
432	2.25×10^{4}	7.0×10^{-16}
389	7.20×10^{4}	9.0×10^{-17}
362	3.46×10^{5}	1.5×10^{-17}
352	1.78×10^{6}	1.1×10^{-17}

Kawasaki and Sakai [170] simplified the above experimental apparatus used by Sippel [169] (by building a silicon semiconductor radiation detector for elastically scattered deuterons) and redid the above gold impurity diffusion experiments in the temperature range 356–440 °C. Their apparatus allowed them to examine diffusion lengths ($=\sqrt{Dt}$) as small as 2×10^{-7} cm in their high purity, polycrystalline, copper specimens. The electroplated gold layers (~ 0.01 μ) were diffused into the copper specimens at temperatures of 355, 409, and 440 °C, for 100 minutes. The calculated gold diffusion coefficients are listed in table 25 and plotted in figure 32 as a function of reciprocal absolute temperature. As can be seen, the results indicate a somewhat larger rate of gold diffusion than the results of Sippel, who used the same technique (although the activation energies are nearly the same). Tomizuka's reliable high temperature tracer data [168] are extrapolated to these relatively low temperatures for comparison. In view of the disagreement in the low temperature results of Sippel [169], Kawasaki and Sakai [170], and Martin et al. [165], one would be more justified in selecting values of the gold tracer diffusion coefficient from the extrapolation of Tomizuka's data.

Choi and Shewmon [180], as a check on the validity of their experimental procedures used to measure surface diffusion coefficients in the copper-gold system, made four measurements of the lattice diffusion coefficient of radioactive gold-198 at 950 °C. The averaged value of the gold tracer diffusion coefficient was 1.1×10^{-9} cm^2/s, in general agreement with the more reliable of the above-mentioned tracer studies.

TABLE 25. Gold impurity diffusion coefficients in copper (after Kawasaki and Sakai [170])

T(°C)	D (cm^2/s)
440	$(1.3-1.4)\times10^{-15}$
409	$(3.3-4.3)\times10^{-16}$
356	$(0.91-2.41)\times10^{-17}$

3.2. Cu → Au

Vignes and co-workers [181–183] used an electron-microprobe analyzer to measure the impurity diffusion coefficient of copper into gold between 700 and 906 °C.

In their technique, a very thin layer of copper ($<2\ \mu$) was vaporized onto the surfaces of polycrystalline gold specimens and then diffusion-annealed. Copper concentration-penetration profiles were determined and impurity diffusion coefficients calculated (see table 26). When the coefficients are plotted as a function of reciprocal absolute temperature, a straight line can be fitted to the data points by the method of least squares (see figure 33). The values of the frequency factor and the activation energy are taken from the plot to give the following Arrhenius equation for the copper diffusion rate in gold.

$$D^{\text{impurity}}_{\text{Cu}\rightarrow\text{Au}} = 0.105 \exp\ (-40{,}650\ \text{cal}\cdot\text{mol}^{-1}/RT)\ \text{cm}^2/\text{s}.$$

TABLE 26. Copper impurity diffusion coefficients in gold [182]

T(°C)	D (cm²/s)
906	3.49×10^{-9}
852	1.36×10^{-9}
823	1.01×10^{-9}
780	4.21×10^{-10}
770	3.95×10^{-10}
739	1.97×10^{-10}
700	8.74×10^{-11}

Since the experimental technique employed depends on the precise determination of copper in very low concentration, it would be interesting to see if the above results can be reproduced in other investigations with electron microprobes.

Leidheiser [184] attempted to measure a copper diffusion coefficient into single crystals of gold at 100 °C. A constant copper concentration source at the gold surface was created by polarizing a gold electrode to the corrosion potential of copper in a boiling solution of

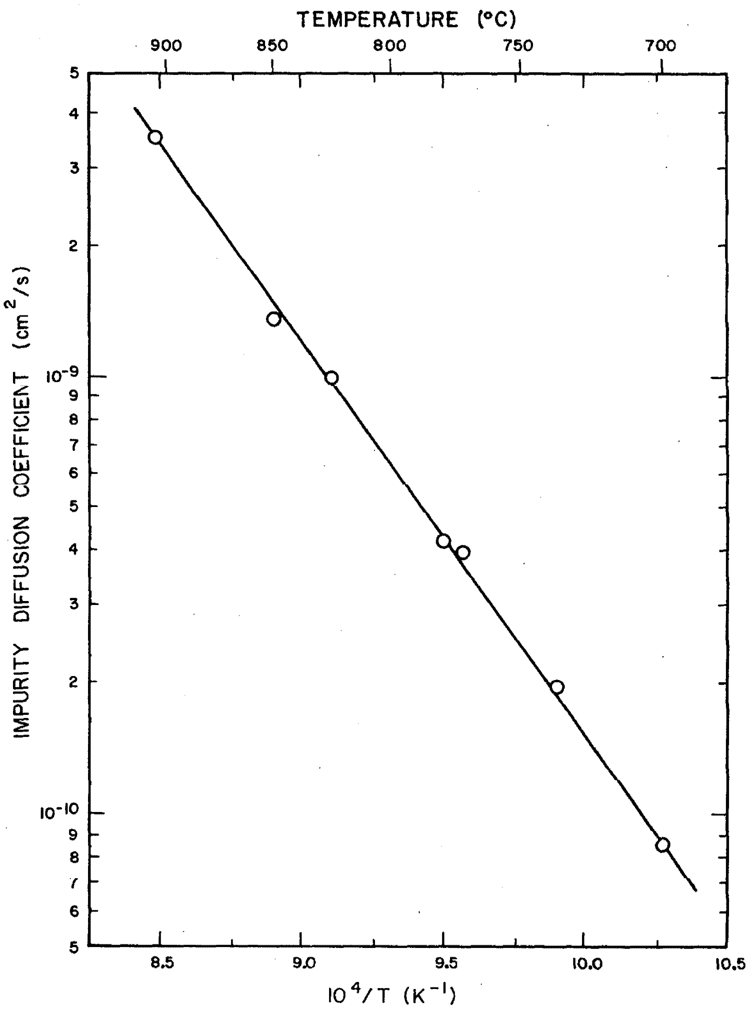

FIGURE 33. Copper impurity diffusion coefficients in gold as a function of reciprocal absolute temperature.

Data taken from Vignes and co-workers [181–183].

2 M hydrochloric acid containing dissolved copper (the concentration of the copper ion was 10^{-2} M). He was not able to detect (gravimetrically) any copper penetration.

3.3. Au* → Cu_3Au

The tracer diffusion coefficient of gold-195 in the *disordered* alloy Cu_3Au has been measured in the temperature range 900 to 500 °C by Benci et al. [185] and by Alexander [186]. Although the details of the latter's experiments are not known, the results are self-consistent, as indicated by the small amount of scatter for this data around the line shown in figure 34. Benci and co-workers relied on the self-absorption method of Zhukhovitsky and Geodakyan [187]. The gold tracer diffusion coefficients calculated from the data are listed in table 27. The temperature dependence of the coefficients is illustrated in figure 34. A least squares adjustment of the data yielded the following Arrhenius equation,

$$D^*_{\mathrm{Au}} = (6.5 \pm 0.9) \times 10^{-3} \exp(-1.66 \pm 0.04\ \mathrm{eV}/kT)\ \mathrm{cm}^2/\mathrm{s}.$$

TABLE 27. Gold-195 tracer diffusion coefficients in Cu_3Au [185]

T(°C)	D^* (cm^2/s)
900	6.31×10^{-10}
850	2.06×10^{-10}
800	8.16×10^{-11}
750	3.91×10^{-11}
700	1.30×10^{-11}
650	5.72×10^{-12}
600	1.68×10^{-12}
550	4.97×10^{-13}

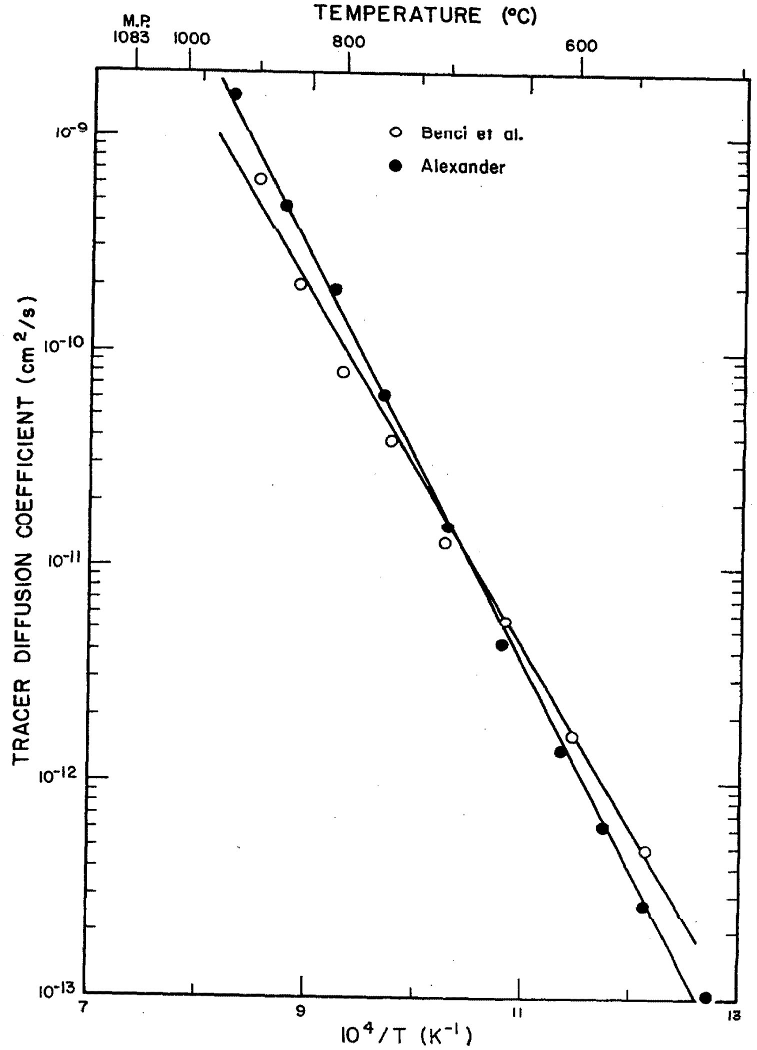

FIGURE 34. The tracer diffusion coefficient of Au-195 in the disordered alloy Cu_3Au as a function of reciprocal absolute temperature.

Data taken from Benci and co-workers [185] and Alexander [186].

Independent of the given errors is an additional uncertainty of ±10 percent in the value of the preexponential factor, D_0, due to the choice of the geometry selected for the activity measurements as well as the value chosen for the absorption coefficient in Cu_3Au. The activation energy is in agreement with the results described in [189] for the energy of formation and migration of vacancies in this alloy.

Million and Kučera [190, 191] have taken the data of Benci and Gasparrini [192] and arrived at a temperature dependence for gold self-diffusion in an *ordered* Cu_3Au alloy expressed by the following Arrhenius equation:

$$D=3.15 \exp(-46{,}400 \text{ cal}\cdot\text{mol}^{-1}/RT) \text{ cm}^2/\text{s}.$$

The details of how the above expression was obtained are described in the previously mentioned papers [190, 191]:

An anelastic effect has been measured by Goering and Norwick [193] from internal friction experiments. The effect has an activation energy of the order of 1.9 eV and it increased by an order of 0.08 eV on going from the disordered state to the ordered state.

