

Copper diffusion in single-crystal α -Zr

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Tracer diffusion of ^{64}Cu in α -Zr single crystals has been measured in the temperature range (615–860)°C. The temperature dependences of the ^{64}Cu diffusion coefficients in directions parallel to and perpendicular to the c axis are given by $D_{\parallel} = 0.40e^{-1.54\text{ eV}/kT}$ and $D_{\perp} = 0.25e^{-1.60\text{ eV}/kT}$ cm²/sec, respectively. The results are discussed in terms of an interstitial diffusion mechanism.

I. INTRODUCTION

Recent tracer studies of solute diffusion in single-crystal α -Zr, made near the upper temperature limit of the hcp phase, have indicated the operation of two basic modes of intrinsic diffusion.^{1–3} Thus a number of solutes were found to have diffusion coefficients compatible with normal substitutional diffusion behavior, while others, in particular Fe, Co, Ni, and Cu, had diffusion coefficients orders of magnitude too large to be reasonably associated with vacancy diffusion.³ The diffusion of these latter elements is most readily interpreted in terms of a predominantly interstitial transport mechanism.

A feature of other metallic systems showing similar ranges of solute diffusion behavior is that the activation energies associated with interstitial solute diffusion are invariably much lower than the activation energy for self-diffusion in the solvent, being about half the latter quantity in many instances.^{4–7} In α -Zr, however, the situation is such that there have been no accurate measurements of the temperature dependence of tracer diffusion in single-crystal specimens, while existing data, referring to diffusion in polycrystalline specimens, must be regarded with caution.³

The main obstacle to the measurement of lattice self-diffusion in α -Zr is the hcp \rightarrow bcc phase transition at 863°C. This transformation limits measurements in pure α -Zr to temperatures below $0.6T_m$,^{1,2} and it is typically at this reduced temperature that extrinsic effects, associated with rapid diffusion along dislocations and grain boundaries, begin to dominate conventional measurements of self-, or substitutional, diffusion in metals. This has certainly proved to be the case for α -Zr self-diffusion studies.³

For interstitial solute diffusion, however, where the intrinsic diffusion coefficients are several orders of magnitude larger than substitutional values, extrinsic contributions may be expected to be correspondingly lower. In these circumstances it may be possible to make reliable measurements of the temperature dependence of solute diffusion.

The object of the present work, therefore, was to determine the characteristic parameters describing the temperature dependence of the diffusion coefficient of one of the very mobile solute species in α -Zr and to compare the results with an estimated best value for Zr self-diffusion.

^{64}Cu was chosen for the present study mainly on account of the ease with which ion-implanted diffusion sources could be made. Preliminary experiments on α -Zr had shown that surface hold-up effects could lead to complex diffusion profiles, particularly at lower temperatures, when diffusion sources were prepared by evaporation. Past and present experience has shown that these effects can, to a large extent, be avoided by implanting the source isotope below the surface oxide layer of the specimens.^{8–10}

II. EXPERIMENTAL

A. Sample preparation

All of the specimens used in this work were from single-crystal rods, 7 mm in diam. These specimens were grown from crystal-bar material in an electron beam furnace.¹¹ The single crystals appeared to be of uniformly high quality, as evidenced by the sharpness of Laue back-reflection x-ray photographs. Furthermore, the impurity contents did not appear to vary significantly from rod to rod. A typical impurity-content analysis, determined by optical emission spectroscopy, is shown in Table I.

Initially, with only one short single-crystal rod available, it was decided to spark-cut right cylindrical disks in order to obtain the maximum number of samples. These specimens had their flat surfaces at an angle of 80° to the c axis. At a later stage sufficient single-crystal material became available to allow the preparation of two additional sets of diffusion samples with plane surfaces parallel and perpendicular to the c axis, respectively; all samples were approximately 7-mm diam by 5 mm thick.

After spark-cutting, the samples were cleaned

by immersion in a solution of 40% HNO₃, 40% H₂O and 20% HF (by volume). Flat surfaces were prepared by grinding on metallurgical abrasives down to 3- μ diamond grit. A high polish was achieved on a metallurgical cloth using a slurry of ignited ammonium dichromate with an increasingly dilute solution of HF in water. The specimens were cleaned and dried prior to vacuum annealing in Ta boats at a pressure of 2×10^{-8} Torr for 48 h. Laue back-reflection photographs were used to check the quality and orientation of each specimen after the preannealing procedure.

B. Formation of diffusion sources and diffusion annealing

The ⁶⁴Cu isotope was made by neutron irradiation of mg quantities of CuCl in the NRX reactor to a fluence of $\sim 10^{18}$ thermal neutrons/cm². The CuCl source was quickly transferred to the source chamber of the CRNL mass separator, where a fluence of $\sim 10^9$ atoms of ⁶⁴Cu was implanted at 40 keV, into a well-defined central area of the specimen. Microtome sectioning, shortly after implantation, showed all the ⁶⁴Cu to be confined to a depth $< 1.5 \mu\text{m}$ from the surface.

