A SIMPLE, INSTRUCTIVE SOLID STATE DIFFUSION EXPERIMENT FOR USE IN TEACHING LABORATORIES

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THE PROCESS OF ATOMIC diffusion in solids is fundamental to many basic processes considered by the materials scientist or engineer. Hence an instructional unit in diffusion is almost mandatory in the education of an engineer who wishes to have even the most rudimentary knowledge of the important basic materials phenomena. However, in attempting to explain the physical significance of the phenomenological equations describing diffusion such as Fick's Laws, many educators have difficulty in presenting tangible evidence of their applicability to relevant materials. It is one thing to describe diffusion mathematically, quite another to "see" the process taking place in a laboratory experiment which illustrates the mathematical description.

In this note we wish to describe an experiment which was developed for use in the undergraduate curriculum in Ceramic Engineering at the University of Washington. The experiment is simple to conduct, the results are easily obtained and it describes diffusion in a common high temperature material, magnesium oxide.

The experiment is based on similar experiments conducted by Zaplatynsky (1) involving cobaltous ion diffusion in single crystal magnesium oxide. The basic principle involved in the determination of the diffusion coefficients and activation energies for the system is the measurement of the rate at which a surface of fixed concentration moves away from a reference interface. The advantages of using this system are: (1) the materials are easily obtainable, (2) the surface of fixed concentration is defined by a sharp color change in the crystal, (3) diffusion coefficients are such that reasonable penetrations are possible at temperatures available in simple laboratory furnaces and for reasonably short diffusion times, and (4) the vapor pressure of cobaltous oxide is such that nearly perfect contact is achieved at the inititial interface.

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PROCEDURE

THE MATERIALS USED in the experiment are easily obtainable. Small magnesium oxide crystals may be obtained for little or no cost from normal suppliers*. The purity is not determined, nor is it felt necessary since the object was to demonstrate the validity of the diffusion equations, not to investigate the effects of impurities on diffusion rates. The cobalt oxide is standard technical grade available from any chemical supply house.

The experimental procedure followed is outlined below. The MgO crystals are cleaved to an approximate sixe of 10x4x4 mm. A corner is ground off each crystal for orientation purposes

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*For example, Norton Co., Worcester, Mass.

and the two short dimensions were measured using a micrometer stage microscope. The crystals are then packed in the CoO powder, which has been dried at 100°C for 24 hrs, in small Al_2O_3 crucibles. These are in turn placed in small fireclay crucibles, much as eggs in egg cups, and covered with a single alumina lid. This double crucible technique is necessary because the high vapor pressure of CoO at elevated temperatures results in the vapor drifting out of the inner container and down the sides. If the second crucible is not present, the furnace will be contaminated. Using this simple technique, the furnace refractories show no sign of the characteristic cobalt blue contamination.

The crucibles are placed in a silicon-carbide-resistance furnace and heated at the desired temperature. At selected times a crucible is withdrawn and the diffusion anneal continued on those remaining. Upon cooling after removal from the furnace, the lump of sintered cobalt oxide is removed, cracked open gently with a hammer and the crystals removed. Three thin sections, about one millimeter thick, are then cleaved transverse to the long dimension of the crystals at approximately the mid-length. These are cemented to microscope slides with epoxy resin. The sections are examined microscopically and the two dimensions of the colorless MgO central portions measured. Care is taken during cleaving and mounting to preserve the orientation, so the dimensions may be matched with corresponding dimensions of the original crystal. The depth of penetration, x, is given by

$$x = (w_o - w_1)/2 \quad \text{or} \quad (d_o - d_1)/2$$

where w_o = original width of crystal
w_1 = corresponding width of colorless crystal after anneal
d_o = original depth of crystal
d_1 = corresponding dimension of colorless crystal after anneal

Thus for two crystals at any one time and temperature a total of twelve measurements may be made of x.

ANALYSIS

FOR THIS GEOMETRY, where the penetration depth is small compared with the size of the specimen and is measured by the distance from the original interface to the region of rapid color change, the solution to Fick's Second Law for one dimensional diffusion into an infinite medium with constant surface concentration is appropriate. This solution is

$$C = C_s\left(1 - \operatorname{erf}\frac{x}{2\sqrt{Dt}}\right) \qquad 1$$

where the error function, $\operatorname{erf} = \frac{2}{\sqrt{\pi}}\int_0^{\frac{x}{2\sqrt{Dt}}} e^{-z^2}\,dz$

and C_s = constant surface concentration
C = concentration at surface of rapid color change
x = penetration distance
D = diffusion coefficient
t = time

From equation (1)

$$\frac{x}{2\sqrt{Dt}} = \operatorname{erf}^{-1}\left(1 - \frac{C}{C_s}\right)$$

where erf^{-1} is the inverse error function.

If the surface concentration and the concentration at the color change surface are known, the relationship between x and t is determined by consulting a table of error functions (2) and is of the form

$$x^2 = kDt$$

where $k = 4\operatorname{erf}^{-1}\left(1 - \frac{C}{C_s}\right)^2$.