There have been a number of papers dealing with the ordering kinetics of Cu_3Au alloys [189, 194–215]. The experiments have concerned themselves with the measuring of properties such as electrical resistivity, etc., all aimed at the calculation of the "self-diffusion energy," activation energy for vacancy migration, etc. Unfortunately, the complex mathematical procedures needed to sort out the many effects (and thus allow the actual calculation of self-diffusion coefficients for the alloying constituents) have yet to be satisfactorily worked out.

3.4. Ordering in Cu-Au

Similar studies such as those mentioned above regarding the alloy Cu_3Au have also been done for CuAu with the kinetics of ordering being studied [208, 216–223] and the characterization of the process by an activation energy [216, 223] which is then compared to activation energies obtained from diffusion experiments (usually the diffusion of copper in gold). Various attempts [208, 209] have been made to describe the diffusion processes occurring in this ordered alloy.

3.5. Cu-Au Interdiffusion

Interdiffusion studies in binary copper-gold alloys have been plentiful even before the year 1940 [221, 224–232]. Bruni and Meneghini [224, 226] published data on the formation of copper-gold solid solutions but did not calculate interdiffusion coefficients. Thompson and Dearden [225] measured the width of the interdiffusion zone (formed at 650 °C after a diffusion anneal of 70 hours) between copper and gold. Jost [227] measured the rate of interdiffusion occurring between gold-plated copper wires in the temperature range 301–616 °C and found his results could be summarized by the following relation:

$$\tilde{D}=1.06\times10^{-3} \exp(-27.4 \text{ kcal}\cdot\text{mol}^{-1}/RT) \text{ cm}^2/\text{s}.$$

In similarly designed experiments, Jost [228] also measured the rate of interdiffusion occurring between a gold-copper (25.6 at. %) alloy and pure gold in the temperature range 443–740 °C, and found that his results could be best described by the exponential relation

$$\tilde{D}=5.8\times10^{-4} \exp(-27.4 \text{ kcal}\cdot\text{mol}^{-1}/RT) \text{ cm}^2/\text{s}.$$

Tanaka and Matano [232, 233] measured rates of interdiffusion in the copper-gold system using X-ray techniques and electrical resistances. Often referred to are Matano's [229] measurements of the rate of interdiffusion between pure copper and copper-gold alloys in the temperature interval 400–950 °C. (Although Matano reports his alloys as containing approximately 10 at. % gold. Jost in his book [234] notes that Matano's alloys contained 2.4 to 3.5 at. % gold). Matano's results can be summarized in the exponential expression

$$\tilde{D}=6.8\times10^{-6} \exp(-22.5 \text{ kcal}\cdot\text{mol}^{-1}/RT) \text{ cm}^2/\text{s}.$$

DuMond and Youtz [231] reported interdiffusion occurring at a rate of 5×10^{-20} cm²/s at room temperature between thin copper and gold vapor deposits.

Mooradian and Norton [230] examined the interdiffusion occurring in the temperature range 150–500 °C between alternate electrodeposits of copper and gold but did not calculate any interdiffusion coefficients.

In more recent years, the interest in interdiffusion in this binary system has continued [235–251]. Where interdiffusion coefficients were measured as a function of composition, they are summarized in figure 35 for temperatures > 500 °C. Most of these high temperature results were obtained by interdiffusing pure gold and pure copper (except for an occasional differential couple). Ziebold and Ogilvie's results [237] were taken from broader, ternary interdiffusion investigations at 725 °C (discussed in detail in the section devoted to copper-silver alloys). The experimental details of Batz and Birchenall's study [236] are unknown, their results only being mentioned in a survey paper of Birchenall [252]. Austin and co-workers [243. 244], while studying the grain boundary diffusion of gold in copper, also measured gold penetration remote from the grain boundary using Matano's [253] and Hall's [254] analyses, and were able to calculate chemical interdiffusion coefficients [see table 28] for the temperature 750 °C. These same coefficients are compared in figure 35 to other high temperature interdiffusion data. Gold interdiffusion coefficients were also calculated at 760, 706, 660, and 625 °C from Gaussian penetration plots obtained from thin source couples. These results are listed in table 29.

TABLE 28. Interdiffusion coefficients in copper-gold alloys at 750 °C (after Austin et al. [243])

Au Concentration (at. %)	$\tilde{D}$(cm²/s)
0.5	3.9×10^{-11}
1.0	4.5×10^{-11}
2.0	5.4×10^{-11}
5.0	7.5×10^{-11}
10.0	1.0×10^{-10}
15.0	1.3×10^{-10}
20.0	3.0×10^{-10}
30.0	6.0×10^{-10}
40.0	1.0×10^{-9}
60.0	1.3×10^{-9}
80.0	1.5×10^{-9}
90.0	1.6×10^{-9}

TABLE 29. Gold interdiffusion coefficients in copper (after Austin et al. [244])

T(°C)	$\tilde{D}$(cm²/s)
760	3.4×10^{-11}
706	8.3×10^{-12}
660	2.0×10^{-12}
625	6.0×10^{-13}

Badia [238], Badia and Vignes [239], Pinnel and Bennett [240], and Borovskii and co-workers [245, 246] made somewhat more detailed studies than the previously mentioned investigators. Badia, using massive polycrystalline specimens, interdiffused his couples at temperatures of 773, 743, 770, and 857 °C.

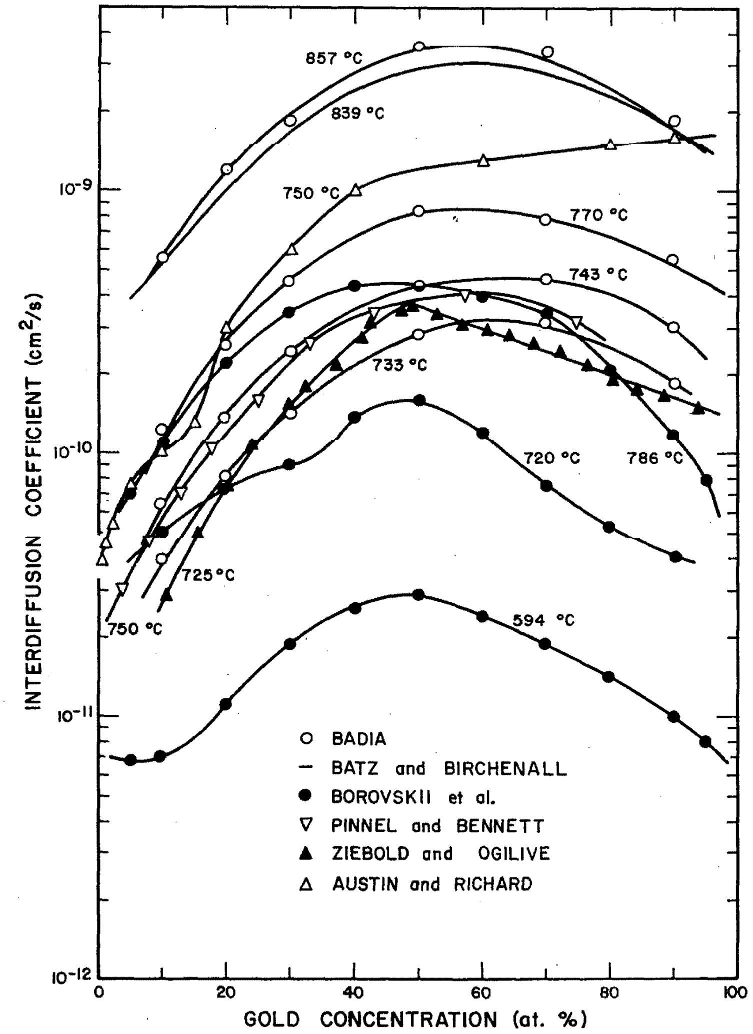

FIGURE 35. Interdiffusion coefficients in the copper-gold system as a function of composition at temperatures ranging from 600 to 860 °C.

Data taken from Badia [238], Austin and Richard [243], Borovskii et al. [246], Pinnel and Bennett [240], Ziebold and Ogilvie [237], and Batz and Birchenall [236].

TABLE 30. Interdiffusion coefficients in copper-gold alloys. (after Badia [238])

Au concentration (at. %)	$\tilde{D}(10^{-10}\ \mathrm{cm^2/s})$			
	733 °C	743 °C	770 °C	857 °C
10	0.43	0.65	1.25	6.0
20	0.8	1.4	2.5	12.0
30	1.55	2.4	4.5	20.0
40	2.4	3.5	7.1	30.0
50	2.9	4.4	9.0	36.0
60	3.3	4.6	9.8	38.0
70	3.3	4.5	9.1	36.0
80	2.7	3.9	7.5	30.0
90	2.0	3.1	5.7	21.0

Concentration-penetration curves were determined with an electron-microprobe analyzer. Interdiffusion coefficients were calculated with the aid of the Matano [253] or Hall [254] analysis (see table 30) and are plotted in figure 35 as a function of composition and as a function of reciprocal absolute temperature in figure 36. Borovskii and co-workers [245, 246], also using massive polycrystalline specimens of copper and gold, interdiffused them at 780, 720, 594, 498, 383, and 370 °C for up to 1,788 hours. Electron-microprobe analysis was used to obtain the concentration-penetration curves. Chemical interdiffusion coefficients (see table 31) were calculated with the assistance of the Matano analysis and are plotted in figures 35, 39, and 40 as a function of composition. The temperature dependence of the interdiffusion coefficient was also determined and activation energies calculated (see figure 37). Germane to the experiments of Borovskii et al. was the effect on interdiffusion of the order-disorder transition occurring in 50 atomic percent copper—50 atomic percent gold alloys at 410 °C. The temperature-dependence of the interdiffusion coefficient at the 50–50 atomic percent compositions is shown in figure 38. The results indicate that a higher activation energy is required for interdiffusion in the ordered state.

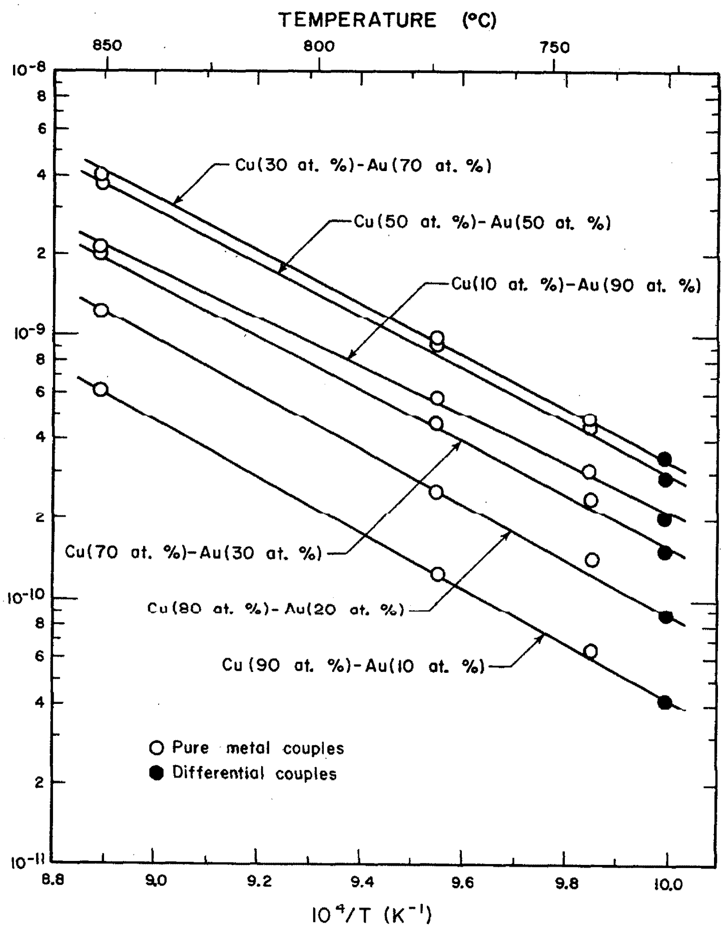

FIGURE 36. Interdiffusion coefficient as a function of reciprocal absolute temperature in the copper-gold alloy system.

