A METHOD OF MEASURING THE DIFFUSION COEFFICIENT IN METALS FOR PENETRATION DEPTHS LESS THAN TEN MICRONS

by

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A Thesis Submitted to the Faculty of the DEPARTMENT OF PHYSICS
In Partial Fulfillment of the Requirements For the Degree of MASTER OF SCIENCE In the Graduate College THE UNIVERSITY OF ARIZONA

1962
STATEMENT BY AUTHOR

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ACKNOWLEDGMENTS

The author wishes to express his gratitude to the following:

To Professor Carl Tomizuka for his financial support under the United States Atomic Energy Commission, Contract AT(11-1)-1041 and for his valuable advice and criticisms during the preparation of this thesis; to Professor Henry Freiser and to Dr James M. Fresco for the use of their Chemistry Laboratory to complete the experiment; to Mr Palmer Weir for his valuable assistance in the laboratory; and to Mr Carl Perceny for his cooperation and helpful suggestions in constructing the sample holder.
ABSTRACT

A method of chemically sectioning metallic specimens for the determination of the tracer diffusion coefficient is developed and tested. An actual measurement for the diffusion of Zn in Cu is made using this method. The results compared favorably with measurements made by the mechanical method of sectioning. It is determined that the method of chemical sectioning is feasible for tracer penetration depths of 10 microns and greater. By proper modification of the equipment it is possible that a decrease in the above penetration limit can be obtained.
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The determination of diffusion coefficients by radioactive tracer techniques is generally limited to materials and temperatures where diffusion coefficients are relatively large (greater than $10^{-12}$ cm$^2$/sec). Complicated and delicate sectioning methods are involved in diffusion measurements at low temperatures using tracer techniques. In many instances such techniques have been abandoned in favor of the method using the activation energy of internal friction (1)* or just plain data extrapolation from a higher temperature region. Hino (2) has shown that the determination of the energy of internal friction does not always give an accurate determination of the tracer diffusion coefficient. Furthermore, Hart (3) has indicated that as lower temperatures are approached short circuiting along dislocations becomes more predominant as a diffusing mechanism. That other mechanisms do become more predominant at lower temperatures has been verified by Tomizuka (4) from experimental data. Accordingly, extrapolation of the present data into the lower temperature

*The figures appearing in parentheses pertain to references appended to this paper.
regions is not necessarily valid. The need for further experimental data in this lower temperature range is evident. Such data will yield additional information on the role these other mechanisms play in the diffusion process. By refinement of the tracer technique it may be possible to obtain this information.

The limitation inherent in the tracer technique is primarily dependent on the method of sectioning used. The precision lathe (5, 6) provides a reliable means of sectioning for diffusion coefficients having magnitude $10^{-12} \text{cm}^2/\text{sec}$ and greater. Slices as small as 5 microns thick can be obtained by this method. This method is confined to metallic specimens and soft specimens of ionic crystals. Another means of sectioning is by use of the microtome (6). Mapother et al (7) obtained 5 micron thick sections using this device which will section non-metallic as well as metallic specimens. Special grinding devices by Nachtrieb et al (6, 8) provided section thicknesses of 0.5 microns. Both metallic specimens and brittle crystals such as germanium and silicon may be used with this method. The difficulties with this method are the complications involved in positioning the specimen face flat on the grinding surface, and then keeping the grinding surface itself flat. In spite of these difficulties the precision grinder offers the best method to
date of sectioning specimens of very small penetration depths.

From the above discussion it becomes obvious that if diffusion coefficients at lower temperatures are to be measured by radioactive tracers either the grinding method must be employed or a new method developed. The purpose of this investigation is to develop and test a method capable of making these measurements at temperatures where the diffusion coefficient is in the interval $[10^{-15} \text{ cm}^2/\text{sec}, 10^{-14} \text{ cm}^2/\text{sec}]$.

Two non-mechanical methods of sectioning were considered; electrolytic and chemical polishing. Electrolytic polishing would entail the use of electrodes which would become radioactively contaminated and create counting problems should the electrolyte be used for radioactivity measurements. Electrolytic polishing also tends to reduce whatever geometrical irregularities are present at the original surface, thereby decreasing the accuracy of sectioning. Chemical polishing alleviates the troublesome electrodes and for this reason was the method chosen to be investigated. The remaining technical problems to be solved in such a method are;
1) to establish a technique to chemically section only one face of the sample consistent with the boundary condition of the ensuing analysis.

