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Room temperature diffusion in polycrystalline materials: an experimental study of interdiffusion in AuCu alloys

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Interdiffusion in the macroscopic volume of an Au28Cu72 alloy at 293 to 435 K is observed by means of the movement of a thin (~ 1 nm) gold overlayer into the alloy during the time of annealing. The measured activation energy of 0.74 ± 0.07 eV is attributed to the migration of mono and divacancies which predominantly takes place in the grain boundaries. The lateral movement of a ~ 0.6 nm gold overlayer in a mechanically polished surface gives data on surface diffusion at around 330 K. Diffusion at room temperature in general is discussed. It is found that the diffusion coefficients exceed $10^{-27}\,\mathrm{m^2\,sec^{-1}}$ and activation energies are in the 40 to $100\,\mathrm{kJ\,mol^{-1}}$ range for low temperature diffusion in the macroscopic volume of most polycrystalline materials.

1. Introduction

A very detailed interpretation of the energetic properties of mono and divacancies in copper exists in the literature [1,2] although experimental data on self and interdiffusion at low temperatures ($\lesssim 600$ K) are lacking. A deviation from a straight Arrhenius relationship ($\mathrm{d}\log D/\mathrm{d}1/T \neq$ constant) in diffusion kinetics is both theoretically and experimentally significant and many sources for such an "anomaly" are proposed [2].

Most materials (with exceptions like semiconductors) used in practice are polycrystalline and serve near room temperature for considerable times. A general view point is that grain boundary diffusion dominates over lattice diffusion at sufficiently low temperature, and it is recognized that extrapolation of high temperature diffusion data down to room temperature is most elusive.

The aim of the present work is to gain better knowledge about the diffusion of polycrystalline materials near room temperature. Primarily the interdiffusion in the macroscopic volume of an Au28Cu72 alloy is measured (grain size ~ 0.2 mm) at 293 to 435 K. These low temperature data are interpreted, together with data from high temperature diffusion in the light of the existing data on vacancies in copper.

The present investigation shows how this low temperature diffusion depends on the grain size. In addition the magnitude of surface diffusion near room temperature in a typical free macroscopic surface is considered.

2. Experimental method

2.1. Terminology, preparation of alloys and creation of gold overlayer for diffusion experiments

The principal locations of diffusion in a polycrystalline sample are sketched in Fig. 1. The terminology in this figure is used in this paper.

The alloys were melted in vacuum and heat treated at 700 to 850° C for times up to 1000 h to produce single phase alloys with various grain size. The homogeneity of the alloys were checked by lateral line scans in a scanning electron microscope with three wave length dispersive spectrometers and one energy dispersive X-ray spectrometer. The chemical composition of the alloys as revealed by this analysis was 28 ± 1 at % and 30 ± 1 at %, respectively (lateral resolution $\sim 1\,\mu$m). The grain size was evaluated by visual inspection after chemical etching in KCN solution. The three different alloys with average grain size are shown in Table I.

Before the experimental work the Au28Cu72 alloy was kept at room temperature for one year. Samples of three alloys were mechanically polished with $1\,\mu$m diamond paste in ethanol except in one case where the chemical etched surface was used. In this condition the samples were immersed in a 1% NaCl containing water (pH $\sim$ 6). During such an immersion a selective dissolution of copper from the alloy surface takes place. The mechanism and kinetics of this phenomenon is discussed in [3]. The excess of gold in the surface due to the removal of copper has been evaluated from gamma spectrometry measurements of the gold and the copper present in the NaCl solution. A surface excess of gold amounting to $1.5\,\mu\mathrm{g\,cm^{-2}}$, slightly depending on time of immersion (50 to 100 h), was found [4].