Data taken from Badia [238].

TABLE 31. Interdiffusion coefficients in copper-gold alloys (after Borovskii et al. [246])

Au concentration (at.%)	$\tilde{D}(10^{-11}$ cm^2/s) [a]					
	370 °C	383 °C	498 °C	594 °C	720 °C	786 °C
5	0.003	0.004	0.076	0.68		7
10	.004	.006	.084	.7	5.0	11
20	.009	.012	.14	1.1	7.4	22
30		.08	.19	1.9	9.0	35
40			.27	2.6	14	43
50		.08	.31	2.9	16	43
60	.008	.015	.28	2.4	12	40
70	.007	.013	.28	1.9	7.5	35
80	.008	.013	.25	1.4	5.3	21
90	.01	.012	.19	1.0	4.1	12
95	.009	.01	.12	0.8		8

[a] Author's quoted errors range from ±6% to ±50%.

Unfortunately, because of the very narrow temperature range over which data was taken (370–383 °C), as well as the scatter in the few data points taken, no activation energy could be calculated for the interdiffusion process in the ordered state. Pinnell and Bennett [240] conducted their interdiffusion experiments with polycrystalline copper/electroplated gold (nominal plating thickness varied from 2.5 to 100 microns) specimens. Interdiffusion temperatures ranged from 750 down to 50 °C. Concentration-penetration profiles were obtained from electron-probe microanalysis. Interdiffusion coefficients were calculated with the aid of the Matano solution [253] and are plotted as a function of composition in figures 39 and 40. Their low temperature results (≦ 500 °C) appear to be complicated by ordering, recrystallization of the gold electroplate and grain boundary diffusion contributions.

TABLE 32. Interdiffusion coefficients and parameters in ordered and disordered AuCu [248]

AuCu State	T(°C)	D(cm^2/s)	D_0(cm^2/s)	Q(kcal · mol^{-1})
Disordered	700	1.94×10^{-9}	2.36×10^{-6}	13.63
	625	1.01×10^{-9}		
	550	5.35×10^{-10}		
Ordered	350	1.20×10^{-11}	7.94×10^{-8}	10.72
	325	8.75×10^{-12}		
	300	5.83×10^{-12}		

Khobaib and Gupta [248] electroplated copper onto a 50 atomic percent copper—50 atomic percent gold alloy and allowed chemical interdiffusion to occur at 300, 325, 350, 550, 625, and 700 °C, after which the couples were sectioned and the copper concentration determined by a colorimetric method. Chemical interdiffusion coefficients for both the ordered and disordered state were calculated using the Boltzmann-Matano analysis (see table 32). On a log D versus 1/T plot, this data fit well on two roughly parallel straight lines, with the line from couples having an ordered gold-copper alloy predicting diffusion values almost an order of magnitude lower than the line determined from couples having a disordered gold-copper alloy. The resulting Arrhenius expressions are for the disordered state:

$$\tilde{D}=2.36\times10^{-6}\exp\left(-13.63\ \mathrm{kcal\cdot mol^{-1}}/RT\right)\ \mathrm{cm^2/s},$$

and for the ordered state:

$$\tilde{D}=7.94\times10^{-8}\exp\left(-10.72\ \mathrm{kcal\cdot mol^{-1}}/RT\right)\ \mathrm{cm^2/s}.$$

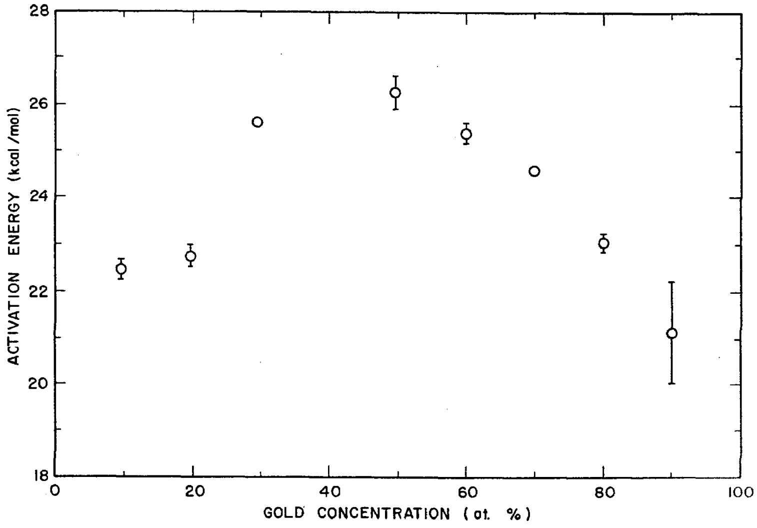

FIGURE 37. Activation energy for interdiffusion in the copper-gold alloy system as a function of gold concentration as determined by Borovskii and co-workers [246].

For concentrations corresponding to Cu_3Au (~30 at.% Au) and CuAu (~50 at.% Au), the activation energy was determined in the temperature interval 498–786 °C, that is, above the order-disorder transition temperature.

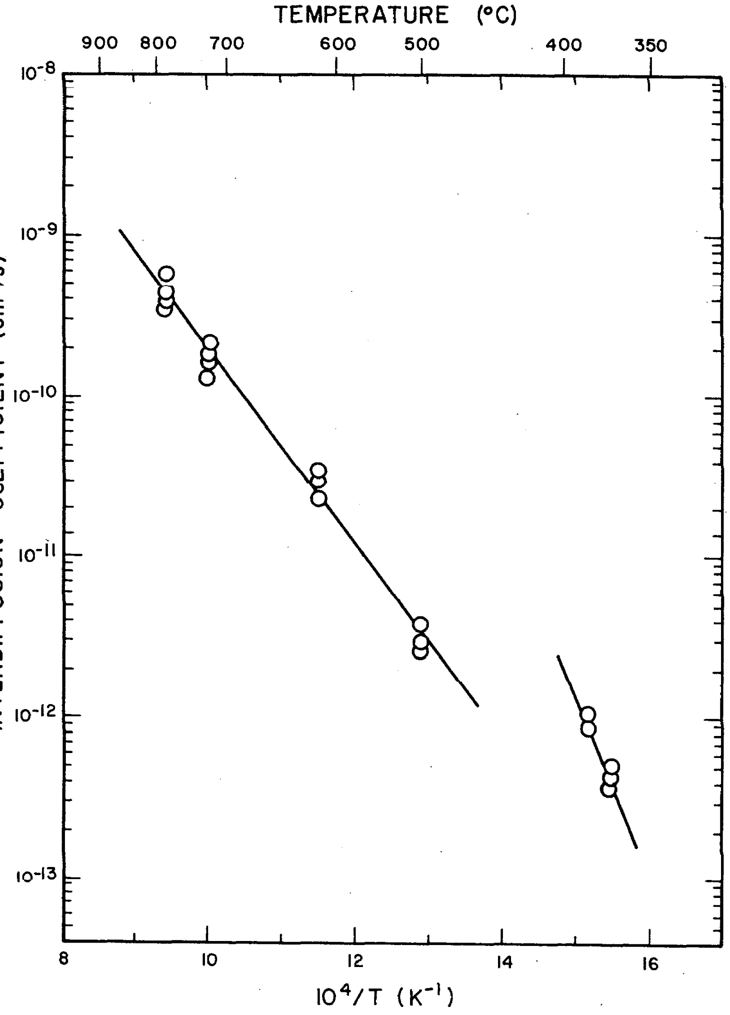

FIGURE 38. The interdiffusion coefficient, measured at the composition 50 at.% copper-50 at.% gold, as a function of reciprocal absolute temperature.

The effect of the order-disorder transition (410 °C) results in a change in the activation energy for interdiffusion. The data shown are that of Borovskii and co-workers [246].

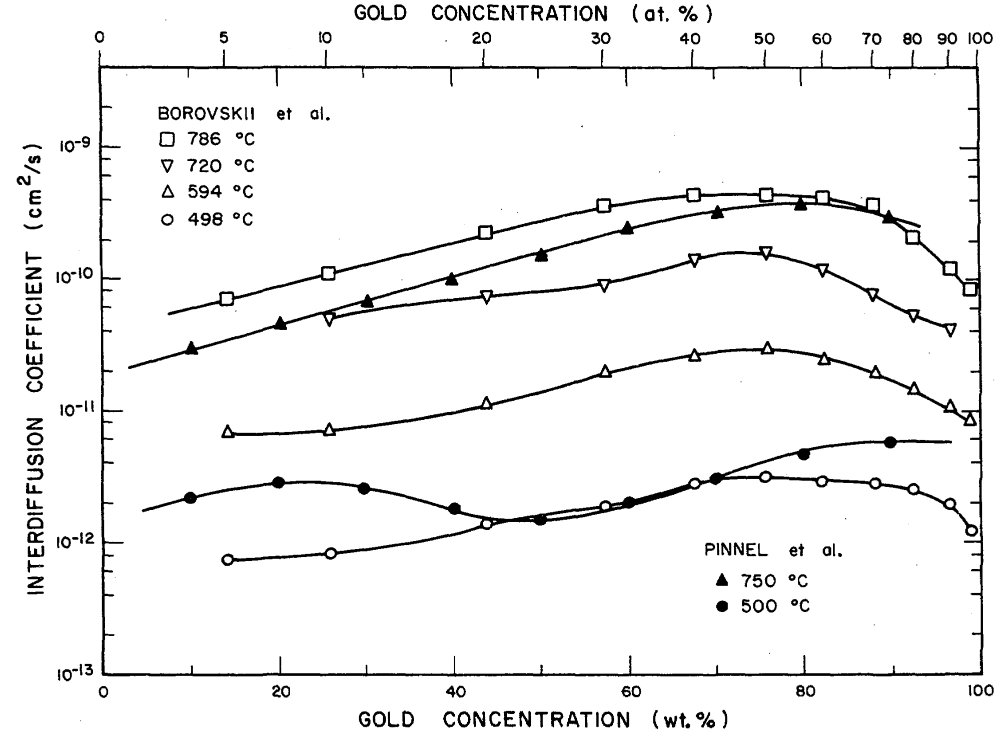

FIGURE 39. Values of the interdiffusion coefficient in the copper-gold alloy system as a function of gold concentration.

Data taken from Borovskii et al. [246]. and Pinnel and Bennett [240].