2) to eliminate pitting of the sample face during the sectioning period.

3) to control and measure the section thickness.

4) to obtain radioactive sections whose activity will be appreciably above the background count of the scintillation counter.

It was the overall objective of this work to develop techniques for chemically sectioning a cylindrical metallic sample and to test this method of sectioning by making a diffusion measurement on a sample of known diffusion coefficient. The feasibility of using the method for determining the diffusion coefficients in the interval $[10^{-15}\text{ cm}^2/\text{sec}, 10^{-14}\text{ cm}^2/\text{sec}]$ could then be ascertained.
2. THEORETICAL BACKGROUND

2.1 Tracer Diffusion

Assume the diffusion process to be characterized by the jump of an atom into the neighboring vacancy; meaning an atom site which is normally occupied, but from which the atom is missing. The validity of this assumption has been shown by Huntington and Seitz (9) who calculated the formation energy of an interstitial in copper to be greater than twice the formation energy of a vacancy. The assumption has been experimentally verified by Simmons and Balluffi (10). Further assume that the diffusion jumps are not completely random, but are influenced to some extent by the direction of the previous jumps. Le-Clare and Liddiard (11) have shown that for such a "correlated random walk" the diffusion coefficient is given by:

\[ D = \alpha a^2 \Gamma P_f \]

where
\[ \alpha \] = correlation factor
\[ a \] = lattice spacing
\[ \Gamma \] = jump frequency
\[ P_f \] = probability of a vacancy being present.
For an atom to make a jump from a given energy position, say I (fig. 1), to the position 3 a barrier 2 must be surmounted. Assume position 2 to be the minimum energy point of the barrier in configuration space, i.e., the saddle point. Assume also the diffusing atom is in thermal equilibrium with the lattice at all times during this jump; in particular when the atom is at the saddle point. That is to say, the process by which the jump takes place is quasistatic.

Let \( R = \) the rate at which particles cross the saddle point barrier

\[
R = (\text{Probability of being in } 1 \text{ or } 2) \times (\text{Number of attempts to jump per unit time}) \times (\text{Probability of success in making the jump})
\]

\[
= P_{1,2} \times v \times e^{-E_m/KT}
\]

where \( P_{1,2} = \) Probability of being in state 1 or 2

\( v = \) Vibrational frequency of the atom

\( E_m = \) Energy barrier for motion into the adjacent site

\( K = \) Boltzmann's constant

Then, we see that

\[
ve^{-E_m/KT} = \text{jump frequency} = \Gamma
\]
Potential Barrier for Motion of Solute Atoms From State 1 to State 3.

Fig. 1
So we have:

\[ D = \alpha a^2 \nu P_f e^{-E_m/RT} \]

Again, from Boltzmann's statistics

\[ P_f = e^{-E_f/2kT} \]

where \( E_f \) is the energy necessary to form a vacancy.

Hence we have

\[ D = \alpha a^2 \nu e^{-E_f + E_m/2kT} \]

Now \( E_f \) and \( E_m \) are not necessarily temperature independent. By Taylor's expansion we see that

\[ E_f + E_m = \left( E_f + E_m \right)_T + \left( \frac{d(E_f + E_m)}{dT} \right)_T T + \ldots \]

The empirical formulation of the diffusion constant is

\[ D = D_0 e^{-H/RT} = D_0 \left( 1 - \frac{H}{RT} + \frac{H^2}{2!R^2T^2} - \frac{H^3}{3!R^3T^3} + \ldots \right) \]

So we have

\[ D \approx D_0 \left( 1 + \frac{H}{RT} \right) \text{ for large } T \]

\( D_0 \) = frequency factor

\( H \) = activation enthalpy

\( R \) = gas constant
Then, $E^+_m + E^-_m$ cannot be greater than first order in $T$. Substituting into the derived expression for $D$

$$D = a a^2 v e^{-\frac{(E^+_f + E^-_m)_{T=0}}{K T}} e^{-\left(\frac{d(E^+_f + E^-_m)}{K d T}\right)_{T=0}}.$$

Thus we have

$$H = N_o (E^+_f + E^-_m)_{T=0}$$

and

$$D_0 = a a^2 v e^{-\left(\frac{d(E^+_f + E^-_m)}{K d T}\right)_{T=0}},$$

where $N_o$ is the Avagadro's number.