The gold overlayers used in the diffusion experiments were 0.6 to 1 nm thick (see experimental method in [3] for the evaluation). The procedure of polishing (whereby $> 10\,\mu$m alloy was removed) and immersion in NaCl containing water (giving the gold overlayers) preceded all diffusion experiments with one exception already mentioned. These experiments were carried out in vaccum ($P_{O_2} < 10^{-4}\,\mathrm{N\,m^{-2}}$). Electron spectroscopy for chemical analysis (ESCA) was used

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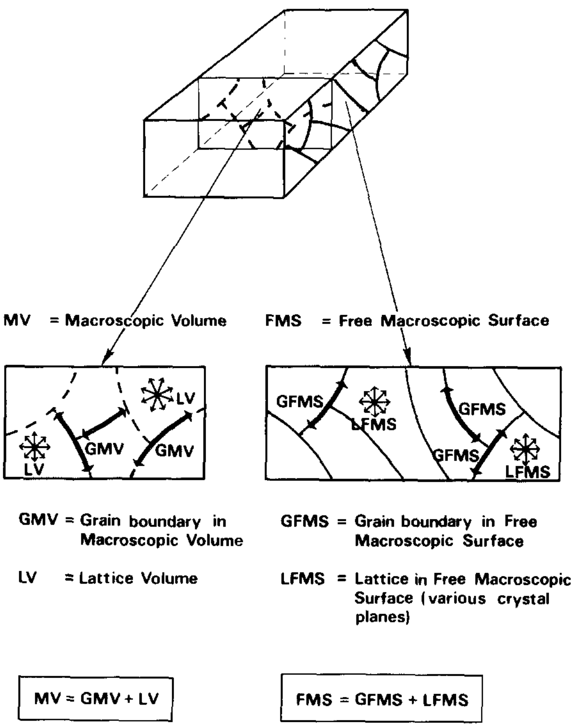

Figure 1 Principle locations of diffusion in a polycrystalline sample.

to probe the gold surface content against time of annealing.

2.2. Evaluation of composition profiles and interpretation of results from ESCA analysis in the experiments of macroscopic volume diffusion

The distribution of gold, (Au)/(Au + Cu), as a function of depth before and during these diffusion experiments of the alloys is given by the expression

$$f(x) = \left(\frac{\text{Au}}{\text{Au} + \text{Cu}}\right)$$

$$= C_0 + \frac{C_s - C_0}{2}\left[\text{erf}\,\frac{x + d_0}{2(Dt)^{1/2}} - \text{erf}\,\frac{x - d_0}{2(Dt)^{1/2}}\right] \quad (1)$$

where C_0 is the inner composition, C_s is the outer composition, d_0 is the thickness of gold overlayer, D is the diffusion coefficient (interdiffusion), and t is the time of annealing.

Graphs of this distribution with $(Dt)^{1/2}$ values 0.2, 0.5 and 2.5 nm with $d_0 = 0.8$ nm of the Au28Cu72 alloy are shown in Fig. 2.

ESCA, Leybold Hereaus LH2000, was used to evaluate the chemical compositions in the alloy surface. Al$K\alpha$ radiation was used for excitation of the photo and Auger electrons. Quantification of the surface compositions of the alloy was based on Cu($2p_{3/2}$), Cu($L_3M_{2,3}M_{4,5}$), Au($4d_{3/2}$) and Au($4d_{5/2}$) lines using standards of gold and copper. The compositions are presented on the form Au/(Au + Cu) (atomic ratio).

TABLE I Characterization of alloys/samples

Nominal alloy composition (± 1 at %)	Average grain size (mm)	Sample dimensions (mm)	Diffusion experiment
Au28Cu72	0.2	14 × 10 × 0.5	volume
Au30Cu70	0.3	15 × 15 × 2	volume, surface
Au30Cu70	0.03	14 × 8 × 0.5	volume

