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Self-Diffusion in Copper*

A. Kuper, H. Letaw, Jr., L. Slifkin, E. Sonder, and C. T. Tomizuka
Department of Physics and Electrical Engineering Research Laboratory, University of Illinois, Urbana, Illinois

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The self-diffusion coefficient of copper has been determined by tracer techniques through the use of a precision grinder and a precision lathe. The temperature dependence over the range 685—1062°C is given by $D=0.468\exp(-47\,140/RT)$ cm²/sec.

INTRODUCTION

SELF-DIFFUSION of copper has been studied by a number of investigators.[1] The temperature range and accuracy of the measurements have been severely limited by the short half-life of the only available isotope, 12.88-hr Cu^{64}. The present determination was undertaken because of the availability of a precision grinding machine for diffusion studies.[2] The precision grinder permits the determination of diffusion coefficients when mean penetrations are of the order 1μ or greater. The high sensitivity of this method is of particular applicability in the case of a short-lived isotope.

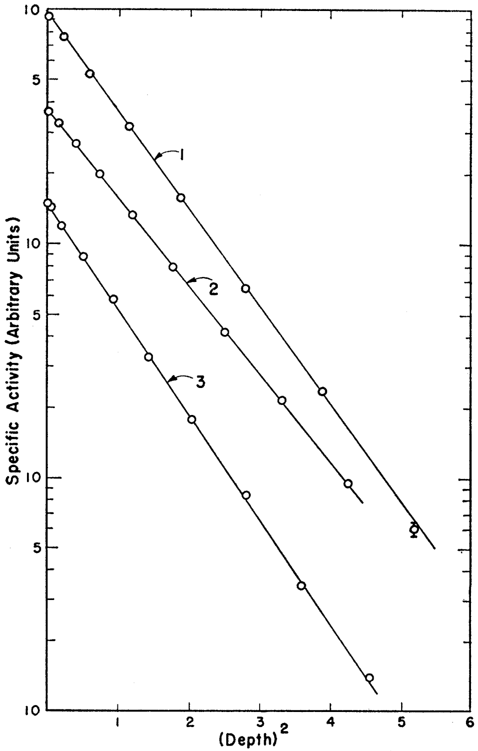

FIG. 1. Penetration curves for specimens sectioned on a lathe. See Table I for the scaling factors for the distance.

EXPERIMENTAL

Cylindrical single-crystal specimens were prepared in vacuum from American Smelting and Refining Company spectroscopically pure copper using procedures described earlier.[3] The specimens were electroplated with layers of Cu^{64} of the order of 50A thick from an acidic $CuNO_3$ solution. The radioactive Cu^{64}, obtained from the Oak Ridge National Laboratory, was found to be contaminated with small amounts of long-lived impurities. These, since they diffused into the samples more rapidly than copper, caused some of the penetration plots to deviate from linearity at the larger penetration depths (curves 4, 6, and 7 in Fig. 2). Diffusion coefficients were determined from penetration curves which were corrected for the residual specific activity of the impurities. This difficulty was subsequently eliminated by the use of spectroscopically pure copper irradiated at Oak Ridge.

The plated specimens were annealed for periods of 8 to 48 hours at temperatures held constant to within ±1°C. Specimens which were annealed at temperatures above 820°C (penetrations $>100\mu$) were sectioned on a lathe and analyzed by beta-counting techniques used previously.[4] The precision grinder was employed to section the other specimens (penetrations $10\text{–}100\mu$), beta counting being carried out as described.[2]

RESULTS

Eight successful measurements were performed over the temperature range 1062—660°C. The penetration

TABLE I. Self-diffusion in copper.

Curve	Unit of (depth)² (cm²)	Slicing method	Temperature (deg C)	Time (sec)	D (cm²/sec)
1	6.45×10^{-4}	lathe	1063	4.1×10^{4}	4.12×10^{-9}
2	2.58×10^{-4}	lathe	936.7	1.26×10^{5}	5.91×10^{-10}
3	6.45×10^{-5}	lathe	839.0	1.49×10^{5}	1.05×10^{-10}
4	7.37×10^{-6}	grinder	812.2	3.32×10^{4}	6.80×10^{-11}
5	5.16×10^{-6}	grinder	765.2	1.06×10^{5}	2.20×10^{-11}
6	2.34×10^{-6}	grinder	715.5	1.21×10^{5}	7.92×10^{-12}
7	1.11×10^{-6}	grinder	684.8	1.40×10^{5}	3.71×10^{-12}
8	7.37×10^{-7}	grinder	660.2	1.40×10^{5}	2.53×10^{-12}

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[1] For instance, B. V. Rollin, Phys. Rev. **55**, 231 (1939); Steigman, Shockley, and Nix, Phys. Rev. **56**, 13 (1939); and M. S. Maier and H. R. Nelson, Trans. Am. Inst. Mining Met. Engrs. **147**, 39 (1942).

[2] Letaw, Slifkin, and Portnoy, Phys. Rev. **93**, 892 (1954); Rev. Sci. Instr. (to be published).

[3] Sonder, Slifkin, and Tomizuka, Phys. Rev. **93**, 970 (1954).