To find the frequency factor and activation energy from first principles involves the calculation of $E^+_f$ and $E^-_m$ which has resulted in approximations and assumptions of the type which are present in the existing theories $(9, 12)$. By measuring the diffusion coefficient as a function of temperature it is possible to obtain $D_0$ and $H$. To extend the range of measurement into the lower temperature regions new experimental methods must be developed.
2.2 Diffusion Equation

Fick's first law of diffusion states that the current density \( J \) is proportional to the concentration gradient of the diffusing atoms.

\[
J = -D \nabla c
\]

where

- \( J \) = current density vector
- \( D \) = Diffusion coefficient
- \( \nabla \) = Nabla operator
- \( c \) = Concentration of diffusion atoms/unit volume

When diffusion is in the \( x \)-direction only

\[
(J)_{x} = (J)_{x + dx} = D[(c_{x})_{x + dx} - (c_{x})_{x}]
\]

\[
= D \frac{(c_{x})_{x} + dx - (c_{x})_{x}}{dx} \ dx
\]

\[
= D \ c_{xx} \ dx
\]

Dividing by \( dx \) gives

\[
c_{t1} = D \ c_{xx}
\]

Similarly for the \( y \) and \( z \) directions

\[
c_{t2} = D \ c_{yy}
\]

\[
c_{t3} = D \ c_{zz}
\]

where the subscripts \( 1, 2, 3 \) imply \( x, y, z \) directions respectively.
We can then write Fick's second law of diffusion

\[ c_t = D \Delta c \]

where \( \Delta \) is Laplace's operator.

2.3 A Solution of the Diffusion Equation

To solve Fick's diffusion equation we shall first solve the initial value problem of finding \( u(x, t), t = 0 \) in a semi-infinite rod of unit cross sectional area where \( u(x, 0) = \psi(x) \). From the solution of this problem we will then be able to determine a form of a trial solution to the problem where the surface concentration is a function of time, i.e., \( u(0, t) = f(t) \).

By separation of variables the diffusion equation becomes,

\[ \frac{1}{\frac{d}{dt}(t)} \frac{\partial T(t)}{\partial t} = \frac{1}{k(x)} \frac{\partial^2 X}{\partial x^2} = -\alpha^2 \]

where \( \alpha \) is real.

This gives

\[ c = e^{-\alpha^2 D t} \cos \alpha (x - \lambda) \]
Assuming \( \psi(x) \) is continuous and bounded the Fourier integral theorem gives,

\[
c(x,t) = \frac{1}{\pi} \int_0^\infty \int_0^\infty \psi(\lambda) e^{-\alpha^2 t D} \cos \alpha (x - \lambda) \, d\alpha \, d\lambda.
\]

Integrating with respect to \( \alpha \) by putting \( y = \alpha \sqrt{D} t \) and \( b \) for \( (x - \lambda)/2 \sqrt{D} t \) we have

\[
c(x,t) = \frac{1}{\pi} \int_0^\infty \psi(\lambda) \int_0^\infty e^{-y^2} \cos 2b \, y \, dy.
\]

Using the formula

\[
\frac{1}{\sqrt{D} t} \int_0^\infty e^{-y^2} \cos 2b \, y \, dy = \frac{1}{2} \sqrt{\frac{\pi}{D t}} \quad e^{-b^2} = \frac{1}{2} \sqrt{\frac{\pi}{D t}} \quad e^{-\frac{(x - \lambda)^2}{4D t}}
\]

we obtain

\[
c(x,t) = \frac{1}{2 \sqrt{\pi} \sqrt{D t}} \int_0^\infty \psi(\lambda) e^{-\frac{(x - \lambda)^2}{4D t}} \, d\lambda.
\]

