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Y₂O₃

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Self-Diffusion in Polycrystalline Yttrium Oxide*

Michael F. Berard[†] and D. R. Wilder

Institute for Atomic Research and Department of Chemistry

Iowa State University, Ames, Iowa

MASTER

Abstract - The self-diffusion coefficient of yttrium in yttrium oxide has been determined for polycrystalline Y₂O₃ in the temperature range 1400 to 1800°C. Radioactive Y-91 was deposited on sintered specimens of 94 to 97% theoretical density. The specimens were annealed under vacuum and sectioned. The following equation describes the temperature dependence of the diffusion coefficient over the range studied:

$$D = 2.41 \times 10^{-4} \exp(-43,900/RT) \text{ cm}^2/\text{sec}$$

I. INTRODUCTION

Yttrium, and its oxide Y₂O₃, are of interest for several reasons. They exhibit properties remarkably similar to those of the heavier lanthanon rare earths due to the electronic configuration and to the lanthanide contraction of the atomic radii. Yttrium occurs fairly abundantly in nature in such minerals as gadolinite, xenotime, and fergusonite but always in complex mixtures with the true lanthanides. Separation of yttrium from these elements usually is by ion exchange, formation of an oxyacid salt, and a calcination to yield the oxide. Ytria (Y₂O₃) crystallizes in the bcc system,¹ and this structure is stable throughout the range of temperature in which the material remains solid.²

This material has a thermal neutron absorption cross section of 1.4 barns,³ lower than any of the rare earths. This property

indicates possible refractory applications for Y_2O_3 in nuclear reactor cores and similar application where neutron flux is all-important.

II. EXPERIMENTAL

(a) Basic Concepts

Assuming an isothermal, isobaric, binary system consisting of a single phase in which diffusion occurs in only one direction, Fick⁴ postulated that the quantity of diffusing material which passes through a unit area in a unit time is proportional to the concentration gradient of the diffusing species. Fick's first law is given by

$$J = - D \frac{\partial c}{\partial x}, \quad (1)$$

where J is the flux, c is the concentration of the diffusing species, x is the direction in which diffusion occurs, and D is the diffusion coefficient. Combining Eq. (1) with an equation of continuity for flow between two adjacent planes normal to the diffusion direction results in Fick's second law,

$$\frac{\partial c}{\partial t} = \frac{\partial (D \frac{\partial c}{\partial x})}{\partial x}, \quad (2)$$

where t is time. Assuming D to be invariant with concentration, Eq. (2) becomes

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2}. \quad (3)$$

Because of its relative experimental simplicity and near freedom from sources of large error, the sectioning technique has been employed for this study. In applying this method it was necessary to first obtain the proper solution of Eq. (3). The boundary conditions that apply are:

$$c = C_0 \quad \text{at } x = 0 \text{ for all } t;$$

$$c = 0 \quad \text{at } x > 0 \text{ and } t = 0;$$

$$c = c(x, t) \quad \text{at } x > 0 \text{ and } t > 0.$$

These conditions, which define the semi-infinite case, give the following solution to Eq. (3).

$$c(x, t) = \frac{C_0}{(\pi Dt)^{1/2}} \exp(-x^2/4Dt). \quad (4)$$

The form of Fick's law used in this treatment is dependent on the valid assumption that the self-diffusion coefficient is independent of the concentration of the diffusing species.

(b) Materials

The yttrium oxide used was made at the Ames Laboratory. An emission spectographic analysis of this material is given in Table I. A stoichiometry analysis indicated Y_2O_3 .

The as-received oxide clinker was crushed, and formed by dry pressing in a cylindrical steel die at a pressure of 70,000 lb/in.² The specimens were placed in a Y_2O_3 crucible and fired in a silicon carbide resistor furnace to 1340°C. The crucible and specimens were then transferred to a graphite-susceptor induction furnace and heated to 2100°C. Based on a density value of 4.64 g/cm³ this firing yielded specimens in the range of 94 to 97% of theoretical density.

The radioactive isotope employed in this study was Y-91, with a 58-day half-life and a 1.55 Mev electron as the predominating emission. The isotope was obtained from Oak Ridge National Laboratory in the form of YCl_3 in approximately three normal hydrochloric acid solution, with a radiochemical purity of greater than 99%. The carrier employed

for tracer preparation was a hydrochloric acid solution in which Y_2O_3 had been dissolved in a concentration of 0.5 g/ml.

Table I. Emission spectrographic analysis of impurities in Y_2O_3 .

