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DIFFUSION IN POLYCRYSTALLINE Y_2O_3 AND Er_2O_3

by

Michael Frank Berard

Ph.D. Thesis, May, 1968

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DIFFUSION IN POLYCRYSTALLINE Y_2O_3 AND Er_2O_3

by

Michael Frank Berard

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of
The Requirements for the Degree of
DOCTOR OF PHILOSOPHY

Major Subject: Ceramic Engineering

Approved:

In Charge of Major Work

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DIFFUSION IN POLYCRYSTALLINE Y_2O_3 AND $Er_2O_3^*$

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ABSTRACT

A study of self-diffusion in Y_2O_3 and Er_2O_3 is presented. A tracer sectioning technique was employed to measure cation self-diffusion coefficients in fully-dense polycrystalline materials under oxidizing conditions. The results are described by the relations

$$D = 1.65 \times 10^{-2} \exp(-69,200/RT) \text{ cm}^2/\text{sec}$$

for Y_2O_3 (1400-1670°C), and

$$D = 1.48 \exp(-102,200/RT) \text{ cm}^2/\text{sec}$$

for Er_2O_3 (1400-1700°C). The greater activation energy for erbium diffusion in erbia is attributed to a mass effect.

Oxygen diffusion coefficients were extracted from observations in the reoxidation of small single crystals of uniformly reduced oxides produced by vacuum fusion. The oxidation process was demonstrated to proceed by the development of

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a fully-oxidized external shell, the growth of which was rate-limited by diffusion of interstitially-dissolved oxygen through the oxidized layer to a sharp interface with the reduced material. The growth of the oxidized shell was followed by means of a thermobalance. Using standard techniques for treatment of diffusion in the presence of a moving boundary, and estimating the saturation limit for interstitial solution of oxygen in the known crystal structure, oxygen diffusion coefficients were calculated. These results are described by

$$D = 6.01 \times 10^{-6} \exp(-19,600/RT) \text{ cm}^2/\text{sec}$$

for Y_2O_3 (1064-1276°C), and by

$$D = 4.76 \times 10^{-5} \exp(-30,100/RT) \text{ cm}^2/\text{sec}$$

for Er_2O_3 (1060-1292°C).

INTRODUCTION

Research Objectives

The study of material transport in rare earth oxides is of interest for several reasons. The unusual openness of the structure of these materials should lead to interesting comparisons of diffusion rates with more densely packed related structures such as the true fluorite structure. Of especial interest might be diffusion studies in a series of structures varying from true fluorite to the defective fluorite common to the rare earth oxides. From a practical standpoint, a number of the rare earth oxides possess both stability at high temperature and extremes in thermal neutron absorption cross-sections. This combination of properties suggests important nuclear applications for rare earth oxides. The ability of these materials to contain fission products, many of which are themselves rare earths, is not known however. As a logical first step in studying either the effects of changes in structure on material transport or the barrier to migration of fission products exhibited by these materials, measurements of self-diffusion must be made.

The objectives of this research were to carry out these necessary self-diffusion measurements in dense Y_2O_3 and Er_2O_3 .

These two materials were chosen because of their nearly identical structures but great difference in molecular weight.

The cation self-diffusion studies were to be carried out on polycrystalline material under oxidizing conditions by a standard radioactive tracer technique. The oxygen diffusion studies were to be based on information extracted from the oxidation rate of partially reduced oxides prepared by vacuum fusion.

Phenomenological Description of Diffusion

Early in the nineteenth century, pioneers in the study of diffusion made qualitative observations which showed that gases tended to intermingle even when great care was taken to avoid mechanical agitation and convection effects (1). Later in that century, Fick proposed a mathematical description of the process analogous to the Fourier expression for heat conduction (2). Assuming an isothermal, isobaric, binary system consisting of a single phase in which diffusion occurs in only one direction, Fick postulated that the quantity of diffusing species passing through a unit area perpendicular to the diffusion direction per unit time is proportional to the negative concentration gradient in the diffusion direction. Subsequently, quantitative measurements in liquids and gases were

found to be adequately described by this postulate (1).

Expressed mathematically, Fick's equation is given by

$$J_i = -D_i \frac{\partial c_i}{\partial x} \quad (1a)$$

where J_i is the flux of the i th species, c_i is concentration in particles per unit volume, x is the dimensional coordinate parallel to the diffusion direction, and D_i is a proportionality coefficient variously called the diffusion coefficient or simply the diffusivity of species i .

Equation 1a is popularly termed Fick's First Law. A more general form of this expression which describes the motion of k diffusing species and is not restricted to a single diffusional coordinate is given by

$$J_i = - \sum_k D_{ik} \nabla c_k, \quad (1b)$$

where D_{ik} is a tensor (3). It may be seen that Equation 1b reduces to Equation 1a under the restrictions specified by Fick.

Fick's First Law is often combined with a continuity equation to yield an equation describing the change in concentration of the diffusing species at a point as a function of time. This equation, known as Fick's Second Law, may be

written for the one-dimensional case as

$$\frac{\partial c_i}{\partial t} = \frac{\partial}{\partial x} \left(D_i \frac{\partial c_i}{\partial x} \right). \quad (2a)$$

If it is assumed that the diffusivity is independent of concentration and therefore is independent of position along the x coordinate, Equation 2a may be simplified to give

$$\frac{\partial c_i}{\partial t} = D_i \left(\frac{\partial^2 c_i}{\partial x^2} \right). \quad (2b)$$

The assumption that the diffusion coefficient is concentration independent is usually not valid; however, in the case of self-diffusion where no gradients in chemical composition but only gradients in isotopic concentration occur, the assumption of the invariance of D throughout the system is acceptable, and Equation 2b should describe the diffusion process.

Darken (3) has pointed out that the driving force for chemical diffusion in an isobaric, isothermal system is not a gradient in concentration but rather is a gradient in the chemical potential of the diffusing species. The flux should thus be the product of the driving force, the mobility, and the concentration of the diffusing species. This may be expressed as

$$J_i = - \frac{c_i b_i}{N} \frac{d\mu_i}{dx} \quad (3)$$

where b_i is the mobility of the i th species. Expressing the

chemical potential in terms of the activity coefficient γ_i of the diffusing species leads to the following expression for the gradient:

$$\frac{d\mu_i}{dx} = \frac{RT}{\gamma_i c_i} \left[\frac{d\gamma_i}{dx} c_i + \frac{dc_i}{dx} \gamma_i \right] . \quad (4)$$

Thus,

$$J_i = - \frac{RTb_i}{N\gamma} \left[\frac{d\gamma_i}{dx} c_i + \frac{dc_i}{dx} \gamma_i \right] . \quad (5a)$$

In the special case where the diffusing species forms an ideal solution in the medium in which diffusion is occurring, which may be considered the case whenever c_i is very small, Equation 5a simplifies to

$$J_i = - \frac{RTb_i}{N} \frac{dc_i}{dx} . \quad (5b)$$

This is the form of Fick's First Law, Equation 1a, and the diffusivity may be identified as

$$D_i = \frac{RTb_i}{N} \quad (6)$$

in this special case. Thus, Fick's laws may be considered as the limits to which the more general and more rigorous descriptions of diffusion reduce under the condition of essentially zero concentration of diffusing species.

Shewmon (4, p. 23) has emphasized that the presence of additional driving forces, for example the presence of an

electric field, will cause additional terms to appear in Equation 3, and Fick's laws can no longer describe the diffusion process.