The activation energies and pre-exponentials obtained by Khobaib and Gupta are unusually low for diffusion in metals and until confirmed by additional experiments should be deemed suspect.

The results of Carpenter and Houska [241] are not displayed as they were only reporting preliminary experimental results utilizing a normal X-ray diffraction technique to study interdiffusion of planar deposits of gold on single crystals of copper. Tenny [242] also used an X-ray diffraction technique to study interdiffusion (750 °C) of thin planar deposits of gold on a copper substrate. No coefficients were calculated although copper was found to diffuse much more rapidly into gold than gold into copper. Also not plotted are the results of da Silva and Mehl [235] who only reported interface and marker motion in their diffusion couples. At 839 °C, after diffusion anneals of 24.5 and 92 hours, they found the copper-gold interface shifting 0.0007 and 0.0020 cm, respectively, toward the gold side of their couple.

The results from these chemical interdiffusion experiments lack good agreement. Why this should be is not readily determined since most of the experiments appear to have been good experiments. Badia [238] though seems to have been most careful in his technique.

In contrast to the above interdiffusion investigations utilizing massive specimens, are the studies performed with thin bimetal films of copper and gold [250, 251, 255–257]. These experiments generally involve equipment and techniques uncharacteristic of the usual bulk interdiffusion study because of the total sample thickness involved (usually several thousand angstroms). Pines and co-workers have used electron-diffraction techniques [260–263] to measure concentration changes occurring during interdiffusion between thin films (~ 10^{-6} cm) of copper and gold [250]. They annealed

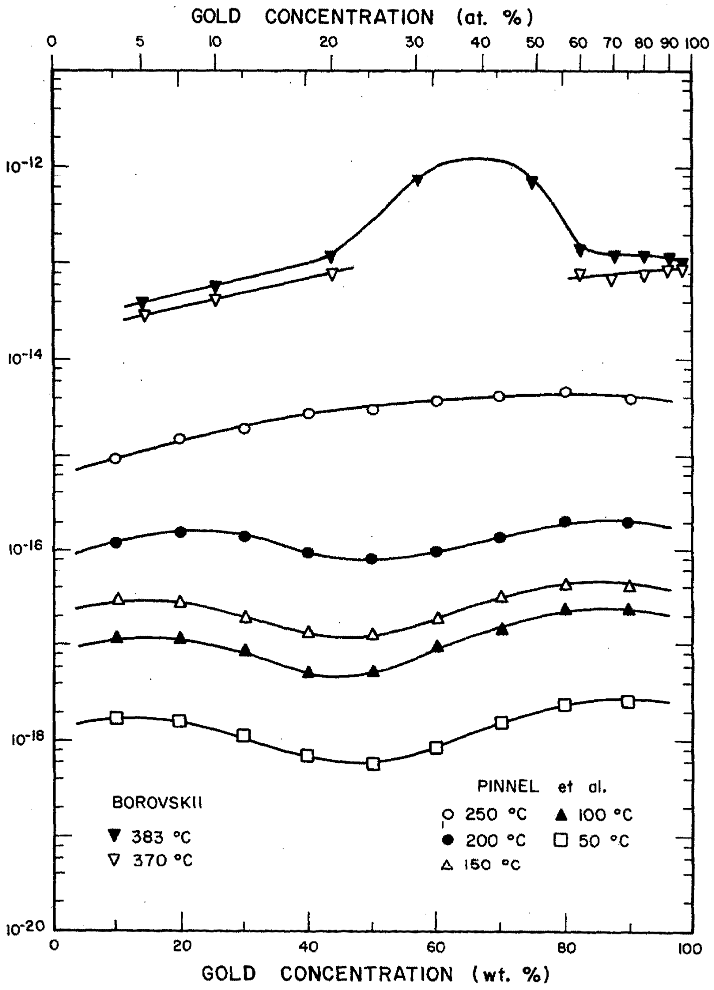

FIGURE 40. Interdiffusion coefficient in the copper-gold alloy system as a function of gold composition.

Data taken from the excerpts of Borovskii et al. [246], and Pinnel and Bennett [240].

thin bimetal films (formed through evaporation and condensation) of copper and gold and observed the kinetics of formation of an ordered copper-gold solution. From this they determined an average interdiffusion coefficient. The diffusion annealing was carried out in an electron-diffraction camera at 150 to 300 °C. The resultant values of this average interdiffusion coefficient, near the 50–50 atomic percent compositions, are plotted in figure 41 as a function of the reciprocal absolute temperature. The equation of the straight line on this figure describing the interdiffusion process is

$$\tilde{D}=4\times 10^{-3} \exp(-26 \text{ kcal}\cdot\text{mol}^{-1}/RT) \text{ cm}^2/\text{s}.$$

Unfortunately, this expression represents a line that in all cases falls below his experimental points. What mathematical analysis employed was not reported. Alessandrini and Kuptsis [251] used electron-micro-

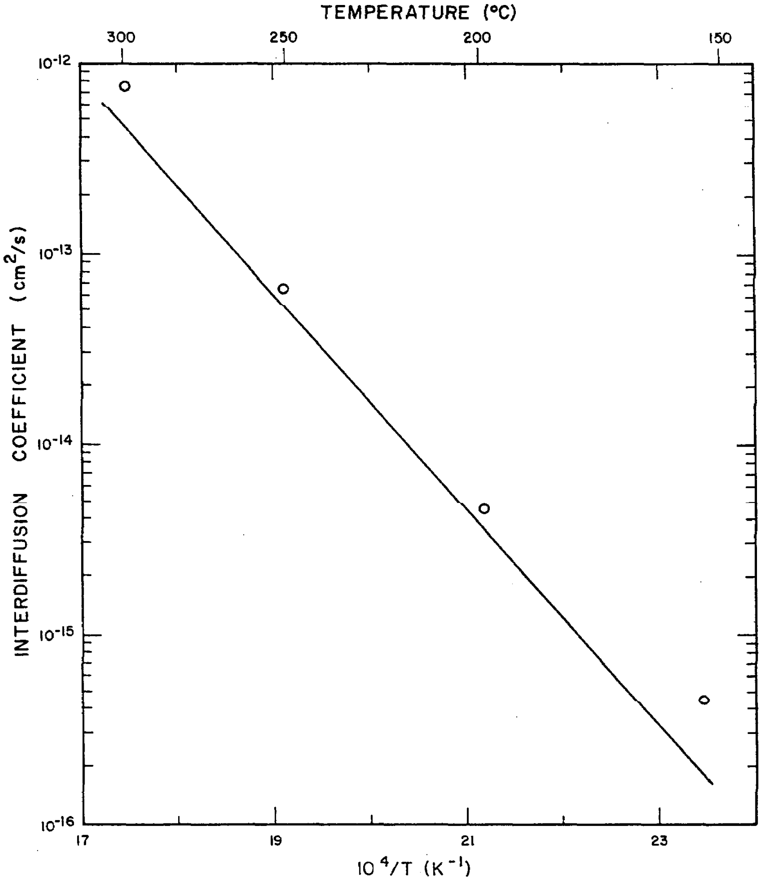

FIGURE 41. Values of an average interdiffusion coefficient (determined near the 50–50 at.% composition) as a function of reciprocal absolute temperature.

Data obtained by Pines et al. [250] using thin films of copper and gold.

probe spectroscopy as the analytical tool in detecting the amount of interdiffusion occurring between thin films of copper and gold. Their thin films were produced by evaporating copper (1500 Å) on top of 100 Å of gold. After the diffusion anneals (which took place in the temperature range 150 to 350 °C), the amount of gold interdiffusion was determined from the enhancement of the characteristic Au *Mα* radiation intensity and by the decrease of the minimum beam voltage necessary to just detect the Au *Mα* signal. The effect of diffusion annealing time and temperature on voltages was observed. From this data activation energies on the order of 0.8 ± 0.2 eV were calculated.

The activation energies determined from the thin film studies of Pines and co-workers and Alessandrini and Kuptsis are somewhat lower than those found in diffusion couples formed from bulk specimens. This is understandable in view of the fact that the studies were performed at low temperatures in thin films, which may or may not be under a high state of stress, and which contain dislocations and very small grains. What is being measured is not pure lattice interdiffusion, but the influence of stress and significant contributions from high diffusivity paths.

Horl and Rieder [257] used electron microscopy to follow the interdiffusion of copper and gold. The tech-

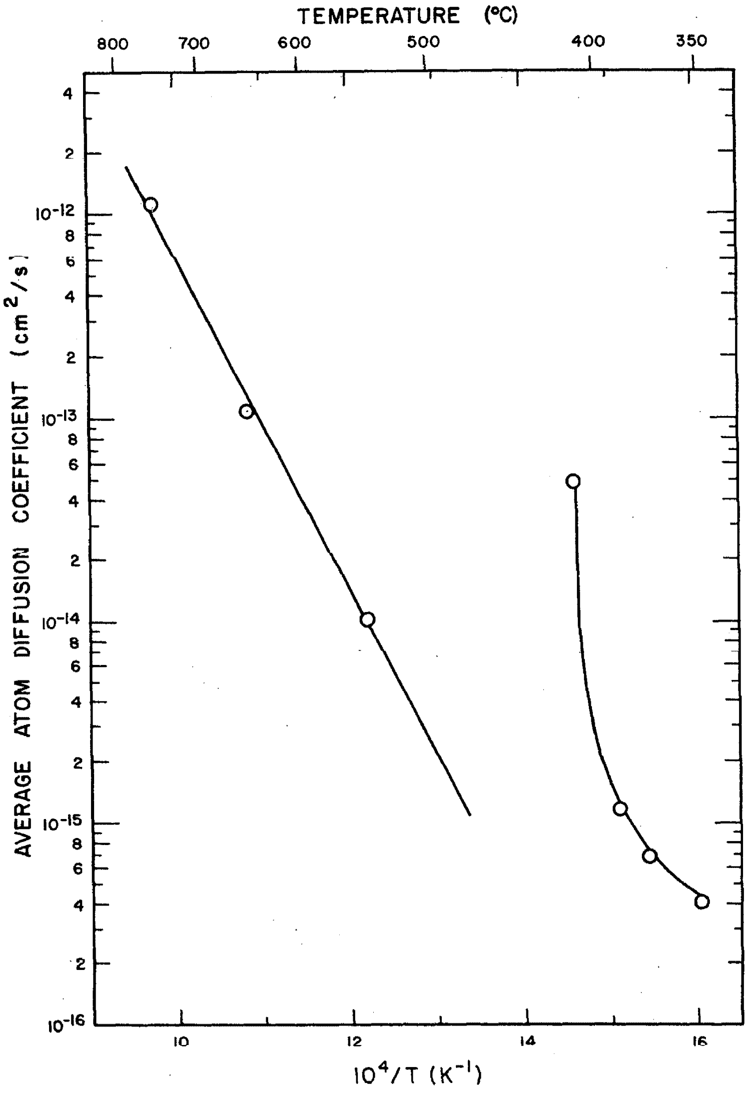

FIGURE 42. "Average atomic diffusion coefficient" as determined from neck width measurements of sintered alloy (50 at.% Au-50 at.% Cu) wires by Tournon and Kuczynski [264].

nique [258] allowed for the continuous observation of the growth of intermetallic phases during the diffusion anneals.