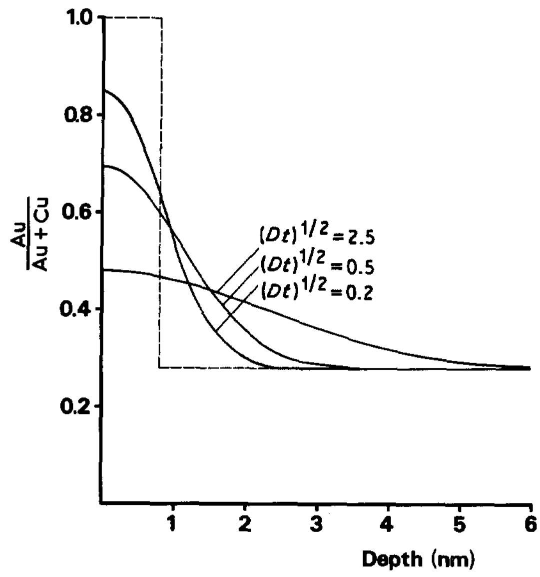

Figure 2 Composition profile before and during diffusion experiment according to Equation 1. $f(x) = 0.28 + 0.36$ [erf($x + d_0/2(Dt)^{1/2}$) − erf($x - d_0/2(Dt)^{1/2}$)] (---) Before diffusion experiment [$(Dt)^{1/2} = 0$].

The ESCA electrons have mean free path λ in the material, so that the relative intensity of electrons emitted at depth x is λ^{-1} exp $(-x/\lambda)$ at the surface. The total signal from the composition profile $f(x)$ in Equation 1 will then be

$$\left(\frac{\text{Au}}{\text{Au} + \text{Cu}}\right)_{\text{meas}} = \int_0^\infty f(x)\,\frac{1}{\lambda}\,e^{-x/\lambda}\,\mathrm{d}x \quad (2)$$

The integral is evaluated to

$$\left(\frac{\text{Au}}{\text{Au} + \text{Cu}}\right)_{\text{meas}} = C_0 + \frac{C_s - C_0}{2}\left\{2\,\text{erf}\,\frac{d_0}{2(Dt)^{1/2}} + \exp\left(\frac{d_0}{\lambda} + \frac{Dt}{\lambda^2}\right)\left[1 - \text{erf}\,\frac{d_0}{(Dt)^{1/2}} + \frac{(Dt)^{1/2}}{\lambda}\right] - \exp\left(-\frac{d_0}{\lambda} + \frac{Dt}{\lambda^2}\right)\left[1 - \text{erf}\left(-\frac{d_0}{2(Dt)^{1/2}} + \frac{(Dt)^{1/2}}{\lambda}\right)\right]\right\} \quad (3)$$

The signal $(\text{Au/Au} + \text{Cu})_{\text{meas}}$ corresponding to different values of $(Dt)^{1/2}$ and d_0 of the Au28Cu72 alloy is shown in Fig. 3 ($\lambda = 1.5$ nm).

3. Experimental results

3.1. Diffusion in free macroscopic surface

The conditions in this experiment are shown in Fig. 4 (○△). The gold overlayer was initially removed from a surface area of 15 mm × 1 mm by mechanical means. The lateral movement of the ~ 0.6 nm thick gold overlayer causes the increase in $(\text{Au/Au} + \text{Cu})_{\text{meas}}$ during annealing. The time, t, required to obtain ~ one new gold monolayer is ~ 1 h and ~ 17 h at 383 K and 325 K, respectively. A diffusion length l equals 5×10^{-4} m used in the relation $l = (2Dt)^{1/2}$ gives diffusion coefficients of $4 \times 10^{-11}\,\text{m}^2\,\text{sec}^{-1}$ at 383 K and $2 \times 10^{-12}\,\text{m}^2\,\text{sec}^{-1}$ at 325 K. These data are