The determination of diffusion coefficients usually begins with a solution to Fick's Second Law. In the more general case, Equation 2a, with D a function of concentration, the equation cannot be solved by the usual techniques. For certain limited conditions, however, the graphical integration method of Boltzman-Matano (4, p. 28) will yield values of the chemical diffusion coefficient describing the redistribution process for all mobile species present. Darken (5) has explained that with additional experiments, the chemical diffusivity can be decomposed into the intrinsic diffusivities of each diffusing species. Jost (6, p. 145) likewise treated this subject in ionic solids.

In the case of self-diffusion, or in impurity diffusion where the concentration of the diffusing species is kept vanishingly small, the variation of the diffusivity with composition can be ignored, and Equation 2b is valid. A great many physically-realizable sets of boundary and initial conditions can be devised, and numerous solutions to Equation 2b are readily available, probably the most comprehensive compila-

tion being that of Crank (7).

The particular solution of Fick's Second Law corresponding to a given set of initial and boundary conditions allows a prediction of the spatial distribution of the diffusing species in the system at any time. An experiment can then be devised which satisfies the restrictive conditions placed on the solution, and the actual distribution of diffusing species after a fixed time can be determined. A value of the diffusion coefficient which exactly superimposes the experimental distribution on the predicted distribution may then be calculated. The methods employed for experimental determination of the distribution of the diffusing species after diffusion are usually based on chemical analysis of the system, either in toto, or performed on thin slices taken at progressively greater distances from the initial concentration discontinuity. Self-diffusion, which implies the diffusion of a substance into its exact counterpart, results in no redistribution of chemical species, and so chemical analysis can yield no useful information concerning this process. The ready availability of concentrated isotopes, both radioactive and stable, has made the mapping of isotopic distributions after diffusion a relatively simple chore, and has made possible the very extensive number

of self-diffusion studies found in the literature today. The ease of isotopic distribution mapping over more conventional analysis techniques has lead investigators to use isotopic techniques for the measurement of chemical diffusion as well. The assumption on which all of these studies are based is that all isotopes of an element may freely substitute for one another in the crystal structure of a solid without affecting the diffusion process. The only possible effect would originate from a difference in masses of the isotopes. Mullen (8) has expressed the ratio of the diffusivity for two isotopes, A and B, in a host material as the following function of their masses, m:

$$1 - \left(\frac{D_B}{D_A} \right) = E_B \left[1 - \left(\frac{m_A}{m_B} \right)^{\frac{1}{2}} \right], \quad (7a)$$

where E_B is a constant for the particular system which closely approximates unity for many systems. Thus, appreciable isotope effects are essentially absent for atomic numbers greater than about ten.

Properties of Yttrium and Erbium Oxides

The sesquioxides of yttrium and erbium possess similar chemical and physical properties. Erbium, atomic number 68, is a member of the group of elements encompassing atomic

numbers 57 through 71, commonly called the lanthanides. This series is built up by addition of electrons in the 4f subshell while the external 6s shell remains filled with two electrons. The similar external electronic arrangement results in similar chemical properties throughout the series with the predominating valence being +3. Valences of +2 and +4 are known to occur in certain of the elements, but erbium has never been reported to show a valence other than +3. Yttrium, atomic number 39, is not a member of the lanthanide series; however, its external electronic arrangement is similar to the lanthanides, and it is commonly grouped together with them under the family name rare earths. Scandium, atomic number 21, is also a member of the rare earth family.

The fully-oxidized forms of the elements, Y_2O_3 and Er_2O_3 , are the only known solid oxides of yttrium and erbium. A comparison of several of the properties of these two compounds condensed from Gibson and Harvey (9) is given in Table 1.

Numerous authors, for example Foex and Traverse (10) and Roth and Schneider (11), report the stable form of both Y_2O_3 and Er_2O_3 , at room temperature and under one atmosphere pressure, to possess the cubic rare earth type C structure. This structure belongs to space group $Ia\bar{3}$ (12a), with sixteen ses-

Table 1. Some properties of Y_2O_3 and Er_2O_3

Property	Y_2O_3	Er_2O_3
Molecular weight	225.81	328.52
$-\Delta H_{298}^{\circ}$, kcal/mole ^a	455.46	453.60
Melting point, $^{\circ}C$	2410 ^a	2400 ^b
Mean CTE (0-1400 $^{\circ}C$), $^{\circ}C^{-1} \times 10^6$ ^a	8.2	7.3
a_0 , $\text{\AA}$ ^c	10.604	10.550
X-ray density, gm/cm ³	5.0308	8.6537

^aFrom Gibson and Harvey (9).

^bFrom Foex (12b).

^cFrom Glushkova and Boganov (14).

quioxide formula units per unit cell. Details of the atomic arrangement have been given by Wyckoff (13). This structure has been described by Eyring (12) as a modified fluorite structure having one anion in four missing in order to balance the trivalent cation charge with a consequent slight readjustment of the positions of the remaining ions. The resulting oxygen vacancies may be considered as forming nonintersecting strings along the four $\langle 111 \rangle$ directions of the cubic cell. These relatively open pathways through the oxygen sublattice

would be expected to enhance material transport in these materials.

A number of determinations of the lattice parameters for the type C structures of yttria and erbia have been reported. The results of Glushkova and Boganov (14) are given in Table 1 along with the corresponding x-ray densities computed from these parameters.

At least one additional crystalline form of both oxides is known at high temperatures. This form, designated type H by Foex and Traverse (10,15,16), is apparently closely related to the hexagonal type A structure common to the lighter lanthanides at room temperature. The type C to type H transformation is a reversible one occurring at 2250 to 2300°C. for both Y_2O_3 and Er_2O_3 (10). A third crystalline form of Y_2O_3 has been reported by Mehrotra et al. (17) as forming reversibly from the type C structure on heating to a temperature of 390°C. This form was stated to be most probably hexagonal, but the possibility of a monoclinic structure was not ruled out. The c/a ratio of this low-temperature hexagonal modification of Y_2O_3 is reported by Mehrotra et al. to be 1.038 at 900°C. which rules out the possibility of this form being a remnant of the high-temperature type H structure

(c/a ratio equal to 1.600 at 2330°C. (10)). The low-temperature transformation of Mehrotra et al. has not been found by other investigators scanning over the temperature region in question by either DTA, dilatometry or x-ray diffraction techniques (10,18,19). No report of a similar low-temperature modification of Er_2O_3 or any other of the normally type C sesquioxides of the rare earths is known to this author.

The effects of pressure on the crystal structure of the heavier rare earth oxides has been studied by Hoekstra and Gingerich (20,21) and by Sawyer et al. (22). It was found that the type C structure can be transformed reversibly into the type B monoclinic structure by pressures above ten kilobars and temperatures above 550°C. (20).

Miller and Daane (23) have produced partially reduced forms of the rare earth sesquioxides by melting under vacuum. Wirkus et al. (24) have reported that material produced in this way reoxidizes to a stoichiometric sesquioxide with an oxygen penetration rate independent of particle size and external oxygen partial pressure, but strongly dependent on temperature. These observations point toward a diffusion-controlled mechanism of reoxidation. The possibility of monitoring the reoxidation process with a thermobalance sug-

gested that diffusion coefficients for oxygen in the sesquioxides might be extractable from weight gain data. Because of the inherently defective anion sublattice in these materials, such a study was expected to yield large diffusivities.