Immediately following implantation the specimens were placed in a Ta boat in a quartz-tube furnace. The diffusion anneals were done at pressures in the range 10^{-8} – 5×10^{-8} Torr. Specimen temperatures were monitored by three calibrated chromel–alumel thermocouples in contact with the Ta boat. Temperatures were controlled to within $\pm 0.5^\circ\text{C}$ during the period of the anneal. For very short diffusion periods the samples were introduced to, and removed from, the hot zone of the furnace using a magnetic slide device.

C. Sample sectioning and ⁶⁴Cu assay

After the diffusion anneals the specimens were cemented to brass holders using a fast-setting resin. Thereafter they were lathe sectioned to depths of from 0.2 to 1.0 mm. For a few samples, specimen diameters were turned down to examine the extent of surface diffusion effects. No significant amounts of ⁶⁴Cu were detected in these surface layers. Because of the small dimensions of the samples and the awkward skew of the specimens oriented for studying diffusion perpendicular to the *c* axis, generally the single-crystal rods had their growth axes nearly parallel to the *c* axis; specimen diameters were not usually turned down. It was felt that this omission was justified on the basis of the null effects noted above. In addition, deformation of the small samples during turning-down procedures sometimes led to undesirable surface distortion. The self-consistency of the results and the apparent absence of artifacts

TABLE I. Impurity levels in α -Zr as determined by optical emission spectroscopy.^a (1) Single crystals used for present work; (2) single crystals used for α -Zr self-diffusion (Ref. 3) (not previously reported). Values are in ppm (atomic fraction).

Impurity	(1)	(2)
B	90	450
Mg	<10	10
Al	35	35
Si	30	1200
Ca	20	40
Cr	<20	20
Mn	<10	20
Fe	55	15
Co	<15	15
Ni	<10	10
Cu	75	30
Mo	50	70
Sn	10	10

^a These analyses were done by Materials Research Corporation, N.Y.

indicated that this approach was reasonable.

The lathed sections were weighed to within a precision of 2%, while the relevant specimen areas were measured to a similar degree of accuracy. The weighed specimens were dissolved in 0.2 ml of a solution of 40% H₂O, 50% HNO₃, and 10% HF (by volume) and made up for liquid scintillation counting by the addition of 4-ml methanol and 12 ml of liquid scintillator.¹ The ⁶⁴Cu activity was measured in a Nuclear Chicago Unilux II liquid scintillation counter. Some activity measurements were also made by γ counting using a well-type NaI(Tl) detector in conjunction with a 112-channel pulse-height analyzer. No differences were detected between the methods. In all cases the measured half-life corresponded well with the published value of 12.8 h. At least 10 000 counts were recorded from each section.

III. RESULTS

The diffusion conditions were equivalent to an infinitely thin source diffusing into a semi-infinite cylinder. The appropriate solution to the diffusion equation is

$$C_{(\chi,t)} = C_0(\pi Dt)^{-1/2} e^{-\chi^2/4Dt}, \quad (1)$$

where $C_{(\chi,t)}$ is the tracer concentration at a depth χ after a diffusion interval t , D is the tracer diffusion coefficient, and C_0 is the initial quantity of tracer at the surface.

In the temperature interval (615–850) $^\circ\text{C}$, the penetration profiles generally corresponded well with a distribution according to Eq. (1) (see Fig. 1). However, as the temperature was decreased,

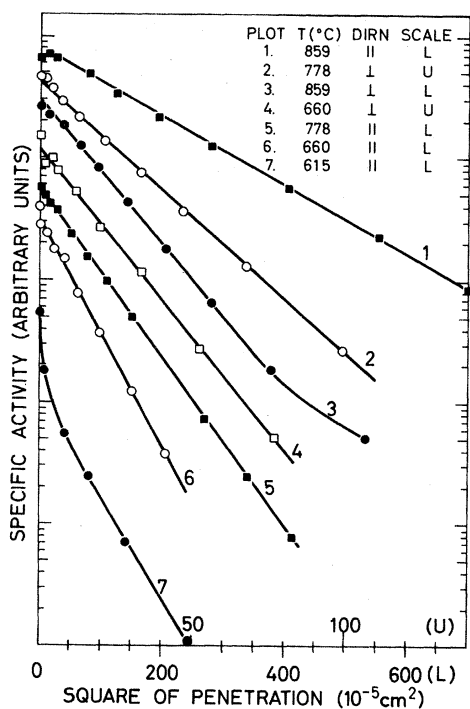


FIG. 1. Typical ^{64}Cu penetration profiles in α -Zr single crystals. The symbols || and \perp refer to diffusion in directions parallel and perpendicular to the c axis, respectively.

a tendency towards curved $\log C$ -vs- χ^2 plots, as indicated by the 615°C profile of Fig. 1, became very pronounced. High surface concentrations and deeply penetrating tails were prominent in these experiments. Data from these lower temperature runs were not considered for the present analysis.