Tu and Berry [256] followed the interdiffusion behavior of pure copper and gold over the temperature range 220 to 160 °C. They used an X-ray method (Seeman-Bohlin diffractometer [259]) to study the kinetics of interdiffusion (and the formation and growth of intermediate phases) in their bimetallic films. A layered structure of Cu | Cu_3Au | $CuAu_3$ | Au was observed to form in the interdiffusion zone, with the ordered phase CuAu conspicuously absent. The reasons for these curious results are speculated on by the authors.

In sintering copper-gold alloys, Duwez and Jordan [249], observed a pseudoequilibrium between copper and the gold-copper ordered phase in sintered powdered compacts containing 75 atomic percent copper and 25 atomic percent gold although the same powder compacts yielded homogeneous $AuCu_3$ alloy at temperatures above 450 °C. Tournon and Kuczynski [264] sintered alloy wires of 50 atomic percent gold—50 atomic percent copper at temperatures ranging from 350 to 750 °C for time intervals from 4 hours to 20 days. After heating, the specimens were sectioned and examined metallographically. The width of the neck formed by the sintered wires was measured and a diffusion coefficient calculated [265]. This "average atom diffusion coefficient" is plotted as a function of reciprocal absolute temperature in figure 42. The effect of ordering in the gold-copper alloy is apparent. In the disordered region, the data can be summarized by the following Arrhenius expression:

$$D_{\text{avg.}} = 2 \times 10^{-4} \exp\left(-39{,}000\ \text{cal} \cdot \text{mol}^{-1}/RT\right)\ \text{cm}^2/\text{s}.$$

The authors speculate that the reason for the high values of the coefficients at 375 and 350 °C are probably due to the lack of equilibrium, ordering still taking place during sintering. In the disordered region, the values of the "diffusion coefficients" are near those of the copper self-diffusion at these temperatures.

3.6. Cu-Au-Ag

The investigations relating to this ternary system are discussed in a previous section on copper-silver-gold alloys.

TABLE 33. Cobalt-57 tracer diffusion coefficients in Cu_3Au [266]

T(°C)[a]	D^*(cm²/s)
900	1.08×10^{-10}
850	4.77×10^{-11}
800	1.78×10^{-11}
750	6.62×10^{-12}
700	1.83×10^{-12}
650	5.40×10^{-13}

[a] Temperatures measured to ±2 °C.

3.7. Cu-Au-Co

The diffusion of radioactive cobalt-57 into a Cu_3Au alloy has been studied [266]. The diffusion coefficients were determined over the temperature range of 650 to 900 °C. A thin layer (~ 100 atomic layers) of cobalt-57

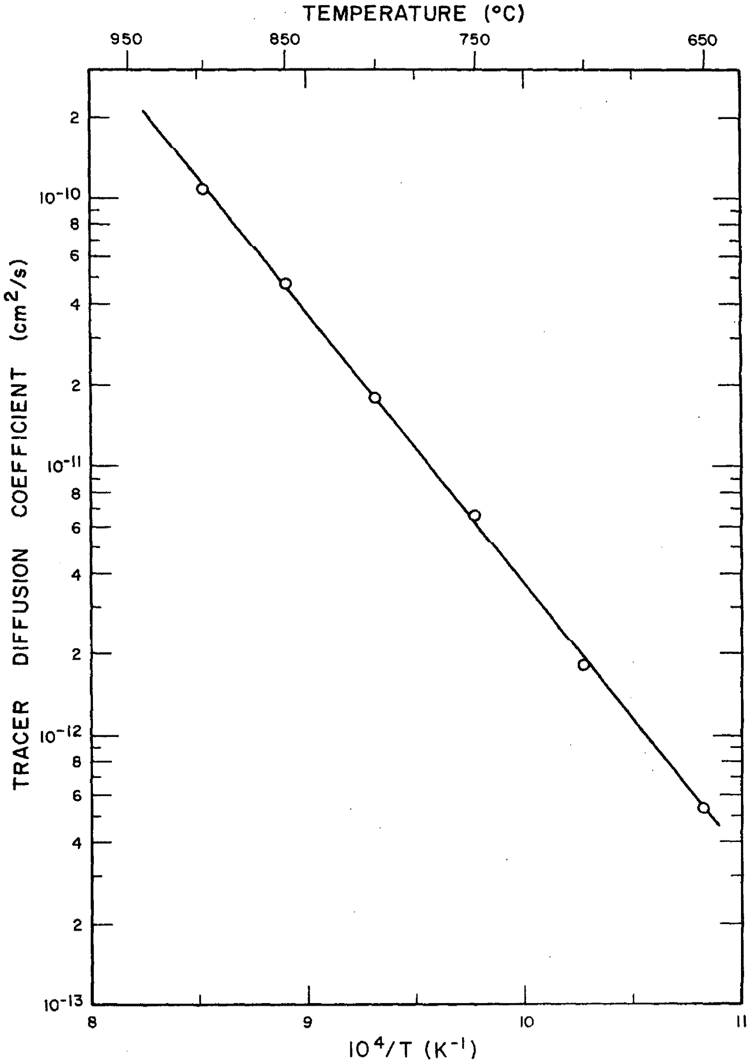

FIGURE 43. Cobalt-57 tracer diffusion coefficients in a Cu_3Au alloy as a function of reciprocal absolute temperature.

Data taken from Benci et al. [266].

was electrodeposited on large-grained polycrystalline alloy specimens (the alloys were made of components of an unspecified purity). After the diffusion anneals, the cobalt–57 concentration gradient was determined through the use of a "self-absorption" method [185–189]. The calculated tracer diffusion coefficients are listed in table 33. A plot of the temperature dependence of these data is shown in figure 43. A least squares analysis of the data over the considered temperature range can be described by the following Arrhenius equation:

$$D^*_{\mathrm{Co}\rightarrow\mathrm{Cu_3Au}} = (4.2\pm0.5)\times10^{-2}\exp\left[-(2.00 \pm0.04)\ \mathrm{eV\ atom^{-1}}/kT\right]\ \mathrm{cm^2/s}.$$

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

3.8. Cu-Au-Fe

Creydt [267] and Creydt and Fichter [268] electro-eposited thin layers (10–20 μm) of copper and gold into an iron substrate and interdiffused them in the emperature range 23 to 212 °C for as long as 11,500 hours only to find that although there was much interdiffusion occurring between the copper and gold deposits, there was no detectable interdiffusion across the iron-gold interface.

3.9. Cu-Au-H

Gol'tsov and co-workers [269] 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 via the conventional experimental techniques [270] used in permeability studies, where a thin membrane of the alloy (while being heated) was subjected to a differential hydrogen pressure. 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 44 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 34). The data for the hydrogen permeability are also plotted as a function of the reciprocal absolute temperature (figure 45), revealing different exponential temperature dependencies. The pre-exponential factors (P_0) and activation energies (Q) calculated for the permeation process are listed in table 34. Near the critical temperature (~ 400 °C), abrupt changes occur in the hydrogen diffusion and permeability rates. The influence of order-

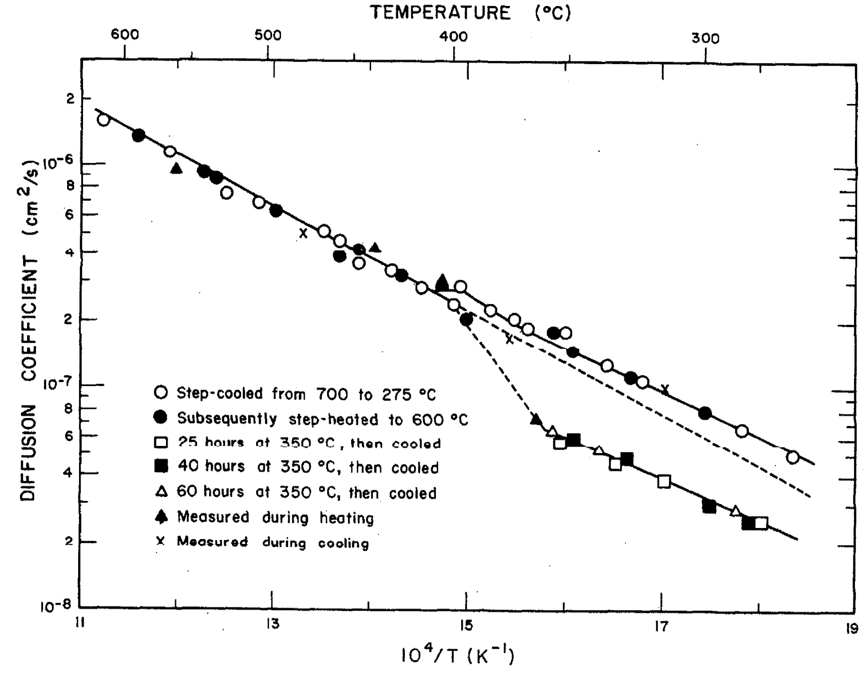

FIGURE 44. The diffusion of hydrogen through a thin alloy membrane of Cu_3Au alloy as a function of reciprocal absolute temperature.

The influence of ordering is apparent. All data taken from the permeability experiments of Gol'tsov and co-workers [269].

TABLE 34. Hydrogen diffusion and permeation parameters in Cu_3Au [269]

T(°C)	Diffusion parameters		Permeation parameters	
	D_0(cm²/s)	Q(kcal·mol⁻¹)	P_0[c]	Q(kcal·mol⁻¹)
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^{-5}	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.

[c] Units are $cm^3 (H_2) \cdot mm \cdot cm^{-2} s^{-1} atm^{-1/2}$.

ing on both quantities is apparent after prolonged isothermal anneals at 350 °C. A model (which is really an extension of Krivoglaz and Smirov's theory [271]) to describe the anomalous changes in the hydrogen diffusion coefficients at the order-disorder transformation has been proposed by the same authors [272–275].