Very little work on diffusion in rare earth oxides has been published, and almost none is available on the sesquioxides possessing the type C structure. Kuntz and Eyring (25) have reported work on praseodymium and terbium oxides, both of which exhibit multiple valences and a very complex series of oxygen-metal stoichiometries (12). In this work, oxygen diffusion coefficients were estimated from the rate at which higher oxides lost weight on heating in a vacuum. Results reported for $\text{PrO}_{1.71}$ range from $1.5 \times 10^{-9} \text{ cm}^2/\text{second}$ at 990°C . to $1.7 \times 10^{-11} \text{ cm}^2/\text{second}$ at 700°C . with an activation energy of 42,000 calories/mole. No specific values for the diffusion coefficient were reported for $\text{TbO}_{1.71}$; however, the activation energy in the temperature range 570 to 643°C . was estimated to be 40,000 to 50,000 calories/mole. Eyring et al. (26) have presented some preliminary results on the diffusion of oxygen in A-type La_2O_3 and Nd_2O_3 and B-type Sm_2O_3 . Over the temperature range 700 - 1000°C ., the data for Sm_2O_3 were found to be described by

$$D = 6.2 \times 10^{-8} \exp(-33,000/RT).$$

Barrett and Barry (27) have studied the behavior of A-type Nd_2O_3 in oxygen by observing pressure decreases in a closed system coupled with electrical conductivity measurements. Their conclusion was that the defective anion lattice can take up oxygen interstitially with charge compensation by holes on neodymium sites. This absorption decreases to very low values at 800°C . and is rapidly reversible indicating rapid oxygen interstitial and hole mobilities.

Wirkus et al. (24) have published some very preliminary data on the diffusion of oxygen in Y_2O_3 and Er_2O_3 , but a change in the analysis approach will result in some modification of their values (28).

Berard and Wilder (29) have reported yttrium diffusion coefficients in polycrystalline Y_2O_3 of fairly low density annealed under vacuum. A single activation energy was found to describe the data in this work, but the magnitude of the coefficients was somewhat higher than might be expected for a trivalent ion such as yttrium. This may be an indication of the enhancing effect of the defective structure or may reflect appreciable transport of material by mechanisms other than pure bulk diffusion. The variation of diffusivity with

temperature in the range 1400 to 1800°C. was described by the equation

$$D = 2.14 \times 10^{-4} \exp(-43,990/RT) \text{ cm}^2/\text{second}.$$

Some discoloration of the specimens annealed at the higher temperature in vacuum was observed. In the light of the work of Miller and Daane (23), it seems possible that this discoloration was due to some reduction of the oxide during the course of the diffusion anneal.

Borchardt (30) has studied the progressive oxidation of yttrium metal in air. It was stated that oxygen diffusion was rate controlling, but no diffusion coefficients for either ion in the oxide were reported.

DIFFUSION LITERATURE

The technical literature pertaining to diffusion is extensive and is growing rapidly. It has been treated in some detail earlier (31), and no attempt will be made to repeat that treatment here. Instead, this discussion will begin by mentioning some of the more important reviews and bibliographies pertaining to the subject, and will conclude with a very brief outline of the history of the development of the diffusion literature.

As is so often the case where a literature is extensive, a number of bibliographies have appeared which are attempts to bring much of this scattered information into one place. Jaumot (32) has prepared an annotated bibliography covering the general subject of diffusion in solids over the period 1890-1955. Askill (33) has prepared a series of bibliographies concerned with diffusion in metals. A number of compilations are available pertaining to diffusion in ceramic materials only. Lindner (34), Lommel (35), and Cumming and Harrop (36) have compiled work on oxides; Vodopivec (37) has compiled work on oxides and sulfides; Berard (38) has compiled work on ceramic systems in general. In 1968 a new periodical (39) devoted exclusively to the compilation of

diffusion literature was inaugurated.

Extensive review works on the subject of diffusion are also available. General works on the subject include those of Jost (6), Barrer (40), American Society for Metals (41), Shewmon (4), and Girifalco (42). Crank (7) and Carlslaw and Jaeger (43) have treated the mathematics of diffusion phenomenology. The general reviews available in article form are too numerous to mention in their entirety. Darken (3) has treated the general subject. Zener (44) has discussed mechanisms, and Bardeen and Herring (45) treated marker movement and introduced the concept of correlation effects. Kingery (46) and Birchenall (47,48) have discussed the general subject of diffusion in crystalline ceramic materials, and Warren (49) has treated the subject in a series on glasses. Perhaps the most exhaustive recent general review article on diffusion in ceramic materials is that by Suptitz and Teltow (50).

Because measurement of diffusion and the related phenomenon of ionic conductivity require special experimental techniques, a considerable portion of the diffusion literature is devoted to the exposition of diffusion methodology. The reviews by Giess (51), Leymonie and Lacombe (52), and Lindner and Johansson (53) are noteworthy in this area. The most

recent reviews for ceramic materials are those of Gorbunov and Izvekov (54) and Suptitz and Teltow (50).

Viewed historically, probably the first qualitative observations on the phenomenon of solid state diffusion were made in the early nineteenth century. For example, it was reported in 1823 by Stodart and Faraday (55) that alloys could be made by interdiffusion of elements in mixed metal powders. In the middle of that century Adolph Fick (2) formulated his famous first law relating diffusion flux and concentration gradient. This relationship was found to satisfactorily describe the experiments on diffusion in liquids and gases being made at that time.

The actual quantitative investigation of diffusion in the solid state remained relatively untouched until 1900 when Roberts-Austen (56) made his pioneering experiment demonstrating the diffusion of gold into solid lead. The diffusion studies made in the early part of the twentieth century, following the work of Roberts-Austen, were solely concerned with chemical diffusion as determined by careful chemical analysis techniques.

The concept of the use of radioactive tracers to study rate processes was introduced by von Hevesy and Paneth (57)

in 1913. The first self-diffusion measurement followed in 1920 when Groh and von Hevesy (58) investigated the diffusion of lead in molten lead. The following year, the same investigators performed the first solid state self-diffusion experiments on solid lead (59). All of these studies were performed with naturally-occurring radioactive isotopes of lead. A number of studies followed, using naturally-occurring isotopes. It was not, however, until the late 1940's, when a plentiful supply of radioisotopes as fission fragments became available, that the areas and materials studied in solid state diffusion broadened appreciably. Since that time considerable data on solid state diffusion have accumulated in the technical literature.

The great interest in the physics of the solid state which has flourished since the early 1930's has provided considerable insight into the actual mechanisms by which atomic migration in the solid state occurs. One of the earliest attempts at a mechanistic approach to explanation of the diffusion phenomenon was given in 1894 by Lord Rayleigh (60) treating atomic motion as a process governed by the statistical laws describing random walk processes. This approach has been often repeated, with the especially comprehensive treat-

ment of Chandrasekhar (61) being most noteworthy. The level of sophistication in knowledge of the solid state by 1942 permitted pioneering calculations by Huntington and Seitz (62) of the energies required to move copper atoms by various proposed diffusion mechanisms in a copper lattice. More of these type of calculations quickly followed (63,64,65) and comparison with experimental activation energies provided strong evidence for a vacancy migration self-diffusion mechanism in fcc metals instead of the direct interchange mechanism popular at that time. Further support for the vacancy mechanism was given in the milestone paper by Darken (5) in which the Kirkendall effect, i.e. movement of inert markers during metallic diffusion in a chemical gradient, was explained in terms of a combination of true diffusion plus a net motion of the diffusion matrix. Darken's analysis has recently been extended to ceramic systems (66).