In Fig. 2 the results of the present work are compared with data from an earlier investigation,¹ where rather large errors, arising from very limited sample dimensions and lower ^{64}Cu activities, are not unexpected. For example, the high $D_{||}$ value at 735°C , from the previous study, was based on a drop of only a factor of 4 in ^{64}Cu specific activity. Within the error limits inherent in the earlier work, the agreement between the data is perhaps not unreasonable.

Also in Fig. 2, the highest temperature point, at 859°C , for $D_{||}$ is significantly low. The origin of this low value is not known. Since the temperature is rather close to the phase-transformation temperature, 863°C , the possibility of an excursion into the β phase was considered. Two observations, however, seem to militate against this possibility. First, since the $D_{||}$ and D_{\perp} measurements at a common temperature were done together in the same furnace, it might be anticipated that the D_{\perp} would also be anomalous at

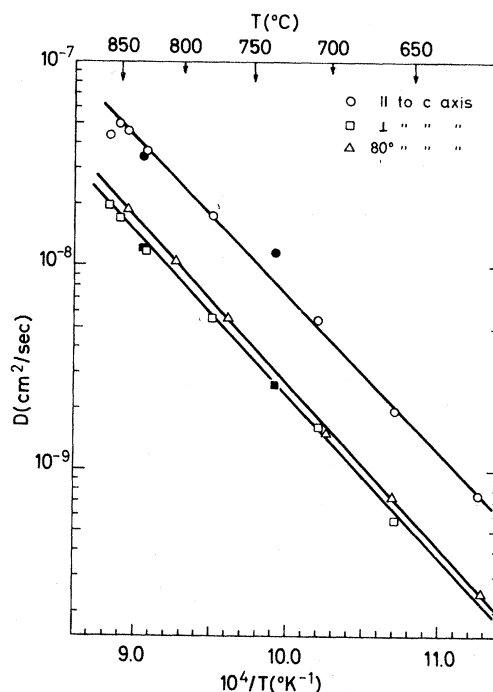


FIG. 2. Temperature dependence of ^{64}Cu diffusion in α -Zr single crystals. The symbols ● and ■ refer to data from a previous investigation (Ref. 1).

859°C , while, second, neither of the diffusion specimens from this experiment displayed any of the characteristic surface distortion usually observed when a Zr specimen has undergone a transformation into the bcc phase. Subsequent Laue x-ray patterns of both specimens, after repolishing, were of excellent quality.

Least-mean-squares analyses of the data, summarized in Table II, led to the following expressions for the temperature dependence of ^{64}Cu diffusion in α -Zr:

$$D_{||} = 0.40e^{-1.54 \text{ eV}/kT} \text{ cm}^2/\text{sec};$$

$$D_{\perp} = 0.25e^{-1.60 \text{ eV}/kT} \text{ cm}^2/\text{sec};$$

$$D_{80} = 0.42e^{-1.62 \text{ eV}/kT} \text{ cm}^2/\text{sec},$$

where $D_{||}$, D_{\perp} , and D_{80} refer, respectively, to diffusion in directions parallel to, perpendicular to, and at 80° to the c axis. The anomalously low $D_{||}$ value at 859°C was not included in the analysis. (A preliminary report of this work¹² erroneously quoted an activation energy of 1.23 eV for Cu diffusion in α -Zr.)

According to an analysis of the diffusion coefficient in terms of

$$D(\theta) = D_{\perp} \sin^2 \theta + D_{||} \cos^2 \theta, \quad (2)$$

where θ is the angle the diffusion direction makes with the c axis,¹³ the results for D_{80} appear to be

TABLE II. Diffusion of ^{64}Cu in α -Zr. The symbols \parallel , \perp , and 80 refer to diffusion in directions parallel to, perpendicular to, and at 80° to the c axis, respectively.