3.10. Cu-Au-Hg

Grain boundary diffusion coefficients of mercury into Cu-Au alloys have been reported [276]. These stress-corrosion studies yielded an indirect method of calculating an approximate diffusion coefficient for large-angle grain boundaries. Values of the grain boundary

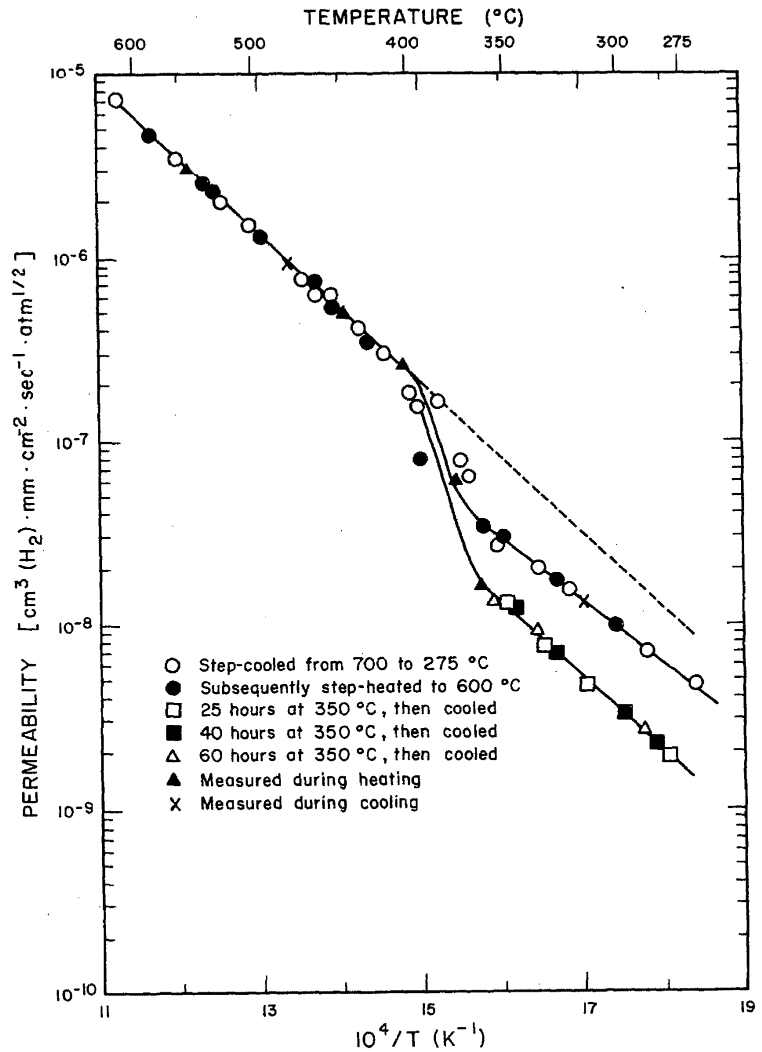

FIGURE 45. The permeability of hydrogen through a thin alloy membrane of Cu_3Au as a function of reciprocal absolute temperature.

The influence of ordering on the permeability rate is apparent. All data taken from the permeability experiments of Gol'tsov and co-workers [269].

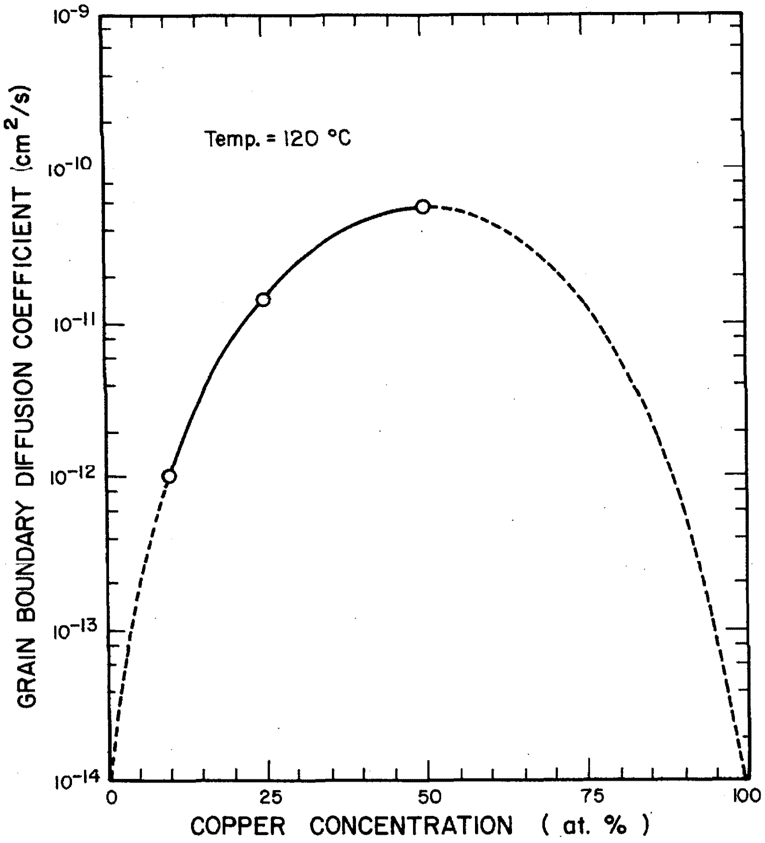

FIGURE 46. The grain boundary diffusion coefficient for mercury into copper-gold alloys as a function of composition at 120 °C.

Data and extrapolations are those of Graf and Klatte [276].

diffusion coefficient at 120 °C calculated from the few experimental points and the author's extrapolations are shown in figure 46.

In view of the way these values were obtained, their use should be with caution.

3.11. Cu-Au-Ni

The influence of small concentrations of gold (0.17 at. %) on the impurity diffusion coefficient of copper in nickel has been measured at 843, 903, and 1000 °C [277]. Thin films of copper were vapor-deposited onto high purity, low dislocation density nickel-gold single crystals. After diffusion, electron-microprobe analysis was used to determine the gold penetration. The copper impurity diffusion coefficients (obtained by using the thin film solution to the appropriate diffusion equations) in the dilute alloy shows very little deviation from the results obtained in pure nickel, except at the lowest temperature 843 °C, where there is a 29 percent increase in the value of the coefficient.

The effect of the mode of preparation of diffusion specimens on radioactive gold diffusion rates in copper-nickel alloys has been reported [278]. The results indicate that although a controlled metal distillation method was more practicable, no advantage over electrodeposition techniques could be found in this alloy system. No gold tracer diffusion coefficients were reported.

3.12. Cu-Au-O

The rate of oxygen diffusion in molten binary copper-gold alloys at 1205 ± 5 °C has been measured by El-Naggar and Parlee [279]. They found that the rate of absorption of oxygen gas by the alloys (containing up to 6 at. % gold) was controlled by diffusion in the liquid phase, thus the rate measurements could be used to calculate oxygen diffusivities in the molten alloy. The 5 atomic percent alloying addition was found to increase the oxygen diffusivity by a factor of 2 compared to pure copper at the same temperature.

3.13. Cu-Au-S

Abbott [280] has studied the mechanism of tarnishing of gold-copper alloys (containing 30, 50, and 70 at. %

gold) while exposed to sulfur and sulfur containing environments at low temperatures (~ 30 °C). The formation of the tarnish film on the alloys was found to be controlled either by diffusion in the surface film or diffusion in the near surface region of the copper-gold alloy.

3.14. Cu-Au-Sn

Interdiffusion between thin films of gold (10–20 μm) and tin (200 μm) electrodeposited on a copper substrate in the temperature range 23 to 212 °C has been described [267, 268]. An electronprobe microanalyzer was employed to measure concentration-penetration profiles after interdiffusion anneals ranging up to 11,500 hours. A wide variety of phases ($AuSn_2$, $AuSn_4$, $Cu_3Au_3Sn_5$, $Cu_4Au_2Sn_5$, Cu_5AuSn_5, and Cu_3Sn) were found in the interdiffusion zone. Interdiffusion coefficients were calculated only for the $AuSn_2$ and $AuSn_4$ phases.

3.15. Cu-Au-Zn

The rate of diffusion of zinc in a copper-zinc (6.5 at. %)-gold (2 at. %) alloy has been studied in the temperature range 870–1020 K by Gertsriken et al. [281].

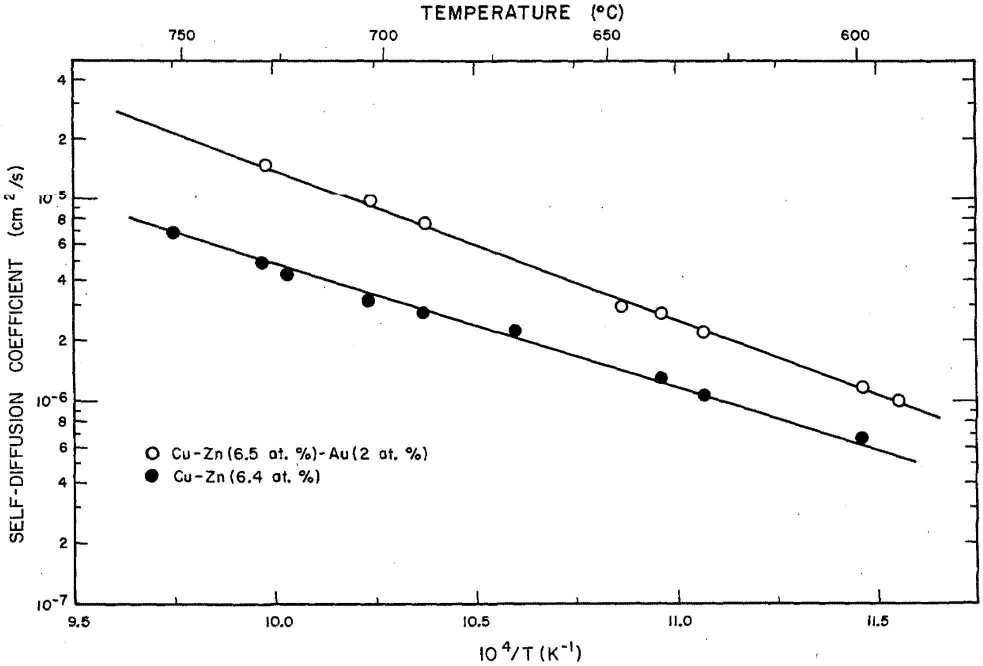

FIGURE 47. The apparent self-diffusion coefficient of zinc in a copper-zinc (6.5 at.%) – gold (2 at.%) alloy as a function of reciprocal absolute temperature.

The effect of a gold alloying addition to the binary alloy increases the zinc mobility. Data taken from the zinc evaporization experiments of Gertsriken and Dekhtyar [281].

The zinc diffusion rate was measured by evaporating the zinc from polycrystalline alloy foil (2 to 30 μm thick) specimens at a constant temperature in a vacuum, and following the weight change on a micro-balance. The weight loss was then related to a diffusion coefficient of the volatile component in the solid phase [282]. The "self-diffusion coefficients" calculated in this manner are plotted in figure 47 as a function of reciprocal absolute temperature, as well as the results from experiments performed concurrently where the specimens contained no gold content. The effect of the gold alloying additions was to increase the zinc mobility. The effects of using thin foils in these experiments (and how such were corrected for) were not discussed by the authors although they may have played important roles in the evaporation processes being measured.

3.16. Cu-Au-X

Thin electrodeposits of gold, silver, tin, and lead have been plated onto copper and brass and then interdiffused at temperatures between 23 and 212 °C [267, 268]. Times of interdiffusion were as long as 11,500 hours. Electron-microprobe analysis revealed the formation of a multitude of phases in the interdiffusion zone. No interdiffusion coefficients were calculated from the data.

Thin electrodeposits of gold, nickel, silver, tin, and copper have been plated onto phosphor-bronze substrates and then annealed at 127, 232, 371, and 538 °C [283]. No interdiffusion coefficients were reported.

3.17. Grain Boundary Diffusion

The grain-boundary diffusion of gold in copper has been investigated by Austin and co-workers [243, 244] and Chatterjee and Fabian [173]. Their results do not agree, the latter authors obtaining an activation energy of 20±3 kcal·mol^{-1} and the former a value of 25 kcal·mol^{-1}.

TABLE 35. Gold grain boundary diffusion coefficients at 750 °C measured by thick layer diffusion into 45° copper bicrystal [243]

Au concentration (at.%)	$D_{gb}\cdot\delta$(cm^3/s)	
	Method 1[a]	Method 2[b]
0.2	2.1×10^{-12}	1.0×10^{-12}
0.5	1.8×10^{-12}	1.0×10^{-12}
1.0	1.3×10^{-12}	1.0×10^{-12}
1.5	1.0×10^{-12}	1.0×10^{-12}
2.0	7×10^{-13}	1.0×10^{-12}
5.0	5×10^{-13}	7×10^{-13}
10.0	3.4×10^{-13}	3.2×10^{-13}
15.0		2×10^{-14}

[a] Calculated from slope of concentration contours.