Around 1950, two additional developments were made in the mechanistic approach to diffusion. The first was the description of the diffusion process by absolute rate theory including provisions for modification of the description to fit any one of various possible mechanisms (67). The second development was the introduction by Bardeen and Herring (45)

of the concept of correlated diffusional jumps. Thus it was shown that a tracer atom moving by a vacancy mechanism is not undergoing a wholly random migration process. The concept of correlation has been especially important in elucidating the mechanism of migration in ionic solids by comparison of self-diffusion and ionic conductivity measurements (68,69,70).

In the 1950's considerable progress was made in development of a mathematical model to describe diffusion along grain boundaries in polycrystalline materials. Fisher (71), Whipple (72), and Levine and MacCullum (73) successively treated the problem with greater sophistication. The latter paper carries the guidelines for unambiguous determination of grain boundary effects in a system in which grain boundary and bulk diffusion both occur. Experimental work has generally shown that atomic migration in metal systems is enhanced by grain boundaries. The somewhat more complex structure of grain boundaries in ceramic materials and the paucity of careful measurements in these systems makes such a generalization dangerous. In a review paper on this subject in ionic systems, Graham and Tallan (74) conclude that cation diffusion rates are usually not enhanced, but anion diffusion rates usually are enhanced by grain boundary regions. The related subject of surface

diffusion has also received considerable study in metal systems since 1950 (75). Little work in this particular area has been published for ceramic systems (74,76).

The advent of atomic power has generated much interest in the subject of radiation effects on solids. Especially since 1960, the enhancement of diffusion rates in materials subject to large fluxes of particles has been the subject of studies in both metal (77) and ceramic systems (78,79,80). Two other topics receiving much attention in recent literature are diffusion in a temperature gradient, commonly called the Soret effect (81,82), and diffusion in systems subjected to pressure gradients (83).

Finally, there is an increasing tendency in the literature of diffusion to critically reevaluate much of the experimental work done to date (48,50,84). Much of the early work has been criticized because of a failure to adequately characterize the materials used and their thermal histories. Many new experiments, meticulously performed, are being reported in the current literature. Some of these experiments are primarily designed to yield reliable diffusivity data as an aid in understanding such diffusion-controlled processes as sintering (85,86), creep (87), and solid state reactions (88).

Other studies are designed less to yield diffusion data than to elucidate the mechanisms of transport (89,90,91) and the effect of crystal structure on the transport process (92,93,94).

EXPERIMENTAL EQUIPMENT AND PROCEDURES

The materials used in these studies were supplied by the Ames Laboratory as oxide clinker resulting from the calcination of hydrated oxalates of yttrium and erbium. An emission spectrographic analysis of the materials as received is given in Table 2. X-ray diffraction powder patterns for both materials indicated the cubic type C rare earth oxide structure as the only form present.

Cation Diffusion Studies

Specimen geometries for cation diffusion studies were made to conform to the so-called thin film solution of Equation 2b. This solution, after Crank (7, p. 10) and Jost (6, p. 16) may be derived in the following manner. Two half-spaces, semi-infinite in extent, share an interface at $x = 0$. At time $t = 0$, all of the diffusing species is concentrated in a plane at $x = 0$. The general form of the solution to the partial differential equation, Equation 2b, is

$$c(x,t) = \frac{\alpha}{(t)^{\frac{1}{2}}} \exp(-x^2/4Dt), \quad (8a)$$

where α is a constant. This may be verified by differentiation of Equation 8a. This equation is symmetrical about

Table 2. Emission spectrographic analysis of starting materials (ppm)

Element	Y ₂ O ₃	Er ₂ O ₃	Element	Y ₂ O ₃	Er ₂ O ₃
Ag	N.D. ^a	N.D.	Mo	N.D.	N.D.
Al	10	<40	Nd	<200	N.D.
Ba	N.D.	N.D.	Ni	N.D.	N.D.
Ca	500	200	Pb	N.D.	N.D.
Cr	N.D.	N.D.	Si	200	<40
Cu	N.D.	N.D.	Sm	<200	N.D.
Dy	<100	<100	Sn	N.D.	N.D.
Er	<400	-	Tb	<200	N.D.
Fe	10	90	Ti	N.D.	N.D.
Gd	<30	N.D.	Tm	N.D.	<10
Ho	<60	<50	Y	-	<10
Mg	Trace	N.D.	Yb	<100	<10
Mn	Trace	N.D.	Zn	N.D.	N.D.

^aNot detected.

$x = 0$, and vanishes everywhere for $t = 0$ except at $x = 0$, where it becomes infinite. To correct for a non-infinite concentration of diffusing species at $x = 0$, $t = 0$, the integral of concentration over all space for a unit cross sectional area is set equal to the amount of diffusing species in the initial plane source,

$$s = \int_{-\infty}^{\infty} c dx, \quad (9a)$$

where s is the total amount of species in the entire system.

Substitution of Equation 8a into Equation 9a gives

$$s = \int_{-\infty}^{\infty} \frac{\alpha}{t^{\frac{1}{2}}} \exp(-x^2/4Dt) dx. \quad (9b)$$

Performing the integration, and rearranging, leads to

$$c(x,t) = \frac{s}{2(\pi Dt)^{\frac{1}{2}}} \exp(-x^2/4Dt) \quad (8b)$$

which describes the case for diffusion from an exhaustible plane source into two semiinfinite solids.

While it is experimentally possible to sandwich a very thin source between, for example, two very long cylinders, this geometry, especially with ceramic materials, is difficult to attain. A much easier geometry to attain consists of a long cylinder one end of which is in contact with a very thin source. This describes the so-called semi-infinite thin film situation, probably the one most commonly used in tracer diffusion experiments.

Equation 8a can be modified to describe the semi-infinite thin film case by permitting solutions only for $x > 0$ and employing a reflection and superposition procedure at the impermeable boundary $x = 0$ (7, p. 11). The reflection and superposition procedure consists of adding concentrations at $x < 0$ to those at $x > 0$ which is simply the addition of two

solutions of a differential equation to arrive at a new solution. Because Equation 8b is linear, this summing procedure is valid. The symmetry of Equation 8b around the boundary $x = 0$, reduces this reflection procedure to that of doubling the concentration at any value of x . Thus

$$c(x,t) = \frac{s}{(\pi Dt)^{1/2}} \exp(-x^2/4Dt) \quad (8c)$$

is the required solution for the semi-infinite thin film case. The cation diffusion experiments were performed in such a way as to conform to the geometry for which Equation 8c is valid.

The diffusion specimens were cut from blocks of dense hot-pressed oxides. The hot pressing operation was carried out in double-acting graphite dies with a 4x3/4-inch cavity placed in a graphite-susceptor induction furnace. The Y_2O_3 densification was carried out at a temperature of 1610°C, held under a pressure of 3300 psi for 15 minutes. The densification conditions for the Er_2O_3 consisted of a 10 minute hold at a pressure of 4000 psi and a temperature of 1610°C. Both materials were cooled after relief of pressure and ejected from the die at room temperature. In both cases, the 4x3/4 x 1/2-inch block fractured on ejection from the die to yield several small pieces. Both oxides were black in color after hot-pressing indicating partial reduction by contact with the

carbon die materials. To determine possible levels of contamination of the oxides by common ash constituents in the graphite, emission spectrographic analyses of the hot pressed materials were made. These analyses are given in Table 3 and when compared with the information in Table 2 show that only minor amounts of iron, silicon and aluminum contamination result from the hot pressing operation.