This indicates we might find a solution to the problem where

\( u(0, t) = f(t); \ t > 0 \) if we use the trial expression

\[
c(x,t) = g(x) \ h(t) \ e^{-\frac{x^2}{4Dt}}.
\]
Substituting this into the diffusion equation we have

\[ g \cdot e^{-\frac{x^2}{4Dt}} \left[ \frac{\partial g}{\partial t} + \frac{x^2}{4Dt} \right] = \frac{\partial^2 g}{\partial x^2} - \frac{x}{Dt} \frac{\partial g}{\partial x} + g \left( \frac{x^2}{4Dt^2} - \frac{1}{2Dt} \right). \]

This equality is satisfied if \( g \) is a constant \( \beta \) and if \( h \) is replaced by \( \frac{1}{\sqrt{t}} \). The solution becomes

\[ c(x,t) = \frac{\beta}{\sqrt{t}} \cdot e^{-\frac{x^2}{4Dt}} \]

which is finite at \( x=0 \) for \( t>0 \) and is zero for \( t=0; \ x>0 \).

The total number of diffusion atoms is given by

\[ c_0 = (\text{Area}) \int_0^\infty c \, dx \]

The area is unity, so the integral becomes

\[ c_0 = \frac{\beta}{\sqrt{t}} \int_0^\infty e^{-\frac{x^2}{4Dt}} \, dx \]

\[ = \frac{\beta}{\sqrt{\pi D}} \cdot \frac{1}{\sqrt{t}} \]

\[ \beta = \frac{c_0}{\sqrt{\pi D}}. \]

Hence we have

\[ c = c_0 / \sqrt{\pi D \cdot t} \cdot e^{-\frac{x^2}{4Dt}}. \]
This relation is used to obtain the diffusion coefficient experimentally. By measuring the concentration of the diffusing atoms at various depths in a given specimen a plot of $\ln c$ vs. $x^2$ is obtained. The slope of this plot then determines $D$ at a given temperature. A number of such measurements is made and the resulting diffusion constants plotted against the reciprocal of the temperature. Using $-\frac{H}{RT}$ the empirical relation $D = D_0 e^{-\frac{H}{RT}}$ the activation enthalpy $H$ and the frequency factor $D_0$ are determined.
3. PROCEDURE

The investigation is divided into two parts: design and test of design; and feasibility test by actual diffusion coefficient measurement.

3.1 Scope

The general scope of the problem is:

1) to chemically remove a thin layer (0.1 μ to 1 μ) of uniform thickness from the sample face without deforming the remaining portion of the sample.

2) To obtain a count of the radioactivity of the removed material.

3) to estimate the thickness of the removed layer with an accuracy of 1% or better.

If these problems are solved it will then be possible to obtain the activity profile of the sample, and using the method discussed at the end of section 2.3, determine the diffusion coefficient.
3.2 Design

The chemical sectioning of a given sample without deforming the remaining portion of the sample is possible by containment of the sample in a special holder. The purpose of such a holder is to allow only one face of the sample to be exposed to the chemicals used. The chemicals chosen for sectioning should be those that produce the most uniform surface, i.e., a surface free of pits, scratches, etc. Depending on the chemicals used and the specimen material it may be necessary to agitate the chemicals over the surface of the specimen to prevent localized chemical processes from occurring. The section thickness will depend on time, chemical concentration and may depend on temperature. These variables should be determined to provide a predetermined section thickness.

During this phase of the investigation (1) the above mentioned sample holder was designed; (2) the chemical suitable for sectioning copper was selected; (3) a procedure was established and tested for the measurement of the tracer diffusion coefficient in copper.
3.2.1 Sample Holder

The sample holder had to be designed such that when it was immersed in the acid bath only the front surface of the cylindrical sample was exposed to the etchant. This was accomplished by machining a 3/4-inch threaded hole 3/4-inch deep into 1-inch thick Teflon*. The hole was continued, unthreaded and tapered inward, through the remainder of the Teflon such that the diameter of the hole was 1/2-inch at the opposite face of the Teflon (fig. 2). A 3/4-inch long Teflon seating bolt, machined to match the threaded hole, completed the sample holder.