Temperature ($^\circ\text{C}$)	Diffusion period (sec)	Diffusion coefficient (cm^2/sec)	Diffusion direction
859	8.91×10^3	4.39×10^{-8} 1.96×10^{-8}	\parallel \perp
851	4.85×10^3	4.90×10^{-8} 1.68×10^{-8}	\parallel \perp
844	8.10×10^2	4.60×10^{-8}	\parallel
844	9.18×10^3	1.89×10^{-8}	80
829	6.09×10^3	3.60×10^{-8} 1.16×10^{-8}	\parallel \perp
808	4.14×10^3	1.06×10^{-8}	80
778	8.91×10^3	1.75×10^{-8} 5.48×10^{-9}	\parallel \perp
706	1.29×10^4	5.43×10^{-9} 1.61×10^{-9}	\parallel \perp
703	1.65×10^4	1.50×10^{-9}	80
662	1.02×10^4	7.19×10^{-10}	80
660	6.3×10^4	1.90×10^{-9} 5.54×10^{-10}	\parallel \perp
615	1.74×10^4	7.30×10^{-10}	\parallel
614	1.06×10^4	2.39×10^{-10}	80

5 or 6% too high. However, for realistic errors of $\pm 2^\circ\text{C}$ in the absolute temperature, $\pm 2^\circ$ in the sample crystallographic alignment and $\pm 5\%$ in the determination of the diffusion coefficients, the observed discrepancy is probably not significant.

IV. DISCUSSION

In agreement with previous work on solute diffusion in α -Zr,¹⁻³ the present results appear to bear out the philosophy that there are two distinguishable intrinsic diffusion processes.

The uniformity of the present data, in terms of both the diffusion profiles (Fig. 1) and the self-consistency of the temperature dependence of the diffusion coefficients (Fig. 2) effectively rules out a process heavily dependent on a random dislocation network. This point has been further substantiated by dislocation density measurements on specimens from the same single crystals used in the present work. Thus the dislocation densities of well-annealed samples are typically $\leq 10^8/\text{cm}^2$, whereas densities of $\sim 10^{10}/\text{cm}^2$ would be required to account for the high values of the diffusion coefficients on the basis of a dominant dislocation diffusion mechanism.^{1,2}

Although the results presented here do not exclude the possibility of substitutional diffusion via tightly bound Cu-vacancy pairs, it is possible to assess the probability of such a mechanism in terms of measured α -Zr self-diffusion coefficients and the impurity content of the specimens used for

these measurements. Table I shows the impurity content of the fast-diffusing solute species Fe, Co, Ni, and Cu, measured in the actual specimens used for the self-diffusion experiments.³

On the basis of a vacancy mechanism small additions of any of the above species would contribute a minimum enhancement to α -Zr self-diffusion which can be estimated in an approximation to the tight-binding limit. In this limit the minimum enhancement of self-diffusion is given approximately by^{14,15}

$$D_m \approx D(0) + 2C_i D_i \dots, \quad (3)$$

where D_m is the measured self-diffusion coefficient in a dilute alloy containing C_i atom fraction of a solute with a diffusion coefficient (in the solvent) D_i and $D(0)$ is the true self-diffusion coefficient in the pure metal, it is assumed that $D_i \gg D(0)$ and that $C_i \ll 1$.

Substituting the measured self-diffusion coefficient³ at 850°C , the appropriate C_i value for Cu (Table I) and an average value for the Cu diffusion coefficient at 850°C in Eq. (3) leads to $5 \times 10^{-14} \approx D(0) + 1.8 \times 10^{-12}$.

The implication of this inequality is that a substitutional mechanism for the diffusion of Cu in α -Zr is not consistent with the data. For the solutes Fe, Co, and Ni, where the diffusion coefficients are about an order of magnitude larger than for Cu,^{2,3} substitution of appropriate values in Eq. (3) leads to an even greater discrepancy and again the elimination of any substantial vacancy contribution to their diffusion.

An alternative approach to the problem of ultrafast solute diffusion in α -Zr, based on observations of diffusion behavior in normal substitutional systems, has also led to the exclusion of a significant vacancy diffusion component to the measured diffusion coefficients of Fe, Co, and Ni in α -Zr.³ The weight of evidence, then, seems to lead inevitably to the adoption of an interstitial mode of diffusion as providing the simplest explanation of ultrafast solute diffusion in α -Zr.

In this context the activation energy for Cu diffusion in α -Zr appears to follow a fairly well-established trend, in that the activation energies Q for diffusion of relatively very mobile interstitial solutes seem to be very much lower than for self-diffusion in the appropriate host metal.^{4-7,16-20} Thus if the previously proposed best value of 2.9 eV for α -Zr self-diffusion³ is adopted, the ratio of $Q(\text{Cu})/Q(\text{Zr})$ in α -Zr is only 0.55.

Although it is difficult to assess the relative contributions of the activation energy and preexponential factor in determining the diffusion anisotropy of Cu in α -Zr, the observation that Q for diffusion parallel to the c axis seems to be smaller than Q

for Cu diffusion perpendicular to the c axis is also in good accord with an interstitial mechanism,¹ the saddle point for interstitial jumps parallel to c being approximately 2% more open than for jumps contributing mainly to D_{\perp} .

In conclusion it may be said that the present tracer diffusion measurements of ^{64}Cu in $\alpha\text{-Zr}$ represent an intrinsic diffusion process which is most reasonably accounted for in terms of an in-

terstitial diffusion mechanism.

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