Table 3. Emission spectrographic analysis of hot-pressed oxides (ppm)

Element	Y ₂ O ₃	Er ₂ O ₃
Al	60	<40
B	Trace	N.D. ^a
Ca	500	300
Cr	N.D.	N.D.
Cu	Trace	N.D.
Fe	100	<20
Mg	Trace	N.D.
Mn	Trace	N.D.
Ni	N.D.	N.D.
Si	400	200
Ti	N.D.	N.D.
V	N.D.	N.D.
W	N.D.	N.D.

^aNot detected.

Water immersion determinations of the bulk densities of the hot-pressed materials showed the Y₂O₃ to have a density of 5.030 gm/cm³ (99.9% of x-ray density) and the Er₂O₃ to have a density of 8.518 gm/cm³ (98.4% of x-ray density).

A diamond saw was used to cut the broken pieces of hot-pressed material into rectangular prisms approximately 1 cm x 1 cm by various lengths up to approximately 2.5 cm. These prisms were then affixed to a short length of $\frac{1}{2}$ -inch drill stock with Loc-Wax-20 (Geoscience Instruments Corp., Mount Vernon, New York) with their lengths parallel to the centerline of the drill stock. The drill stock was then chucked into the head of a small laboratory lathe attached to the bed of a surface grinder, and a diamond wheel was used to grind the rectangular prisms into right circular cylinders of approximately 1 cm diameter. The cylinders were then sliced perpendicular to their centerlines to form short cylinders of approximately 1 cm length.

The short cylindrical specimens thus prepared were heated in air in a silicon carbide resistance furnace for 24 hours at 1250°C to oxidize the materials back to the stoichiometric sesquioxides. After the oxidation treatment, the oxides again possessed their characteristic colors, white for Y_2O_3 and pink for Er_2O_3 . Photomicrographs of the materials following oxidation are shown in Fig. 1. The average grain size was estimated to be 18 μ for the Y_2O_3 and 12 μ for the Er_2O_3 . The almost complete lack of porosity is especially noteworthy.

(a) Y_2O_3 ; 400 X

(b) Er_2O_3 ; 400X

Figure 1. Microstructure of hot-pressed oxides

Water immersion bulk densities for each small cylinder were determined, and all exceeded 96.8% of x-ray density for both materials.

A sectioning device was constructed which was designed to grind very thin slices from the surface of the cylinders perpendicular to their axes. This device, which is pictured in Fig. 2, was built around a rigidly-mounted four-speed phonograph turntable (Collaro, Model No. 4TR-200). A $\frac{1}{2}$ -inch aluminum plate was supported at three points above the turntable and parallel to it. The plate was provided with a bushing which maintained the shaft of the specimen holder perpendicular to the plane of the turntable, but allowed free rotation and vertical movement of the specimen holder. The specimen holder itself consisted of a $\frac{1}{2}$ -inch Jacobs chuck that was weighted by the addition of a $\frac{1}{4}$ -inch brass sleeve.

A small jig, pictured in Fig. 3 was built to hold a diffusion specimen in a reproducible alignment on a short piece of $\frac{1}{2}$ -inch drill stock with both ends machined parallel. The drill stock and specimen were clamped into the jig, and the entire assembly was heated to approximately 150°C to allow development of a bond of Loc-Wax-20 between specimen and

Figure 2. Sectioning device with specimen in place

Figure 3. Specimen mounting jig

drill stock. After cooling to set the wax, the assembly was removed from the jig and the drill stock was gripped in the Jacobs chuck.

The three jaws of the chuck maintained the cylindrical axis of the drill stock and specimen perpendicular to the plane of the turntable. A provision was made in the center of the turntable to mount $1\frac{1}{2}$ -inch diameter aluminum discs approximately 0.1-inches in thickness covered with silicon carbide paper. The centerlines of the turntable and the specimen holder were displaced $5/8$ -inch so that material removed from the specimen would be deposited on the abrasive paper in an annular pattern rather than in a single spot. Figure 4 shows the specimen holder and several abrasive-covered discs.

The sectioning device was used to grind the face of the short cylinders perpendicular to their axes, first with 180 grit paper and followed by a final finish with 600-grit paper. The specimens were removed from the drill stock and inspected under low magnification for flaws. Using a 35 mm camera on a rigid mount with oblique lighting, an end-on-view photographic slide of each specimen was made. These slides were projected onto a flat surface at a magnification of 229X as determined by a projection of a carefully measured piece of

Figure 4. Specimen holder and abrasive-covered discs

Figure 5. Diffusion annealing furnace

$\frac{1}{2}$ -inch drill stock photographed with the same camera set-up. Traces of the projections were measured with a polar planimeter (K&E Model 4236) to yield cross-sectional areas of each specimen. Spot checks showed that no measurable changes in specimen cross-sectional area resulted from the high-temperature diffusion anneals described below.

The product of the measured densities and cross-sectional areas of each specimen yielded a thickness factor having units of gm/cm which was used to convert the weight of a slice ground from the specimen to the thickness of the slice.

The isotope used in the Y_2O_3 studies was Y91, a β^- emitter of 59-day half-life. This material was supplied by Oak Ridge National Laboratory in the form of an acid solution of YCl_3 having a radiochemical purity greater than 98% and an estimated specific activity of 2.5 mc/ml. The isotope used in the Er_2O_3 studies was Er169, a β^- emitter of 9.4-day half-life. This material was supplied by Nuclear Science and Engineering Corporation in the form of an acid solution of $ErCl_3$ having a radiochemical purity of greater than 98% and an estimated specific activity of 5 mc/ml. Both isotopes decay to stable products.

Tracer solutions of approximately 2 $\mu\text{c/ml}$ in distilled water were prepared for both isotopes. These solutions also contained approximately 7.5×10^{-2} gms/ml of dissolved stable oxides added as acid solutions. The purpose of the addition of the stable oxide was not to act as a carrier, but rather, to give a visible deposit after evaporation. The activation technique for the diffusion specimens consisted of three to four repetitions of the following cycle: 50 microliters of the diluted tracer solutions were pipetted onto the polished surface of the specimen and allowed to remain in contact with the surface for 30 minutes, during which time exchange of radioactive ions and ions in the surface of the specimen took place. Evaporation of the solution was minimized by covering with a small inverted beaker. After the 30-minute exchange period had elapsed, the beaker was removed and the tracer solution allowed to evaporate leaving behind a hydrated chloride of the tracer. After several repetitions of this procedure, the specimen was placed in a small electrically heated tube furnace and heated to 800°C for 4 hours. This operation converted the excess tracer material to the sesquioxide. After removal from the furnace, the oxidized tracer deposit appeared highly adherent to the specimen surface. A

sectioning analysis of a specimen activated in this manner showed no detectable activity below a depth of 8 microns from the surface for Y_2O_3 and 10 microns for Er_2O_3 .