To use the holder the cylindrical sample is first placed in a snug fitting Teflon sleeve so that the sleeve extends just beyond the face to be sectioned (sectioning face). Both the sample holder and the sleeve are inserted, sectioning face first, in the sample holder. The seating bolt will now force the sample and sleeve into the tapered hole. The greater the seating torque applied to the bolt the more the Teflon sleeve is compressed about the sample. If the seating torque is too small the chemicals.

* Teflon is a registered trade mark of the E.I. duPont de Nemours and Company (Inc.).
Cutaway View of Sample Holder
(Seating bolt not shown)

Fig. 2
used work between the sleeve and the sample and etch the cylindrical sides of the sample. If the torque is too great the Teflon sleeve is forced over a portion of the face thus protecting a part of the face from chemical attack. A seating torque should be found for a given size sample and sleeve where the entire face is allowed to be attacked by the etchant while the remainder of the sample is protected.

3.2.2 Chemical Sectioning

Because very little experimentation has been done regarding the physical processes involved in the chemical polishing of metals (13) it is necessary to either rely on the tested methods of others or to develop a method by trial and error. It was decided to use the first alternative since any trial and error testing would probably duplicate what has already been done.

Tegart (13) has suggested the following acid bath (used at 70° C) for the chemical polishing of copper:

- 20 ml. Nitric acid 63.02% Specific gravity 1.4
- 55 ml. Ortho-phosphoric acid 98% Specific gravity 1.84
- 25 ml. Glacial acetic acid 60.05% Specific gravity 1.065
This mixture, with 85% phosphoric acid instead of the orthophosphoric acid, was chosen as the basic acid bath for the experiment. The final mixture was diluted with water and used at 45°C (see section 3.2.3.3).

3.2.3 Sectioning

Three variables contribute to sectioning with the above apparatus: 1) Acid bath agitation

2) Seating torque

3) Strength of acid bath

To define these variables preliminary sectioning tests were made using a short length of 1/2-inch diameter copper rod as a dummy specimen. The sample sleeve was approximately 5/8-inch O.D. with rounded edges to prevent binding in the sample holder. These preliminary tests were accomplished by repeated sectioning of the dummy specimen while varying but one of the above variables for a given test. Prior to each of these preliminary tests the dummy specimen was mechanically polished, washed with a liquid detergent, rinsed with water and dried by blowing air at room temperature, over the specimen. This assured that the quality of sectioning obtained from a given test was not dependent on the previous test. The final version of the sectioning technique must
however, provide a smooth sample surface for every section removed. Preparation of the specimen surface just prior to sectioning must be unnecessary.

3.2.3.1 Agitation Tests

Agitation of the acid bath is necessary to remove gas bubbles which form on the sample surface. These bubbles cause the sectioned surface to be pitted and irregular by hampering the polishing processes.

The first device to be considered was the magnetic stirrer. A 1 1/4-inch long, glass sealed magnet was used in conjunction with a Precision Scientific Mag-Mix M-1 magnetic stirrer. The acid bath was contained in a 400 ml. beaker along with the stirrer. The assembled sample holder was suspended face down in the acid and the stirrer activated. The sample holder was adjusted so the sample was directly over the vortex formed by the rotating stirrer. Time spent in the acid bath was between one and three minutes.
After determining a satisfactory seating torque (see section 3.2.3.2) a number of runs were made this way. Visual inspections of the sample indicated pitting along the edges of the sectioning faces in almost all cases. It was decided that this method of agitation was too dependent on the placement of the sample face relative to the vortex to be reliable in obtaining a satisfactory polish.

High frequency sonic agitation was considered. This method was abandoned since cavitation in the acid would probably create as many surface bubbles as would be removed.

The second method tested, and the one ultimately employed for diffusion measurements, was to allow the acid to lie directly on the top of the sample face. Agitation was accomplished with a motor-driven glass propeller mounted 3/8-inch directly over the sample. The propeller consisted of a single blade approximately 5/8-inch across with a 30° attack angle. By diluting the acid (see section 3.2.3.3.) with water this method was found to be satisfactory.