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Zaplatynsky, in his work on this system, assumed a value of four for k regardless of the surface concentration. He found as a result that the apparent diffusion coefficient for cobalt diffusion in MgO was an order of magnitude lower if a surface concentration of 30 m/o CoO was imposed rather than 100 m/o. The difficulty in assigning a value to k arises from not knowing what the concentration of CoO is at the color change surface. On the basis of Zaptalynsky's chemical analysis of

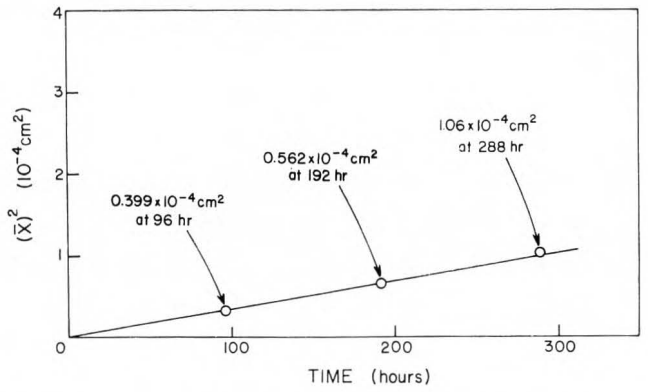

FIGURE 1. Plot of Average Penetration Depth Squared, $(\bar{X})^2$, as a Function of Time for Diffusion of Co^{++} into MgO at 1250°C.

his specimens together with his measurements of penetration depth it would appear that this concentration is nearly 60 m/o CoO; however, this is impossible since he had a color change surface when the surface concentration was held at only 30 m/o. If one assumes a value of, say, 20 m/o, then a value of k may be obtained for each value of the surface concentration used. For the surface concentration used by Zaplatynsky, the values are:

Surface Concentration	k
100 m/o CoO	3.6
30 m/o CoO	1.2

Recalculation of Zaplatynsky's diffusion coefficients for Co in MgO yields values which are much more nearly equal for the two conditions of surface concentration.

On this basis all that is required for the determination of a diffusion coefficient is a series of penetration depths, x, and corresponding times, t. A plot of x^2 as a function of t should be a straight line of slope kD. By plotting ln D against corresponding values of reciprocal absolute temperature, for diffusion coefficients measured at various temperatures, activation energies, Ea, and diffusivity constants, Do, may be determined from the slope and intercept.

RESULTS OF TRIAL RUNS

AS A TRIAL CASE, six crystals were run under the procedure outlined above at 1250°C for three times, 96, 192 and 288 hours. The results of the tests are shown in Figure 1. Each point represents an average of twelve independent measurements of the penetration depth, two measurements on each of three sections from two different crystals. The diffusion coefficient at 1250°C calculated using a value of k = 3.6 was 2.6 x 10^{-11} cm^2/sec. Zaplatynsky's data yield a diffusion coefficient at the same temperature of 3.9 x 10^{-11} cm^2/sec. This result suggests that whatever the shortcomings of the analysis, the results of the experiment are reproducible.

USE OF THE EXPERIMENT

THE LONG TIMES INVOLVED in the diffusion anneals probably require that specimens be prepared before the students are introduced to the experiment. In our program, the specimens are given to the students mounted on microscope slides and ready for measurement (Fig. 2). A good description and/or demonstration of the preparation of the specimens is given, together with some background information on the analysis of the data. The students then measure the specimens, plot the data and derive values for the diffusion coefficients, activation energies and diffusivity constants.

The laboratory report written by the student requires a description of the procedure, presentation of data and an evaluation of the results. The student is led to examine certain aspects of the experiment by including in the syllabus for the experiment a few questions which he should discuss.

REFERENCES

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2. Jahnke, Eugene and Emde, Fritz, *Tables of Functions with Formulae and Curves*, Dover Publications, Inc., New York, 1945.

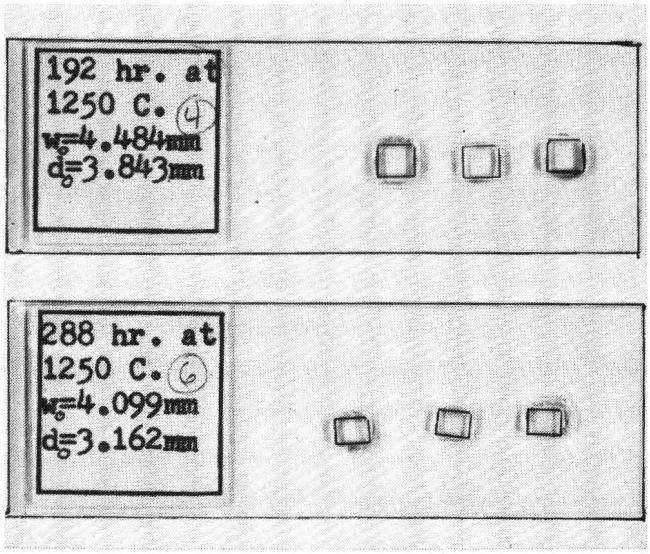

FIGURE 2. MgO-Co^{++} Diffusion Specimens Prepared for Student Use. (Note that temperature, time duration of diffusion anneal, and w_o and d_o are marked on each slide.)