The activated specimens were placed in a covered crucible composed of the same oxide and were placed in the furnace for diffusion anneals. The furnace, shown in Figure 5 was of a muffled construction allowing the use of oxidizing atmospheres for the diffusion anneal. The heating element consisted of a tungsten mesh cylinder 3 inches diameter by 2 inches long. The heater was surrounded by tantalum radiation shields, and the entire assembly was enclosed by a water-jacketed stainless steel furnace shell. The muffle consisted of a gas-tight tube of either ZrO_2 or Al_2O_3 , $1\frac{1}{4}$ -inches I.D. and having a $1/8$ -inch wall thickness. The muffle was sealed into the furnace shell at top and bottom by packings of refractory fiber mat (Carborundum Company - Fiberfrax Lo-con). The entire volume of the furnace between the muffle and the furnace shell was continuously purged with argon during operation. The interior of the muffle was open to the air. As a precaution to offset the effects of argon leaking through the bottom seal into the muffled volume of the furnace, a flowing stream of pure oxygen having a flow

rate of 0.1 SCFH was introduced through the furnace bottom. A ZrO_2 pedestal was used to position the specimen crucible in the hot zone of the furnace.

Furnace temperature was sensed by a tantalum-sheathed W-5% Re vs W-26% Re thermocouple with the hot junction projecting through a slit in the heating element and located approximately 1/16-inch from the outside of the muffle. Specimen temperature was measured by a Pt-6% Rh vs Pt-30% Rh thermocouple inside the muffle with the hot junction in contact with the specimen crucible.

The output of the control thermocouple was fed to a manual set-point controller-recorder (Minneapolis-Honeywell Regulator Co. Model Electronik 18). The controller generated an error signal proportional to the difference in set-point and furnace temperature which in turn was fed to a silicon-controlled rectifier (SCR) power amplifier (Loyola Industries, Inc. Model L607 (12KVA)). The output of the power amplifier was fed through a step down transformer and thence to the furnace heating element. The recorder provided a permanent record of the furnace temperature. Specimen temperature was determined periodically during an anneal with a manual potentiometer. Temperature variation

of the specimen during an anneal was never greater than $\pm 5^{\circ}\text{C}$ around the nominal value.

Heating and cooling rates of the furnace were controlled by adjustment of the manual set point. Both rates were 50-60 $^{\circ}\text{C}$ per minute for all runs. The times for all runs were measured from the recorder records and were judged to be accurate to within one minute.

Diffusion anneals made at temperatures below 1450 $^{\circ}\text{C}$ for long time periods were carried out in air in a silicon carbide resistance furnace. Diffusion specimens were heated uncovered on a plate of the same oxide. Temperature was measured by a Pt vs Pt-10% Rh thermocouple placed adjacent to the specimen and coupled to a strip chart recorder (Minneapolis-Honeywell Regulator Co. - Model Elektronik 19). The furnace control system consisted of a Pt vs Pt-10% Rh thermocouple feeding a proportional controller (C. J. Tagliabue Corporation (N.J.)-Celectray). A saturable-core reactor, controlled by the output signal of the proportional controller, fed power to the furnace heating elements.

The duration of most diffusion anneals was approximately four hours except for those made at 1400 $^{\circ}\text{C}$. These latter anneals were made for periods of approximately 24 hours

(Y_2O_3) and 50 hours (Er_2O_3) to allow greater penetration at the low diffusion rates expected at these temperatures.

After a diffusion anneal, the activated surface of the specimen was cleaned with a cotton swab soaked in acetone to remove any loose tracer deposit. The swabs were generally found to remain inactive even after vigorous scrubbing of the surface, indicating a tightly adherent tracer layer. The specimen was then mounted on the drill stock with Loc-Wax-20 using the jig to ensure alignment. Prior to sectioning, the mounted specimen was chucked into the head of a small lathe, and a few microns were turned off the cylindrical surface to eliminate any effects of surface diffusion. With the exception of the anneals made above 1600°C , no measurable activity was found in the material removed from these surfaces. In the exceptions noted, the levels of activity were barely above background and were considerably below the activity levels of the slices removed during sectioning.

Following the removal of material from the cylindrical surface, the mounted specimen was placed in the Jacobs chuck of the sample holder and assembled into the sectioning device. Aluminum discs covered with 500-grit silicon carbide paper and preweighed to the nearest 0.0001 gram were used to remove

consecutive slices a few microns thick from the flat surface of the diffusion specimen. The sample holder was turned continuously during the sectioning operation to offset any effects of slight misalignment in the bushing carrying the shaft of the specimen holder.

When sufficient thickness of material had been removed, an operation usually taking about 1 to 1½ minutes, the abrasive-covered disc was reweighed. Using the thickness factors previously computed, the gain in weight of the disc was converted into thickness of the slice removed. All material removed appeared to be ground into the surface of the abrasive disc with no loose powder in evidence. This greatly reduced the hazard of material loss during transfer of the disc to the balance after sectioning. As a last step in the sectioning operation, the abrasive disc containing the active material was covered with mylar tape.

The covered discs were positioned under an end-window (2.0 mg/cm²) Geiger-Müller tube (Tracerlab, Incorporated, Type TGC-1/1883) for counting. A binary scaling unit (Nuclear Instrument and Chemical Corporation, Model No. 165) integrated the output of the tube. A brass positioner was employed to ensure that all specimens would be counted in the same geom-

etry. The separation distance from the window of the G-M tube to the surface of the disc was approximately $5\frac{1}{2}$ cm for most counts. Figure 6 shows the counting chamber with a specimen in position. Counting time was usually one minute for the more active slices. When the activity levels were below approximately 1000 counts per minute, the counting time was lengthened. Since the radioactive decay process follows a Poisson distribution (95, p. 111) the standard deviation on a single determination of a counting rate is given by

$$\sigma_R = \frac{\sigma_S}{t} = \frac{(S)^{\frac{1}{2}}}{t} = \left(\frac{R}{t}\right)^{\frac{1}{2}} \quad (9)$$

where R, S, and t represent, respectively, the counting rate, the total number of counts recorded, and the time over which a count is taken. Thus, quadrupling the counting time will halve the standard deviation on the counting rate. Counting times for the slices of low activity were adjusted to keep the ratio (σ_R/R) less than about 0.03. Occasionally, counting times as long as 50 minutes were required.

The number of slices removed during sectioning of a sample ranged from ten to twenty covering total depths investigated of thirty to sixty microns below the original surface. The data yielded by a typical sectioning procedure are given in Table 4.

Figure 6. Specimen counting arrangement

Table 4. Sectioning data--Er₂O₃ specimen E-1 (Anneal time = 1.44×10^4 sec; anneal temperature = 1560°C)

Section No.	Slice weight, gm	Slice thickness (t), cm	x, cm	x ² , cm ²	A, counts/min	(A/t) <u>counts</u> min-cm
1	.0006	1.569×10^{-4}	0.784×10^{-4}	0.615×10^{-8}	4426	2.82×10^7
2	.0012	3.138×10^{-4}	3.137×10^{-4}	9.84×10^{-8}	3312	1.06×10^7
3	.0013	3.399×10^{-4}	6.405×10^{-4}	4.10×10^{-7}	2673	7.86×10^6
4	.0012	3.138×10^{-4}	9.673×10^{-4}	9.36×10^{-7}	1611	5.13×10^6
5	.0013	3.399×10^{-4}	12.94×10^{-4}	1.67×10^{-6}	966	2.84×10^6
6	.0011	2.876×10^{-4}	16.08×10^{-4}	2.58×10^{-6}	1109	3.85×10^6
7	.0013	3.399×10^{-4}	19.22×10^{-4}	3.69×10^{-6}	780	2.29×10^6
8	.0012	3.138×10^{-4}	22.48×10^{-4}	5.05×10^{-6}	434	1.38×10^6
9	.0015	3.923×10^{-4}	26.01×10^{-4}	6.77×10^{-6}	505	1.29×10^6
10	.0014	3.661×10^{-4}	29.80×10^{-4}	8.88×10^{-6}	459	1.25×10^6
11	.0013	3.399×10^{-4}	33.33×10^{-4}	1.11×10^{-5}	396	1.16×10^6
12	.0014	3.661×10^{-4}	36.86×10^{-4}	1.36×10^{-5}	308	8.41×10^5
13	.0016	4.184×10^{-4}	40.78×10^{-4}	1.66×10^{-5}	328	7.84×10^5
14	.0011	2.876×10^{-4}	44.31×10^{-4}	1.96×10^{-5}	274	9.52×10^5
15	.0016	4.184×10^{-4}	47.84×10^{-4}		174	4.16×10^5