Element	wt%
Sm	≤ 0.05
Gd	≤ 0.01
Tb	≤ 0.05
Dy	0.01
Ho	≤ 0.05
Er	≤ 0.05
Yb	Trace
Mg	≤ 0.001
Fe	0.04
Ca	Trace
Ta	≤ 0.04
Total Impurity	≤ 0.301

(c) Equipment

The furnace used for the diffusion anneals was a water-cooled vacuum resistance furnace employing a molybdenum heating element.

A pellet lathe was constructed to allow removal of material from the diameter of the diffusion specimens following annealing..

A special sectioning device was designed to remove successive thin layers from the active face of the diffusion specimens. The device was in many respects similar to the one described by Goldstein.⁵ Provision was

made in the center of a turntable to mount a 1 3/8 in. diameter alumina disc 1/8 in. in thickness covered with 400-grit silicon carbide paper. The center lines of the turntable and the specimen holder were displaced 5/16 in. so the material removed from the specimen would be deposited on the abrasive disc in an annular pattern. This provision was made to facilitate counting and to utilize a greater portion of the abrasive disc for grinding.

The detector used was an end-window Geiger-Müller tube with a binary scaling unit to integrate the output. A brass positioner assured that all discs would be counted in the same geometry.

(d) Procedures

The tracer was applied in the form of a hydrochloric acid solution of Y_2O_3 containing Y-91 to the extent of about five microcuries per milliliter. Although yttria is fairly soluble in hydrochloric acid, no appreciable etching of the surface was observed, and preliminary investigations showed that penetration of active solution through the surface pores of the specimens did not exceed twenty microns prior to annealing.

The oxidation of the tracer material to yttria was carried out in a drier and finally in a small electric furnace operating at 900°C in air.

The activated specimens were placed in a small molybdenum dish and suspended within the annealing furnace.

The temperature of the annealing furnace was controlled by means of a manually-operated variable transformer. Temperature was read

with an optical pyrometer previously calibrated against a standard tungsten filament bulb and corrected for sight-glass absorption.

After the anneal, the excess tracer material which did not take part in the diffusional process was removed with a stiff brush. The specimens were weighed to the nearest 0.0001 g and their height was measured to the nearest 0.0001 cm with a micrometer. They were then placed in the pellet lathe, and a few microns of material were turned off their cylindrical surface.

Previously weighed alumina discs covered with 400-grit paper were used to remove succeeding thin sections from the active face of the specimens in the sectioning device. The rate of material removal was controlled by varying the grinding time and the speed of the grinding table. The gain in the weight of the alumina discs during grinding was converted to the thickness of the section removed.

The discs were covered with transparent Mylar tape and counted. The duration of the counting period varied with the amount of activity on the disc, at least 1000 total counts being taken in all cases to limit the counting error to less than 3%.⁶

III. Results

The data resulting from the sectioning and counting operations are shown in Figs. 1 through 5. In these graphs x is the distance from the initial surface of the specimen to the mid-point of the section under consideration. An activity, A , defined as counts/min/micron thickness was calculated by dividing the total activity of each section removed by the section thickness. This procedure assumes a linear activity gradient across each section.

The data were found to fall on straight lines described by equations of the form

$$\ln A = \ln K - (x^2/4Dt), \quad (5)$$

where K is a constant depending upon the initial amount of activity deposited on the specimen. This equation is simply the logarithm of Eq. (4) with the substitution of activities for concentrations. The slope of this curve is $-(1/4Dt)$.

In each case a least-squares fit for the data points was obtained, and the diffusion coefficient, D, was calculated from the resulting slope. Table II gives a summary of the diffusion coefficients resulting from these calculations.

Table II. Summary of results.

Specimen	Specimen Density (g/cm ³)	T (°K)	D (cm ² /sec)
#10	4.36	1673	2.90×10^{-10}
#14	4.44	1773	6.86×10^{-10}
#9	4.43	1873	1.90×10^{-9}
#11	4.30	1973	3.50×10^{-9}
#16	4.49	2073	5.09×10^{-9}

With few exceptions, diffusion coefficients vary with temperature according to the equation

$$D = D_0 \exp (-Q/RT), \quad (6)$$

where T is the absolute temperature, R is the gas constant, D_0 is a constant known as the frequency factor, and Q is the enthalpy of activation, more commonly known as the activation energy. The logarithm of

Fig. 1. Curve of $\ln A$ vs x^2 for $T = 1400^\circ\text{C}$, $t = 14400$ sec.

Fig. 2. Curve of $\ln A$ vs x^2 for $T = 1500^\circ\text{C}$, $t = 7200$ sec.

Fig. 3. Curve of $\ln A$ vs x^2 for $T = 1600^\circ\text{C}$, $t = 14400$ sec.