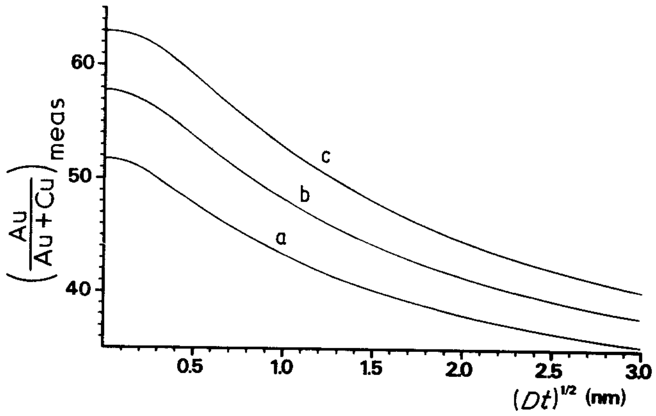

Figure 3 Measured gold surface contents, (Au/Au + Cu)$_{meas}$ against $(Dt)^{1/2}$ according to Equation 3. (Au/Au + Cu)$_{meas}$ = $\int_0^\infty f(x)\ 1/\lambda \exp(-x/\lambda)\ dx$, with λ = 1.5 nm. (a) d_0 = 0.6 nm, (b) d_0 = 0.8 nm, (c) d_0 = 1.0 nm.

plotted in Fig. 5 for the purpose of comparison with data from macroscopic volume diffusion.

3.2. Diffusion in macroscopic volume

The decrease rates of the measured gold surface content (Au/Au + Cu)$_{meas}$ against time of annealing are illustrated in Fig. 4 (●▲). Similar results, (Au/Au + Cu)$_{meas}$, after anneal of the alloys at various temperatures and times are summarized in Table II. From the curves of the (Au/Au + Cu)$_{meas}$ against $(Dt)^{1/2}$ (as shown in Fig. 3) the diffusion coefficients, D, are calculated and shown in Table II. Mean values of these diffusion coefficients are plotted in Fig. 5 together with data from the literature on high temperature diffusion of gold in gold [5], gold in copper [6] and copper in copper [7].

In Table III the energetic properties of mono and divancancies in copper from [1] and [2] are collected together with pre-exponential factors from high temperature diffusion experiments. These data determine the straight lines D_3 and D_4 as well as the slopes of D_1 and D_2 illustrated in Fig. 6. The pre-exponential factors of D_1 and D_2 are extracted from a fit of the sum $D = D_1 + D_2 + D_3 + D_4$ (solid line in Fig. 6) to the experimental data.

In a plot against temperature, Fig. 7 displays the activation energy of self diffusion from [8]. The solid line in this figure corresponds to the slope of the solid line in Fig. 6, while the hatched line is a simple approximation to all data with the numerical value indicated in the figure caption.

4. Discussion

4.1. Diffusion in macroscopic volume

The total diffusion D of a material can be considered as superposition of n partial diffusion coefficients D_i

$$D_i = D_{0_i} \exp - \frac{Q_i}{kT} \qquad D = \sum_{i=1}^{i=n} D_i$$

Each value of Q_i corresponds to a descrete activation energy. A perfect single crystal in thermal equilibrium has Q values corresponding to the formation and migration ($Q_i = E_F + E_M$) of dislocations as mono and divacancies. In a polycrystalline sample there is a considerable concentration of vacancies in the grain boundaries at all temperatures. Consequently, the Q values at low temperatures for polycrystalline materials are expected to be determined by the energies associated with migration of already existing dislocations (E_M) rather than with formation and migration ($E_F + E_M$).

The activation energies of grain boundary diffusion for fcc metals are approximately half the values for lattice diffusion. The energy required for migration of monovacancies is roughly half the energy needed for formation plus migration of these dislocations. These circumstances support the above interpretation of the Q values.

The present study gives a Q value of 0.74 ± 0.07 eV as shown in Fig. 5. In resistivity annealing of quenched copper around 400 K an activation energy of 0.85 ± 0.15 eV was found [9]. The activation energy for grain boundary diffusion at 700 K of gold in