Oxygen Diffusion Studies

In order to produce homogeneous reduced oxides for the oxidation study, both Y_2O_3 and Er_2O_3 were vacuum melted by the procedure of Miller and Daane (23). The construction of the induction furnace used is shown schematically in Fig. 7. The susceptor was a tantalum can approximately 3-inches diameter by 8-inches long with a tantalum cover containing a small black body hole. The susceptor was placed in a fused quartz tube $5\frac{1}{2}$ -inches in diameter with the space between the susceptor and the tube packed with graphite felt insulation (National Carbon Company - Grade DF). The top of the susceptor can was also covered with several layers of graphite felt. The ends of the quartz tube were sealed to water-cooled brass fittings with provisions for evacuation and purging of the furnace chamber.

The oxides were pressed into $3/4$ -inch diameter slugs up to $1\frac{1}{2}$ -inches long which were placed in a uncovered rhenium crucible of tapering square cross section about 1x1 inches at the top and about $1\frac{1}{4}$ -inch deep. The loaded crucible was placed in the tantalum can on a short rhenium pedestal.

After the furnace was loaded and sealed, a mechanical forepump and an oil diffusion pump were used to evacuate the

Figure 7. Furnace for vacuum fusion of oxides

chamber to a pressure below 1×10^{-5} torr. The induction coil was then energized and the temperature was raised rapidly, reaching 2500°C in approximately 15 minutes. Temperatures were determined by viewing the sample surface through a sight glass in the top plate of the furnace with an optical pyrometer. No sight glass corrections were made. Peak temperature was held for one hour and the power was shut off allowing rapid cooling. The furnace was back filled with argon and allowed to cool to room temperature.

The fused oxides were broken out of the crucible in the form of massive lumps. Both oxides were glassy black in color as is usual with oxygen-deficient oxides. Well defined grain boundaries were visible on the free surface of the fused mass with considerable striating. The previous work of Miller and Daane (23) had shown that the preparation technique resulted in less than 10 ppm rhenium contamination. The results of an emission spectrographic analysis of the fused materials showed that with the exception of several hundred parts per million tantalum from the heater, no appreciable contamination of the samples resulted from the melting procedure. Examination of the fused oxides by x-ray diffraction showed only the C forms present with no evidence of the H modification. This

is in agreement with the results of Foex and Traverse (10) on examination of fused rare earth oxides. The metal-oxygen ratios of the two reduced compounds were determined by gain in weight on reoxidation. The results of these measurements are compared in Table 5 with metal-oxygen ratios reported by Miller and Daane (23) on materials prepared in a similar manner. In the material prepared for this study, the oxygen deficiency is seen to be slightly less than one oxygen ion per unit cell for the Y_2O_3 and slightly less than one oxygen ion per five unit cells for the Er_2O_3 .

Table 5. Properties of fused oxides

Material	Particle diameter, cm	Metal-oxygen ratios	
		This study	Miller and Daane ^a
Y_2O_3	5.02×10^{-2}	$YO_{1.484}$	$YO_{1.491}$
Er_2O_3	5.41×10^{-2}	$ErO_{1.494}$	$ErO_{1.489}$

^aMiller and Daane (23).

The reduced oxides were crushed by impact in a mortar and pestle, were separated into size fractions by use of National Bureau of Standards woven wire screens, and were stored in a desiccator over CO_2 and water absorbents until used. A single size fraction was used for diffusion studies,

NBS -40+60 mesh. The average particle diameters for each material were determined by microscopic measurement using a filar eyepiece precalibrated against a dimensional standard. Approximately 500 particles from each fraction were measured. The results of these measurements are also given in Table 5.

Several of the larger particles of each oxide were examined separately in an x-ray powder camera. The spot patterns resulting indicated that the individual particles were single crystals, but that the presence of twinning was most probable. The surface striations reported above would seem to verify the presence of twinning.

The rate of weight change during reoxidation of these partially-reduced oxides was determined by suspending a sample from an electrobalance (Cahn Instrument Co., Model RG) in a constant-temperature furnace. A recorder (Minneapolis-Honeywell Regulator Co., Model Electronik 19) traced the weight of the sample as a function of time. The furnace was heated by means of molybdenum winding operating in helium atmosphere. An impervious Al_2O_3 tube permitted the hot zone of the furnace to be operated under oxidizing conditions. Previous work (24) had shown the rate of oxidation of these materials to be the same in air and in oxygen enriched atmos-

pheres, so for simplicity of operation, all runs were carried out in air.

A small Al_2O_3 crucible suspended by a fine platinum wire was used as a sample container. In order to minimize thermal lags during heating, very small samples of the oxides were used. The typical sample size for Y_2O_3 was 150 mg, while for the denser Er_2O_3 , an approximately 350-mg sample was employed.

Prior to insertion of the sample, the furnace was heated and allowed to come to equilibrium as measured by a Pt vs Pt-10% Rh thermocouple suspended in the exact position the sample container would later occupy. As the furnace was reaching equilibrium, a weighed sample was suspended from the balance beam above the furnace, and the electrobalance and recorder were turned on and allowed to warm up for at least 30 minutes. To initiate a run, the furnace was quickly raised into position around the sample. Since no balance motion occurred during this operation, readings could be taken almost at once. However, to allow time for the sample to reach thermal equilibrium, the data for the initial minute or so was somewhat erratic. The beginning or zero point was back calculated after each run from previous data on weight change experienced by the material on returning to the stoichiometric

sesquioxide. Figure 8 shows the thermobalance and furnace arrangement. Blank runs with fully-oxidized materials were used to determine platinum losses which were slight except at the higher temperatures.

Figure 8. Thermobalance and furnace for oxidation studies

RESULTS AND DISCUSSION

Cation Diffusion Studies

The sectioning procedure carried out on each diffusion specimen yielded a penetration profile giving the distribution of activity after the high-temperature anneal. The expected distribution, Equation 8c, consists of a very high concentration at the surface ($x = 0$) which drops off exponentially with the square of the distance from the surface. Therefore, a plot of the logarithm of the specific activity of a slice vs the square of the distance of its centerpoint from the original surface should yield a straight line, i.e.

$$\ln(A/t) = \ln A_0 + \left(\frac{-x^2}{4Dt} \right) .$$

In this equation, the quantity (A/t) is the activity of a slice divided by its thickness, and is directly proportional to the concentration of the tracer at the midpoint of the slice. The value of the constant A_0 is proportional to the initial concentration of activity on the surface, but an exact measurement of this quantity is not necessary for determination of the diffusion coefficient. The slope of a penetration curve, $-1/4 Dt$, for a known diffusion time t gives a direct calculation of the diffusivity D for the tem-

perature at which annealing took place.