Fig. 4. Curve of $\ln A$ vs x^2 for $T = 1700^\circ\text{C}$, $t = 7200$ sec.

Fig. 5. Curve of $\ln A$ vs x^2 for $T = 1800^\circ\text{C}$, $t = 7200$ sec.

Eq. (6) is

$$\ln D = \ln D_0 - (Q/RT) \quad (7)$$

which is a straight line function.

Plotting the logarithm of the values of D given in Table II vs the reciprocal of the corresponding absolute temperatures gave the curve shown in Fig. 6. The slope of this curve is equal to $-(Q/R)$.

A least-squares fit was obtained for this curve, and the activation energy for diffusion as well as the frequency factor was determined from the resulting equation. These values were then placed in Eq. (6) to yield the temperature dependence equation of the diffusion coefficient.

$$D = 2.41 \times 10^{-4} \exp(-43,990/RT) \text{ cm}^2/\text{sec}$$

This equation may be considered valid in the temperature range 1400-1800°C.

The uncertainties in the measured values of the annealing time and the annealing temperature were less than 1% in all cases. Due to the small amounts of tracer employed and the diminishing specific activities at increasing depths below the specimen surface, the convenience of the duration of counting become the controlling factor in limitation of uncertainty in counting measurements. An upper limit of 3% was arbitrarily chosen for the uncertainty in these measurements necessitating the taking of about 1000 total counts.⁶ The greatest source of error in the entire procedure stemmed from the uncertainty involved in determining the gain in the weight of the abrasive discs during sectioning. The maximum uncertainty encountered in these determinations was approximately 6%.

Condit⁸ states that the total uncertainty in the diffusion coefficient may be as large as the sum of the absolute values contributed by each parameter, but states further that this is unlikely. Based on Condit's

Fig. 6. Curve of the temperature dependence of the diffusion coefficient.

calculations, the maximum uncertainty in the diffusion coefficients measured in this study has been estimated to be about 10 - 15%.

IV. DISCUSSION

The fact that the diffusion of yttrium in yttrium oxide exhibits only one activation energy throughout the entire range of temperatures considered suggests that a single mechanism or unvarying combination of mechanisms of mass transport predominates over this range. A study of a compilation of cation diffusion coefficients in oxide systems⁷ shows a general trend toward increasing activation energy with increasing ionic charge. It should be emphasized that this is only a very general trend, and discrepancies often occur. The activation energy of yttrium in yttria, observed to be about 44,000 calories/mole, is approximately one-half of the value predicted by the general trend.

It is of interest to speculate on the possible causes of this departure from the general trend. The inordinately low observed activation energy may be due to a combination of mass transport mechanisms in which diffusion along grain boundaries exerts a sensible effect. The activation energy for grain boundary diffusion will be considerably lower than that for volume diffusion due to the nature of the ion bonding in grain boundaries as compared to that in the interior of the crystal.

The lack of any break in the temperature dependence curve, Fig. 6, is, however, indirect evidence that some volume diffusion is taking place, and may, in fact, be the predominating diffusional path. It is generally accepted,⁹ that diffusional transport paths at high temperatures are predominantly through crystal volumes, with transport along grain boundaries predominating at lower temperatures. Since no change in activation energy,

and hence no change in predominance, takes place in yttria, even at high temperatures, it would seem that some volume diffusion is taking place over the entire range in which measurements were made. Unfortunately, no data are available at this date on the diffusion of yttrium in single crystals of yttria, and hence the fraction of the total mass transport that takes place through the grains of the specimen material cannot be separated from that which takes place along the grain boundaries. Work is in progress along such lines.

In addition to the effect of grain boundary diffusion, the activation energy of the over-all diffusional process may be further reduced by high nonequilibrium vacancy concentrations in the specimen material prior to annealing. Coble¹⁰ has suggested that oxides prepared by calcination at fairly low temperatures will show this effect. If it is assumed that nonequilibrium vacancies are present in the specimen, it follows that more units capable of taking part in the diffusional process would be available, and the coefficient of diffusion would be raised.

V. SUMMARY

A method of sectioning using a radioisotope tracer has been described for determination of self-diffusion of Y in polycrystalline Y_2O_3 . The analysis of the results yields the following relationship between the diffusion coefficient and temperature:

$$D = 2.41 \times 10^{-4} \exp(-43,900/RT) \text{ cm}^2/\text{sec}$$

This relationship is valid between 1400 and 1800°C.

A continuous temperature dependence was observed, indicating one mechanism or constant relation between two or more mechanisms.

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