[4] C. T. Tomizuka and L. Slifkin, Phys. Rev. **96**, 610 (1954).

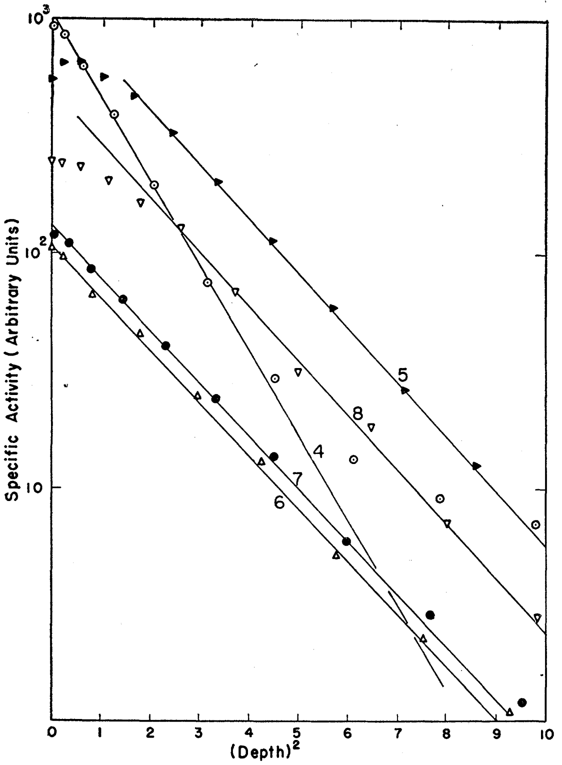

FIG. 2. Penetration curves for specimens sectioned by a grinding machine. See Table I for the scaling factors.

curves for the three specimens sectioned on the lathe are shown in Fig. 1, while those obtained on the precision grinder are plotted in Fig. 2. The scaling factors for these curves as well as a summary of the data are shown in Table I. The logarithms of the diffusion coefficients are plotted against the reciprocal of the absolute temperature in Fig. 3. A least-squares calculation gives the temperature dependence over the range 1062–685°C as

$$D=0.468\exp(-47\,140/RT)\ \text{cm}^2/\text{sec}.$$

The number of measurements and the temperature range *statistically* determine the activation energy to 0.005 percent and the frequency factor to 6 percent. These figures seem too optimistic, since systematic errors of unknown origin probably can exceed the estimated range of errors.

The three upper points in Fig. 3 were double-weighted in the calculation since the maximum probable error in the lathe technique was 2 percent, while the grinding machine yielded data with an accuracy of about 5 percent. The lowest-temperature point in Fig. 3 was not included in this calculation since its deviation from the best least-squares straight line was much greater than could be accounted for by possible systematic errors. Further diffusion coefficients will be obtained in the neighborhood of this temperature in

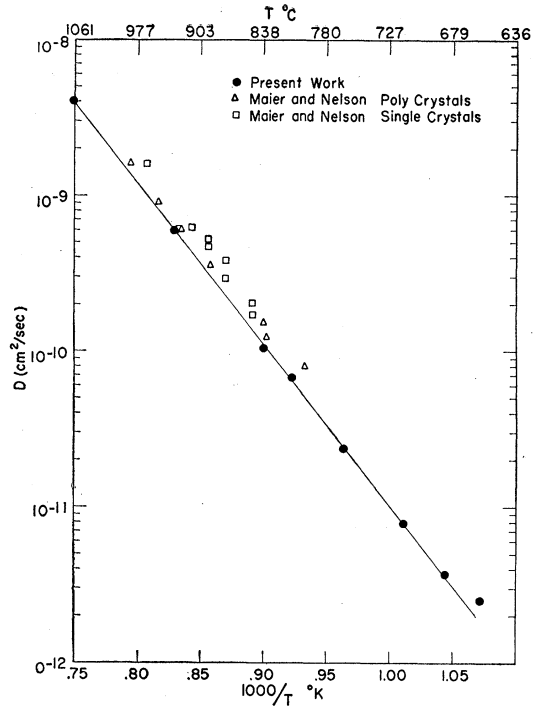

FIG. 3. Diffusion data plotted as log$D$ *versus* $1/T$.

order to determine whether or not a real deviation exists.

The results of the present work are seen to agree rather well with the data of Maier and Nelson[1] which are shown in Fig. 3. Those authors suggest different values of the activation energy of self-diffusion in copper depending on the crystalline state of the sample. The present data agree better with their results for polycrystals even though only single crystals were used in this research.

It is of interest to compare data from previous calculations and experiments relating to diffusion processes in copper with those reported here. The frequency factor calculated by Zener's theory[5] is 0.28 cm²/sec as contrasted with the experimental value of 0.47. The present experiment does not alter the estimate by Overhauser[6] of the energy of formation of a vacancy because the activation energy obtained by Maier and Nelson[1] differs from our value by only 0.02 ev. Also, the conclusions of Huntington and Seitz[7] remain valid.

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[7] H. B. Huntington and F. Seitz, Phys. Rev. **61**, 315 (1942) and H. B. Huntington, Phys. Rev. **61**, 325 (1942).