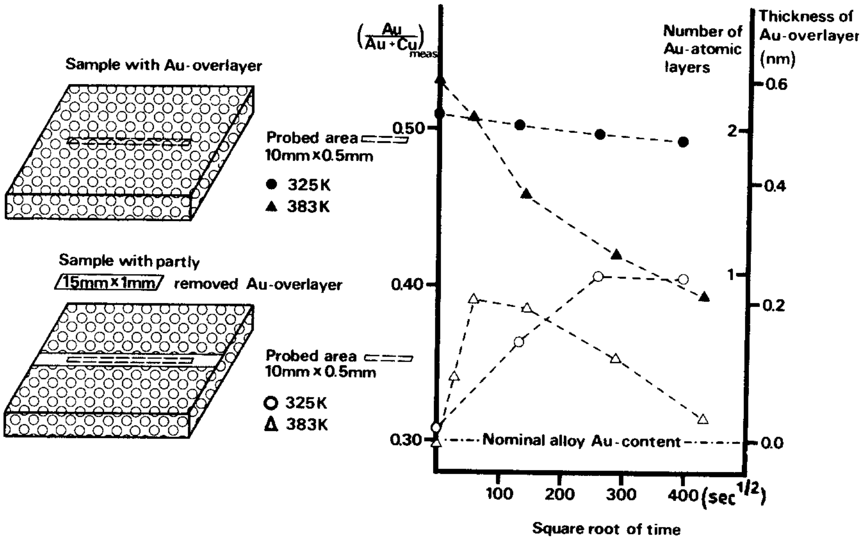

Figure 4 Interdiffusion in free macroscopic surface (○△) and macroscopic volume (●▲) of an Au30Cu70 alloy (0.3 mm grain size). The ordinate to the right is valid for: (○△) time ⩾ 0, (●▲) time = 0.

TABLE II Results on gold surface contents: before diffusion experiments as thickness of pure gold overlayers and after as $(\text{Au}/\text{Au} + \text{Cu})_{\text{meas}}$. Diffusion coefficients according to Equation 3

~ grain size (mm)	d_0(nm)	T(K)	$(\text{Au}/\text{Au} + \text{Cu})_{\text{meas}}$	$(Dt)^{1/2}$(nm)	t(h)	D(m^2 sec^{-1})
0.2	0.97	293	0.550	0.75	816	1.9×10^{-25}
0.2	0.97	293	0.535	0.87	1872	1.2×10^{-25}
0.2 (etched)	0.97	293	0.500	1.19	4200	9.4×10^{-26}
0.2	0.88	293	0.530	0.95	2980	8.4×10^{-26}
0.2	0.64	309	0.505	0.38	52	8.0×10^{-25}
0.2	1.0	325	0.584	0.56	40	2.2×10^{-20}
0.2	1.0	325	0.514	1.12	96	3.6×10^{-20}
0.2	1.0	325	0.473	1.55	212	3.1×10^{-20}
0.2	0.95	335	0.503	1.11	50	6.8×10^{-24}
0.2	0.79	373	0.512	0.68	2	6.4×10^{-23}
0.2	0.79	373	0.442	1.45	16	3.7×10^{-23}
0.2	0.79	373	0.411	2.04	28	4.1×10^{-23}
0.2	0.76	435	0.479	0.94	0.08	2.9×10^{-21}
0.2	0.76	435	0.430	1.56	0.58	1.2×10^{-21}
0.2	0.94	435	0.350	5.3	2	3.9×10^{-21}
0.2	1.0	435	0.33	8	14	1.3×10^{-21}
0.2	1.0	473	0.287	> 25	50	$> 5 \times 10^{-21}$
0.3	0.60	325	0.497	0.20	19	9.0×10^{-25}
0.3	0.60	325	0.493	0.30	43	6.0×10^{-25}
0.3	0.66	383	0.504	0.45	1	5.6×10^{-23}
0.3	0.66	383	0.458	0.93	6	4.0×10^{-23}
0.3	0.66	383	0.420	1.45	23	2.4×10^{-23}
0.3	0.66	383	0.393	2.0	51	2.3×10^{-23}
0.03	0.98	325	0.516	1.13	40	9.0×10^{-24}
0.03	0.98	325	0.455	1.88	96	1.0×10^{-23}
0.03	0.98	325	0.408	2.9	212	1.1×10^{-23}
0.03	0.56	383	0.441	0.6	0.5	5.6×10^{-22}
0.03	0.56	383	0.389	1.4	1.5	3.6×10^{-22}

copper was measured to 0.87 ± 0.13 eV [6]. According to Table III the migration energies of mono and divacancies in copper are 1.06 and 0.67 eV, respectively. The activation energy obtained in the present work agrees well with the previous measurements [6, 9] and shows that divacancy migration dominates over monovacancy migration in room temperature diffusion.