[b] Calculated from grain-boundary concentration penetration.

Austin and co-workers prepared their grain boundary diffusion couple, both thick layer (125 μm) and thin layer (0.5 μm) sources by electroplating gold onto copper bicrystals having a 45° tilt boundary along a common [001] axis. The diffusion anneals were made in the temperature range 625 to 760 °C. After diffusion, gold concentration contours were measured on the specimens by electron-microprobe traverses. Results from the thick layer source couples were obtained by applying Whipple's solution [285]. The product of the gold grain-boundary diffusion coefficient (D_{gb}^{Au}) and grain-boundary width (δ) was calculated from values of parameters obtained from an exact solution to Whipple's analysis (Whipple's exact solution to the idealized grain-boundary diffusion problem was evaluated numerically for ranges of parameters appropriate to the experimental data) [243] and are listed in table 35. Suzuoka's solution [286] was applied to the results for the instantaneous or thin source case. The product of the gold grain-boundary diffusion coefficient and grain-boundary width for each temperature studied were averaged. These values are listed (with estimated errors) in table 36. Assuming the half-width of the grain boundary to be 2.5×10^{-8} cm, the gold grain-boundary diffusion rates are calculated and plotted as a function of reciprocal absolute temperature in figure 48. A linear temperature-dependence results and gives an activation energy of 25±2 kcal·mol^{-1} for the grain-boundary diffusion process.

Chatterjee and Fabian [173], obtained grain-boundary diffusion rates of gold in polycrystalline copper in the temperature range 400–700 °C using the instantaneous-source technique and radioactivation analysis (already described in some detail in an above section dealing with tracer diffusion). To obtain values for the gold grain-boundary diffusion coefficient, the logarithm of the gold concentration was plotted against the 6/5 power of the penetration distance for temperatures from 400 to 700 °C, and the results interpreted using Suzuoka's method [286]. When the coefficients (with an expected error of 10%) are plotted (see figure 48), a linear temperature-dependence is revealed. The activation energy obtained from the slope of the line is 20±3 kcal·mol^{-1}.

When one realizes the experimental and computational problems encountered and the many possible sources of error are considered, the order of magnitude difference between these two results does not seem surprising.

TABLE 36. Gold grain boundary diffusion coefficients measured from thin layer diffusion into 45° copper bicrystal [244]

T(°C)	$D_{gb}\cdot\delta$(cm^3/s)[a]
760	1.25×10^{-13}
706	6.4×10^{-14}
660	3.8×10^{-14}
625	1.9×10^{-14}

[a] Author estimates error to be ±20%.

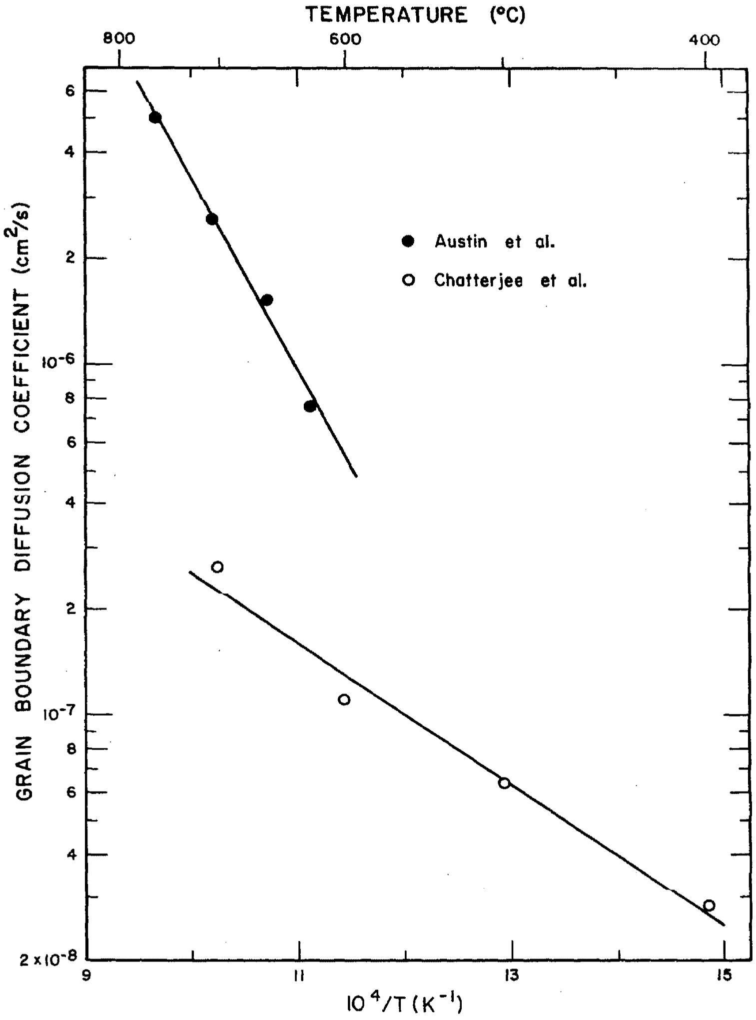

FIGURE 48. The grain boundary diffusion of gold in copper as a function of reciprocal absolute temperature.

A grain boundary half-width of 2.5×10^{-8} cm is assumed in the calculations. Data taken from published results of Austin and co-workers [244], and Chatterjee and Fabian [173].

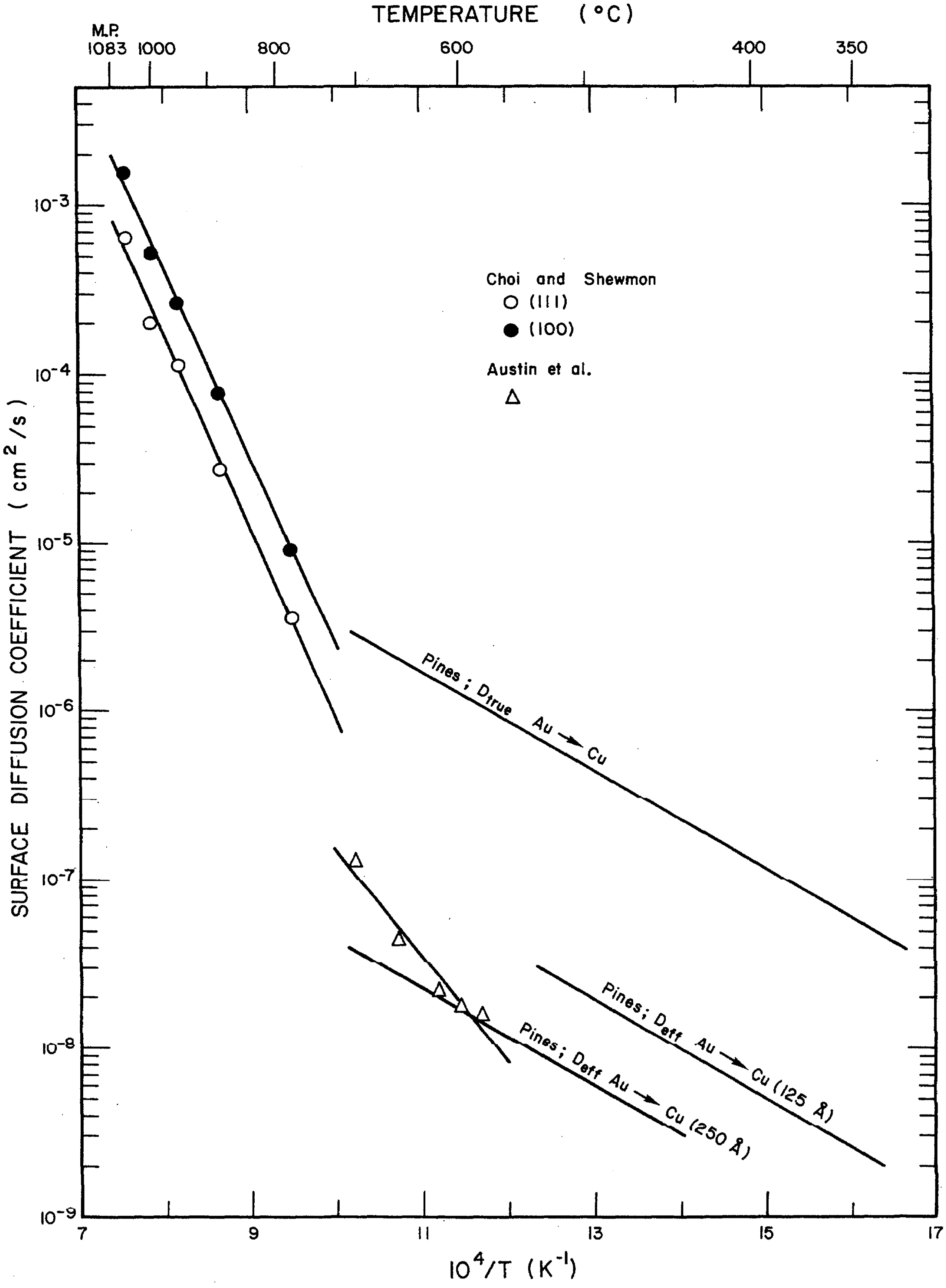

FIGURE 49. The surface diffusion coefficients of gold on copper as a function of reciprocal absolute temperature.

The results of Choi and Shewmon [180] are for gold diffusing on the (100) and (111) faces of pure copper. The straight line shown drawn through the data of Austin et al. [244] is obtained from a least squares analysis of their tabulated data and yields an activation energy of ~ 28 kcal·mol^{-1}. See the text for more detailed description of the coefficients measured by Pines and co-workers [255].

3.18. Surface Diffusion

The surface diffusion investigations in the copper-gold system [180, 244, 250, 287] are not in general agreement with each other (when it is possible to compare results). The disagreement (see figure 49) may be in part due to the fact that a different experimental technique was employed in each investigation as well as different mathematical approaches to the computations of the coefficients.

Choi and Shewmon [180] used a radioactive tracer (gold-198) and a "thin-layer" model (with a mathematical analysis given by Shewmon [288]) for the spreading of a tracer from a point source on the surface. With this approach, surface diffusion coefficients of gold-198 on the (100) and (111) surfaces of copper were measured in the temperature range between 780 and 1050 °C. The results are plotted as a function of reciprocal absolute temperature in figure 49. A straight line can be fitted to the data points and an Arrhenius expression obtained. The surface diffusion of the gold tracer on the (100) plane can be described by

$$D_s = 2.1 \times 10^5 \exp(-52{,}000 \text{ cal} \cdot \text{mol}^{-1}/RT) \text{ cm}^2/\text{s},$$

and on the (111) plane by

$$D_s = 3.6 \times 10^5 \exp(-51{,}100 \text{ cal} \cdot \text{mol}^{-1}/RT) \text{ cm}^2/\text{s}.$$

Choi and Shewmon, in their original paper, obviously interchanged the pre-exponential factors in the two Arrhenius equations. If one uses their original expressions, straight lines, somewhat removed from the data points, are obtained. Simply interchanging the values of the pre-exponential factors in the two equations will yield lines very close to the appropriate data points as well as comparing favorably with the Arrhenius plots shown in their paper.