To use this technique the sample holder had to be modified. A 1/2-inch deep 1 1/2-inch O.D., 1 7/16-inch I.D. circular channel
was machined about the center of the tapered side of the hole in the sample holder. A 3-inch length of glass tubing was placed in the channel and sealed with silicon grease. This provided the sample holder with its own acid bath container into which the stirrer could easily be positioned (fig. 3, 4).

3.2.3.2 Seating Torque

The seating torque was measured with a Torque Control TS-100 adjustable torque screwdriver. The torque was varied for a number of sectioning runs until a value was obtained where the face edges were left unpitted and the remaining faces were not attacked by the acid. Inspection was visual with the aid of a magnifying glass. For the acid mixture finally used (section 3.2.3.3) the desired torque measured 48-inch ounces.

3.2.3.3 Strength of Acid Bath

The rate of sectioning will be a function of the strength and temperature of the acid bath. To determine the strength to be used in the feasibility test a sectioning rate of 0.5 microns/min. was chosen. By weighing the sample before and after each etch it was possible to obtain the thickness removed and thus the sectioning rate for a given temperature. This was only an approximation
Figure 3 - The sample holder components.

Left to right: sample holder and acid bath container;
seating bolt; specimen sleeve with specimen.

Figure 4 - The sample holder and stirrer in position for sectioning.
since no means was provided to maintain the acid bath temperature constant while sectioning was being completed.

Using the above sectioning rate the acid mixture described in 3.2.2, made 35.5% dilute with water, was chosen as the acid bath for sectioning copper; the acid bath temperature at the start of sectioning being 45°C. Actually there was very little difference between the sectioning rates at 70°C and 45°C. 45°C was chosen because the evaporation rate is less.

3.3 Feasibility

To test the feasibility of chemical sectioning for the determination of diffusion coefficients it is necessary to compare results with those obtained by other methods. The diffusion of Zn in Cu was chosen to be compared with the work already done by Hino (2). One diffusion coefficient was determined at a given temperature and a comparison made with Hino's results.

3.3.1 Tracer Diffusion of Zn in Cu

Zn 65 was used as a tracer for diffusion in a single crystal of copper. A single crystal specimen was employed to
prevent short circuiting of the tracer element along the grain boundaries. The specimen was cut from a larger single crystal and then treated to remove the cold worked material.

The sectioning face of the specimen was ground flat using a series of abrasive papers down to 3-0 coarseness. The face was then polished on a series of three polishing wheels of diminishing coarseness, washed with liquid detergent, and etched in a 50% dilute mixture of HNO₃ and water. After this etching the specimen was sealed in an evacuated vycor capsule and heated at 300°C for twenty-four hours. The annealing temperature was then increased at approximately 50°C per hour, held at 900°C for twenty-four hours and cooled slowly to room temperature. Further etching of the specimen indicated that no grain boundaries appeared as a result of this process.

The specimen was then electroplated with Zn 65 and sealed in an evacuated vycor capsule. This assembly was placed in the diffusion furnace for a predetermined time and at a predetermined temperature - 2.78 hours at 789°C (see section 2.1) - and then rapidly cooled by submerging the capsule in ice water. The cylindrical surface was then turned down on a lathe in order
that effects of surface diffusion and diffusion through this surface be eliminated. It was observed that the soft copper lapped over the sectioning face during the cutting process. It became apparent after chemically sectioning the sample that attempts to remove this lap-over (burr) without defacing the sectioning face were unsuccessful. A new specimen was prepared and the burr removed by applying a small file to the burr as the sample rotated on the lathe.

The sample was weighed using a Mettler B-6 semi-microbalance and then placed in the Teflon sleeve and sample holder. After positioning the sample under the rotating stirrer, 25 ml of the acid bath at 45°C were quickly poured into the sample holder apparatus. The first eleven cuts were made by allowing the acid to work for two minutes. The acid bath was then quickly transferred to a beaker and the sample was washed with the greater portion of 7 ml water. The wash water was forced onto the sample using a 10 ml polyethylene bottle converted to a wash bottle. The wash water was then allowed to "slosh" about on the sample for approximately one minute, after which it was added to the beaker containing the used acid mixture. The remainder of the water in the wash bottle was used to rinse the stirrer. This rinse was added to the beaker containing the used acid mixture. 4 ml of the solution were then...
transferred from this beaker to the counting bottle. A graduated pipett was employed for this transfer. The specimen was then removed from the sample holder and sleeve and then weighed. Ample time for the specimen to dry was allowed before the specimen was weighed. The difference between the weights before sectioning and after sectioning gave the section mass $\Delta M$. The section thickness was calculated by measuring the density and diameter of the specimen sectioning face.