If we denote the activation energy for divacancy migration with Q_{m_2} then the corresponding diffusion coefficient D_{T} is

$$D_{\text{T}} = D_{0_{\text{m}_2}} \exp - Q_{\text{m}_2}/kT$$

and $D_{\text{T}=\infty} = D_{0_{\text{m}_2}}$ is the diffusion coefficent when all existing divacancies are activated to migrate. The pre-exponential factor D_{0_1} in Fig. 6 is coupled to the grain size 0.2 mm. By changing the grain size by a factor of ten we also expect a change of D_{0_1} by a factor of ten. This is also fairly well supported by the experimental results in Fig. 5. By extrapolating the grain size down to the size of the grain boundary, $\sim 10^{-9}$ m, we find the pre-exponential factor $D_{0_{\text{m}_2}} = (2 \times 10^{-4}/10^{-9}) \times 10^{-13} = 2 \times 10^{-8}$ m^2 sec^{-1}. In the same way we find $D_{0_{\text{m}_1}} = (2 \times 10^{-4}/10^{-9}) \times 10^{-9} = 2 \times 10^{-4}$ m^2 sec^{-1}. Furthermore, we find that the concentration of divacancies is equal to

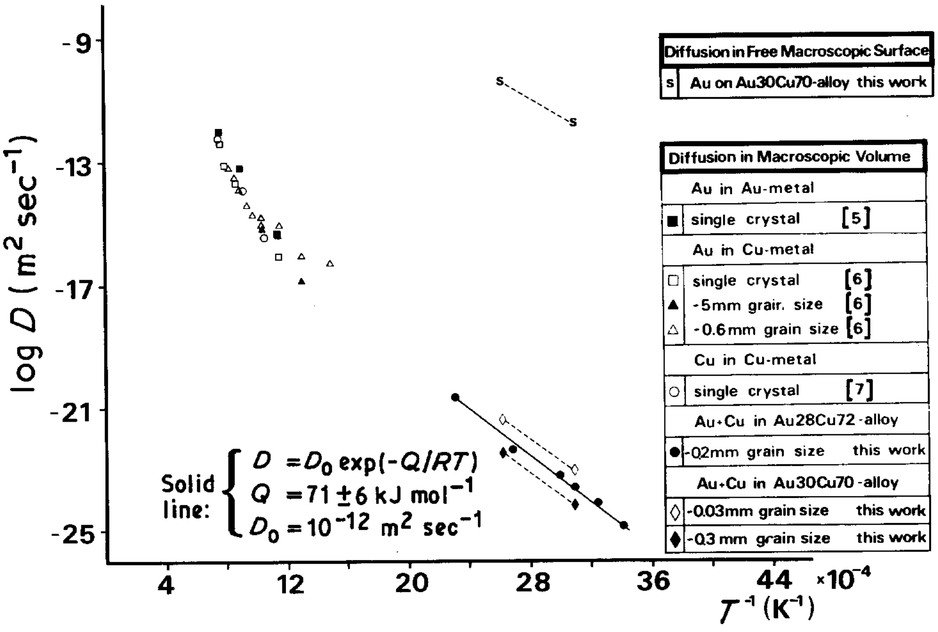

Figure 5 Logarithm of diffusion coefficient against $1/T$ where the present data are fitted by straight lines.