Austin and co-workers [244] employed an infinite half-plane thin source and Whipple's analysis [285, 289]

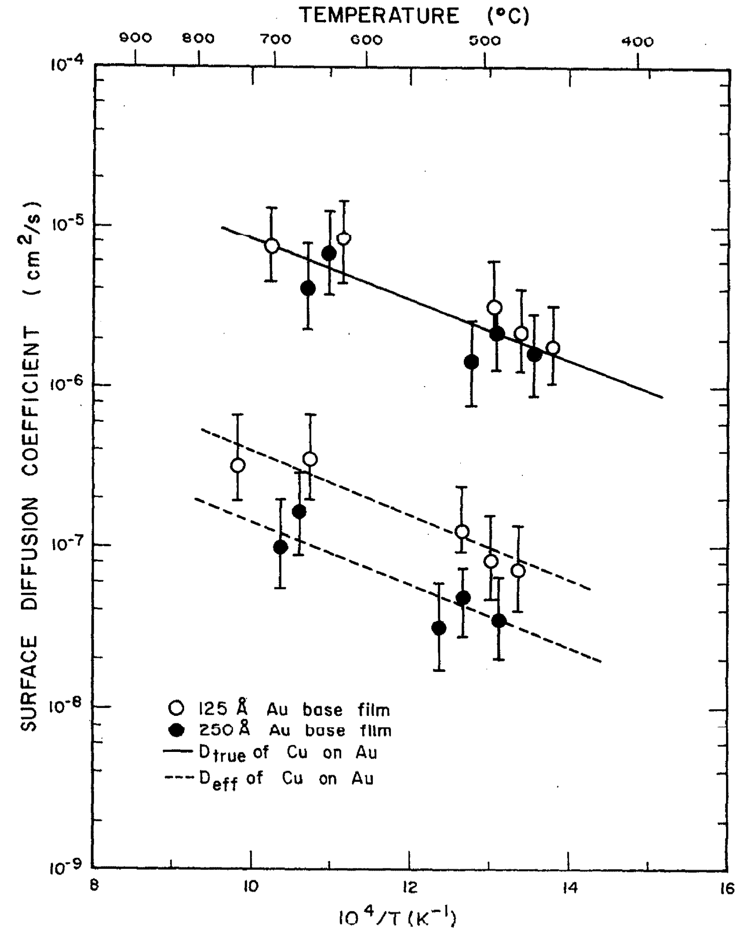

FIGURE 50. Surface diffusion coefficients of copper on gold as a function of reciprocal absolute temperature.

Data from the experiments of Pines et al. [255].

to measure the surface diffusion rate of gold on the copper (100) surface. Electron-probe microanalysis revealed the gold concentration gradients obtained from surface diffusion. The calculated values of the coefficients are plotted in figure 49. Although the mean slope of the straight line fitted to the data is for an activation energy of ~ 28 kcal·mol^{-1} the activation energy could vary from 20 kcal·mol^{-1} at 600 °C to as much as 30 kcal·mol^{-1} at 700 °C.

Pines and co-workers [255], working with thin films ($\sim 10^{-6}$ cm thick) of gold and copper, have measured surface diffusion coefficients with the aid of an electron diffraction technique [250, 261, 290]. The experiments though were plagued by complications arising from film thickness [255]. They tried to sort out some of the effects and report measuring a "true" as well as an "effective surface diffusion coefficient." Using thin film couples of different thicknesses (125 Å and 250 Å) such surface diffusion coefficients for gold on copper (200–500 °C) and copper on gold (480–930 °C) were obtained and are plotted in figures 50 and 51. The authors were able to fit straight lines to their data and calculate activation energies (for the surface diffusion of gold on copper $\simeq 16$ kcal·mol^{-1}; for copper on gold $\simeq 14$ kcal·mol^{-1}) for the processes. They also concluded that the values of both of the types of surface diffusion coefficients were dependent not only on the thickness of the specimens, but also on the lattice diffusion coefficients as well as the solid solubilities of the metals in each other.

Geguzin et al. [287] concerned themselves with surface self-diffusion occurring in surface layers of copper-gold alloys. Mullin's mass-transfer technique [291] was the essential mode of experimentation, with several modifications (as described in [292, 293]). Calculated from the data was the product $D_s\delta_s$, where D_s is a surface diffusion coefficient and δ_s is the depth of the subsurface layer (the depth of which is greater than the

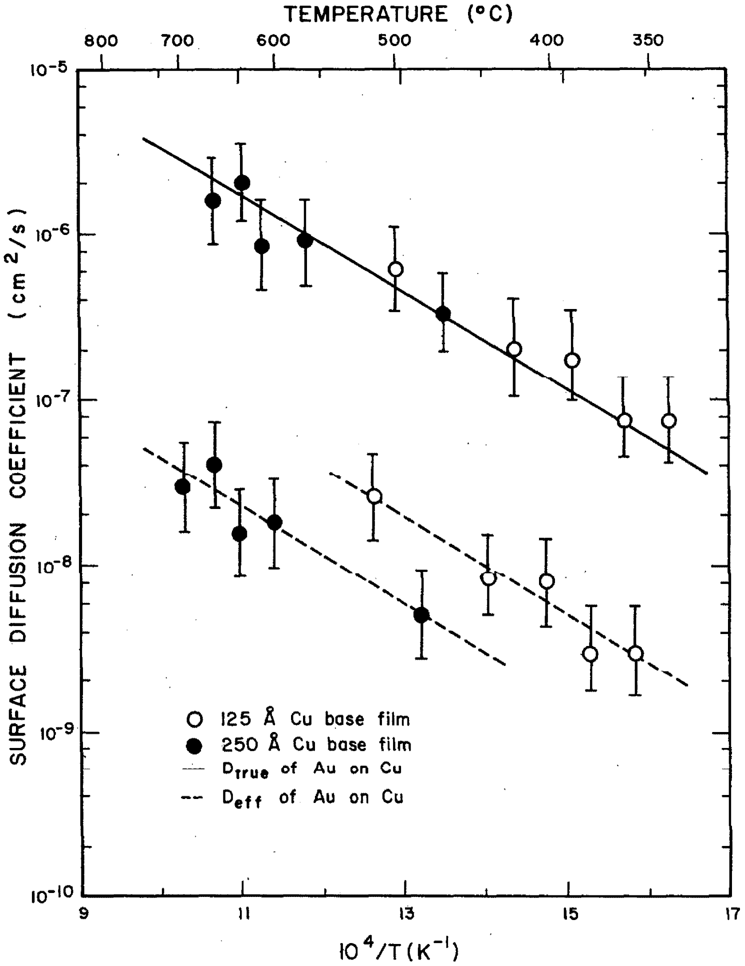

FIGURE 51. Surface diffusion coefficients of gold on copper as a function of reciprocal absolute temperature.

Data taken from the experiments of Pines et al. [255].

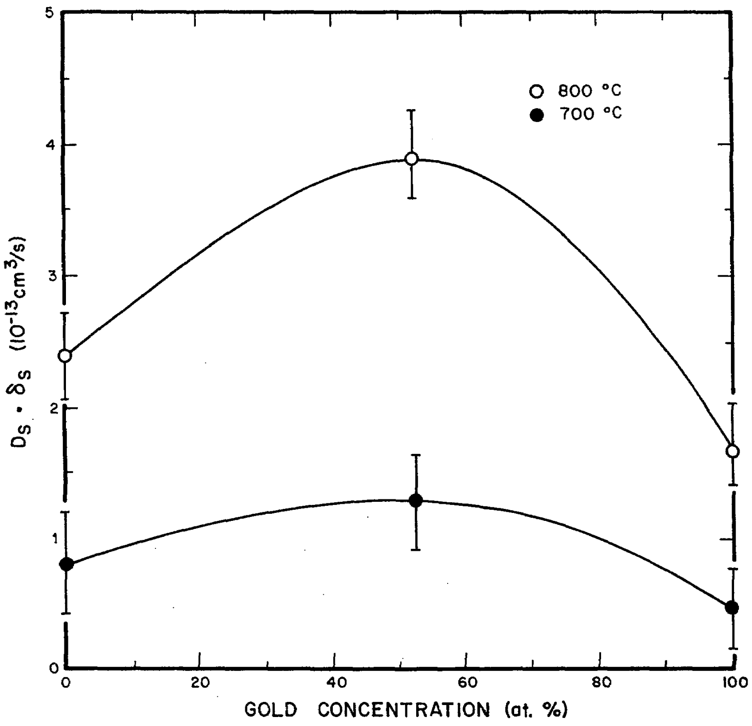

FIGURE 52. Product of an "average atom surface self-diffusion coefficient" and the depth of a subsurface layer as a function of composition.

In the subsurface layer, lattice diffusion contributions to the surface diffusion processes are occuring. The coefficient does not distinguish between copper and gold atoms. Data excerpted from the paper of Geguzin et al. [287].

interatomic spacing). The concentration dependence they obtained for the product $D_s\delta_s$ is plotted in figure 52. The surface self-diffusion coefficient being described here is some sort of "average atom surface self-diffusion coefficient" containing volume diffusion contributions.

3.19. Electromigration

Nehlep et al. [294] investigated the effects of passing a current (41,000 A/cm^2) through copper-gold alloys (containing approximately 35 wt % copper) at temperatures near 750 °C. X-ray analysis of the specimens after three months of current flow revealed that the gold concentrated at the anode, and the copper at the cathode.

3.20. Thermomigration

The phenomena of thermomigration in copper-gold alloys has been observed by Jaffe and Shewmon [295] and Darken and Oriani [296]. The latter investigation utilized alloy specimens containing 26.5 atomic percent gold whereas the former employed dilute alloys, containing radioactive gold-198 as an impurity. These experiments showed apparently opposite effects.

Darken and Oriani [296] found that after 32 days of holding one end of their alloy specimens at a temperature of 830 °C and the other end at 435 °C, copper had migrated to the hotter side. Lattice parameter measurements obtained from X-ray diffraction patterns revealed an enrichment in gold towards the lower temperatures. Oriani [297] indicates that the measured heat of transport in these experiments has a positive sign although no values for the quantity are reported.

Jaffee and Shewmon in their study [295] employed a steady-state technique which measured the stationary redistribution of radioactive gold-198 in a linear temperature gradient (the mean temperature being approximately 1000 °C). After sectioning and counting the amount of redistributed radioactivity in their diffused specimens, they found that the hotter side of their specimens had become *enriched* in gold rather than the colder side (as in the experiments of Darken and Oriani). Jaffee and Shewmon did calculate from their data an effective heat of transport (−4800±3000 cal/mol) using a rather elementary mathematical analysis.

The reason for the disagreement in the results is not readily apparent. Although Kostyukov's calculations [298] appear to lend some weight to the observations of Darken and Oriani, his mathematical analysis [299] (based on the model of Palatnik and Lynbchenko [300]) is incorrect, and thus cannot validate the results of either of the two above experimental investigations. Jaffee and Shewmon do appear to have performed a more elegant experiment which should give a more reliable result.

3.21. Molten Metals

Diffusion of oxygen in liquid copper-gold alloys is discussed in the above section on the Cu-Au-O system.

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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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