The 1.11 Mev gamma activity of the solution in the counting bottle was then measured using a detector and counting system composed of a Baird Atomic Model 810B scintillation detector (powered by a Baird Atomic Model 312A power supply), a Baird Atomic Model 215 linear amplifier and RIDL's Model 33-2 pulse height analyzer, Model 49-26 counter and Model 54-7 timer. Knowing $\Delta M$ the specific activity was determined. To assure accurate weight measurements great care was exercised at all times in handling the specimen.

Drift in the base line of the pulse height analyzer made it necessary to adjust the base line before each count. This was achieved using the specimen's lathe turnings to furnish the Zn 65 spectrum. The total number of counts for each case was limited to 900 due to the unfortunate weak activity of the sections. Rerunning the same sample yielded very good reproducibility. A background measurement (of the
scintillation counter) was made after each activity measurement, and the result was used to correct the specific activity. In all cases the background counts were about 2 counts per minute.

The section thickness of the first eleven cuts was approximately 0.3 microns. A plot of these points indicated that the activity spread may not be great enough to give meaningful results. Sixteen more cuts were made using an etching time of three minutes instead of two. This increased the average section thickness to approximately 1.1 microns.

3.3.2 Results

The activity profile plot (ln c vs. $x^2$; section 2.3) with a mean square fit is shown in figure 5. The probable error is 0.034. From this fit the diffusion constant at 789\textdegree C is

$$D_{789} = 1.40 \times 10^{-10} \text{ cm}^2/\text{sec}.$$
4 DISCUSSION

The value of $1.40 \times 10^{-10} \text{ cm}^2/\text{sec}$ obtained by the present method agrees well with the same diffusion constant estimated from Hino's results ($D=1.45 \times 10^{-10} \text{ cm}^2/\text{sec}$) obtained by the lathe sectioning method. It is quite feasible then that this chemical sectioning technique is a valid method for determining diffusion coefficients for small penetration depths; at least down to 10 microns. In all probability, the above limit can be lowered to penetration depths less than 10 microns by modifying the apparatus slightly (see section 4).

The above method of chemical sectioning may be improved upon in a number of ways:

1) Increase of the number of radioactive atoms per unit volume of liquid.
2) Reduction of the burr formed during sectioning of the cylindrical surface.
3) More accurate determination of the section thickness.

To increase the sensitivity of the method, the amount of acid and wash water must be decreased. This would insure a greater
number of tracer atoms (present in the acid bath after sectioning) be contained in the counting bottle. Ideally the total volume of acid mixture and rinse would be equivalent to the volume of the counting bottle. This can most effectively be done by decreasing the diameter of the acid bath container mounted to the sample holder. This acid bath container can be machined right into the sample holder. Then the diameter of the acid container need not be much greater than the specimen diameter. It may also be possible to obtain a more reproducible section thickness if a heating mantle is placed around the acid bath to keep the acid at a constant temperature.

Since this experiment the machining of copper crystals has been greatly enhanced and burr formation was reduced by the modification which lowered the lathe cutting tool. Elimination of burr formation is also possible by chemically etching the cylindrical sides while protecting the sectioning face.

The section thickness can be more accurately obtained by using a micro-balance instead of the semi-micro balance used in this experiment. Sample weights could then be determined to 1 microgram.
By plating a larger quantity of tracer on the specimen, a greater activity per section will be obtained. This will allow a smaller section thickness to be counted. To decrease evaporation of the tracer from the surface, diffusion can take place in an atmosphere of an inert gas such as argon.

In conclusion, the above method may prove useful, not just for metallic specimens, but for the determination of diffusion constants in very brittle crystals such as calcite. Of course, other acid baths and different apparatus would have to be employed, but the idea would remain essentially the same.
REFERENCES