TABLE III Properties of mono and divacancies in copper from [1] and [2]

	monovacancies	divacancies
Activation energy of migration	1.06 eV	0.67 eV
Activation energy of formation plus migration	2.09 eV	2.67 eV
Pre-exponential factor formation plus migration	$2 \times 10^{-5}\,\mathrm{m^2\,sec^{-1}}$	$2.8 \times 10^{-3}\,\mathrm{m^2\,sec^{-1}}$

10^{-4} times the concentration of monovacancies (D_{0_1}/D_{0_2} in Fig. 6).

Thick overlayers and thin samples can naturally suppress the net mass transport due to saturation in the grain boundaries at low temperatures. However, this is not the case in the present study as indicated by the time independent diffusion coefficents found in Table II.

In one experiment a chemically etched sample surface was used instead of the 1 μm mechanically polished surface finish. However, the rate of diffusion as seen in Table II was similar for both surface preparations which indicates the density of grain boundaries is the most important parameter for the diffusion kinetics in the present experiments on room temperature diffusion.

Since most metals have energies for vacancy migration in the 0.5 to 1 eV range we expect to find these values whenever measurements of activation energies are made near room temperature. This prediction is supported in Fig. 7 where all listed data on self diffusion from [8] are collected.

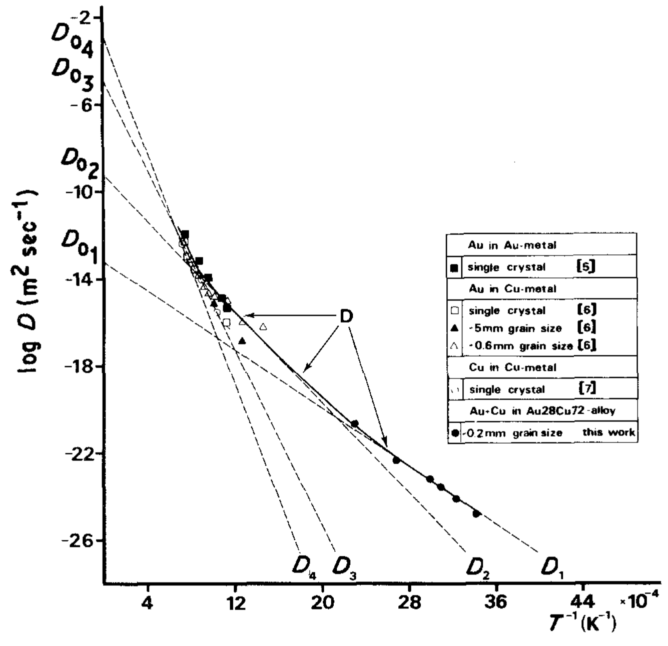

Figure 6 Logarithm of diffusion coefficient against $1/T$ where the present data and literature data are fitted by the sum (D) of four diffusion coefficients (D_1, D_2, D_3, D_4) given by solid line. Grain boundary diffusion: $D_1 = D_{0_1} \exp(-Q_1/kT)$, $Q_1 = 0.67\,\mathrm{eV}$, $D_{0_1} = 10^{-13}\,\mathrm{m^2\,sec^{-1}}$. $D_2 = D_{0_2} \exp(-Q_2/kT)$, $Q_2 = 1.06\,\mathrm{eV}$, $D_{0_2} = 10^{-9}\,\mathrm{m^2\,sec^{-1}}$. Lattice diffusion: $D_3 = D_{0_3} \exp(-Q_3/kT)$, $Q_3 = 2.09\,\mathrm{eV}$, $D_{0_3} = 2 \times 10^{-5}\,\mathrm{m^2\,sec^{-1}}$. $D_4 = D_{0_4} \exp(-Q_4/kT)$, $Q_4 = 2.67\,\mathrm{eV}$, $D_{0_4} = 2.8 \times 10^{-3}\,\mathrm{m^2\,sec^{-1}}$.

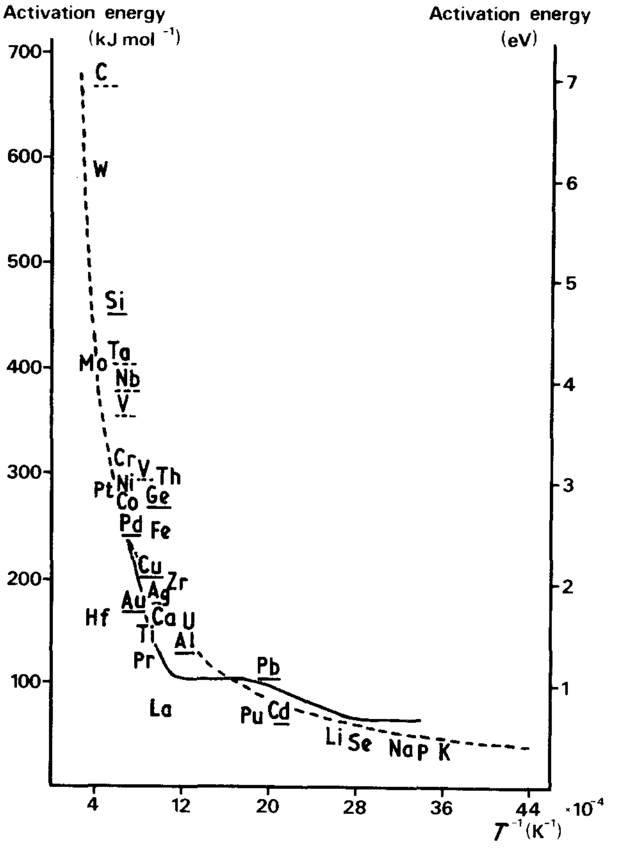

Figure 7 Activation energy against $1/T$ in self diffusion according to [8]. Temperature T is mean temperature in a temperature interval where the activation energy is given in [8]. $\underline{\times}$ Single crystal, × polycrystal, × single and polycrystal. (——) From solid line in Fig. 6. (– – –) $Q/T = 0.17\,\mathrm{kJ\,mol^{-1}\,K^{-1}} = 1.7 \times 10^{-3}\,\mathrm{eV\,K^{-1}}$.

A study [10] of the parabolic oxidation kinetics of copper, iron and chromium, gives the following results for the apparent diffusion coefficent and the activation energy in the temperature interval 295 to 450 K: $10^{-24}\,\mathrm{m^2\,sec^{-1}}$ and 0.9 eV respectively, for copper oxide, $10^{-25}\,\mathrm{m^2\,sec^{-1}}$ and 0.8 eV respectively, for iron oxide and $5 \times 10^{-27}\,\mathrm{m^2\,sec^{-1}}$ and 0.5 eV, respectively, for chromium oxide. These data indicate relatively small variations in transport rates of different polycrystalline materials near room temperature.

5. Conclusions

5.1. Macroscopic volume diffusion

1. The interdiffusion at room temperature in an Au28Cu72 alloy with grain size ~0.2 mm range is measured, and the following values are obtained for the diffusion coefficient, the pre-exponential factor and the activation energy: $10^{-25}\,\mathrm{m^2\,sec^{-1}}$, $10^{-13}\,\mathrm{m^2\,sec^{-1}}$ and $0.74 \pm 0.07\,\mathrm{eV}$.

2. The diffusion in the temperature range $295\,\mathrm{K} < T < 1000\,\mathrm{K}$ in gold–copper can be expressed as a superposition of four independent contributing diffusion coefficients, each one of the form $D_i = D_{0_i} \exp - Q_i/kT$.

3. Two Q values correspond to the migration of mono and divacancies and another two Q values are associated with the simultaneous formation and migration of mono and divacancies.

4. The Q values are 40 to 100 kJ mol^{-1} in most polycrystalline materials near room temperature. Only a perfect single crystal can give a higher value at room temperature.

5. The present author believes that the diffusion coefficients generally exceed 10^{-27} m^2 sec^{-1} in polycrystalline materials at room temperature.

5.2. Macroscopic free surface diffusion

Surface diffusion in a mechanically polished free surface gives a diffusion coefficient in the 10^{-12} m^2 sec^{-1} range at 325 K.

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