Penetration plots for all specimens used in this study are shown in Figures 9 and 10. Least-squares fits for all plots are indicated. The initial few points on each plot were ignored in making these fits because of unusually high activities due to residual tracer and some penetration of the tracer solution during activation.

The penetration plot for Y_2O_3 specimen A-2 ($1400^{\circ}C$), as shown in Figure 10, consists of two distinct linear regions indicating the probability of two distinct zones of diffusion in this sample. A fit for each zone was obtained and will be discussed below. Only one diffusion zone was found for all other samples investigated including that for Er_2O_3 at $1400^{\circ}C$.

The diffusivities calculated from the slopes of the least-squares fits of the penetration plots are tabulated in Tables 6 and 7 along with specimen densities and diffusion anneal temperatures. The two diffusivities corresponding to the penetration plot of Y_2O_3 specimen A-2 are given. All results are represented graphically in Figure 11 as a plot of logarithm of the diffusion coefficient vs the reciprocal of the absolute annealing temperature. Rate process data giving a linear plot of this type is said to conform to the

Figure 9. Penetration plots for Er_2O_3 specimens

Figure 9. (Continued)

Figure 10. Penetration plots for Y_2O_3 specimens

Figure 10. (Continued)

Figure 10. (Continued)

Table 6. Cation diffusion coefficients--Y₂O₃

Specimen No.	Density, gm/cm ³	Temperature, °C	D, cm ² /sec
D-1	4.928	1670	2.67x10 ⁻¹⁰
E-1	4.949	1610	1.35x10 ⁻¹⁰
D-2	4.920	1575	1.13x10 ⁻¹⁰
F-1	4.925	1500	5.43x10 ⁻¹¹
A-2	4.974	1400	1.38x10 ^{-11a} 1.58x10 ^{-10b}

^aSmall penetration distances.^bLarge penetration distances.Table 7. Cation diffusion coefficients--Er₂O₃

Specimen No.	Density, gm/cm	Temperature, °C	D, cm ² /sec
B-1	8.444	1700	2.67x10 ⁻¹⁰
C-2	8.384	1625	9.05x10 ⁻¹¹
D-1	8.405	1625	8.30x10 ⁻¹¹
E-1	8.491	1560	2.46x10 ⁻¹¹
C-1	8.360	1490	1.19x10 ⁻¹¹
C-3	8.430	1490	1.32x10 ⁻¹¹
D-3	8.446	1400	2.16x10 ⁻¹²

Figure 11. Cation self-diffusion coefficients

Arrhenius equation. For diffusion, this equation may be written

$$D = D_0 \exp(-Q/RT) \quad (10)$$

where D_0 is a constant termed the frequency factor, R is the gas constant, T is the absolute temperature, and Q is a constant called the activation energy. A least-squares fit of the results for Y_2O_3 , using only the lower value from specimen A-2, gives

$$D = 1.65 \times 10^{-2} \exp(-69,200 \text{ calories/mole}/RT) \text{ cm}^2/\text{sec} \quad (11)$$

for the temperature range investigated, 1400-1670°C. A similar treatment of the Er_2O_3 results gives

$$D = 1.48 \exp(-102,200 \text{ calories/mole}/RT) \text{ cm}^2/\text{sec} \quad (12)$$

for the range 1400-1700°C.

A comparison of the diffusion coefficients of yttrium in Y_2O_3 from this study with those of Berard and Wilder (29) is shown in Figure 12. The earlier data, curve BW, lies above that for this study by approximately an order of magnitude at all temperatures. The activation energy for the diffusion process in this study is also found to be approximately one-third greater than that of earlier work (29), i.e., 69,200 vs 44,000 calories per mole. These differences are no doubt reflections on the differences in materials and annealing conditions used in the two studies. The work of Berard and

Figure 12. Comparison of Y_2O_3 diffusion data

Wilder was carried out in vacuum on fairly porous material averaging about 87.5% of x-ray density. The present study, however, was carried out under oxidizing conditions with very dense material averaging 98.2% of x-ray density.

An appreciable contribution of surface diffusion along pore walls was probably present in the early work (29), although a single activation energy was capable of describing their data. Surface diffusion rates are usually orders of magnitude above volume diffusion rates (75), and hence a surface contribution would result in an increased apparent diffusion coefficient. In addition, any reduction of the oxide at high temperatures under vacuum would result in a loosening of the structure by introduction of excess oxygen vacancies. This, in turn, would be expected to enhance diffusion rates and decrease the activation energy. The observation by Berard and Wilder that samples were darkened by high temperature treatment indicates that some reduction may have occurred.

In the present work, surface diffusion along pore walls is probably negligible due to the high specimen density. Because an oxidizing atmosphere was maintained during diffusion annealing, reduction of the oxides was not probable. A single activation energy describes these data at all tempera-

tures except 1400°C (Specimen A-2). At this single temperature, two distinct zones of diffusion were found in the specimen. Near the surface, the diffusivity was low having a value that fitted well with those of higher temperatures and is probably representative of true volume diffusion. Deeper within the specimen, however, the penetration profile yielded a second diffusivity approximately one order of magnitude greater than that near the surface. Of especial note is the fact that this anomalously high diffusivity is approximately the same as that found by Berard and Wilder (29) at the same temperature. This may be an indication of an area of sub-surface porosity in the specimen giving the unusually high apparent diffusivity. It is not expected that the anomaly in the 1400°C run is due to a clear cut grain boundary contribution to diffusion. The work of Levine and MacCallum (73) shows that for experimentally-attainable conditions, the ratio of the grain boundary diffusivity to the volume diffusivity must be on the order of 10^4 or larger before a definite separation on the penetration plot of the two contributions is possible. The single order of magnitude difference found in the two diffusivities at 1400°C would seem to exclude pure grain boundary diffusion as a possible interpretation of the

second diffusion zone. Such a splitting of diffusion penetration data into two distinct regions has been reported by Austerman et al. (96) for oxygen diffusion in polycrystalline BeO. The investigators were not, however, able to explain this phenomenon.

The diffusion coefficients for erbium in Er_2O_3 , Figure 11, are seen to fall below those for yttrium in Y_2O_3 over the temperature range investigated. The difference is approximately an order of magnitude at 1400°C , but decreases with increasing temperature. Indeed, if the data are extrapolated to the melting points, the diffusivity in Er_2O_3 is found to be about four times that in Y_2O_3 . Equations 11 and 12 show that the activation energies for diffusion in Er_2O_3 and Y_2O_3 are in the ratio of 3:2. Also, the frequency factor in the case of Er_2O_3 is about 100 times that for Y_2O_3 . Interpretation of these differences is aided by using the approach of Zener (44) which yields, for a vacancy migration mechanism in a cubic material,

$$D = \gamma a_0^2 \nu \exp(-\Delta G/RT) \quad (13)$$

and

$$\Delta G = \Delta G_f + \Delta G_m$$

where γ is a geometrical constant characteristic of the

structure and diffusion mechanism, a_0 is the lattice parameter, ν is a characteristic frequency, and ΔG_f and ΔG_m are the free energies of vacancy formation and vacancy migration, respectively. The similarity in structures of the two materials causes the product νa_0^2 to be nearly the same in both. Thus, Equation 13 can be rewritten for the two materials as

$$D = [K\nu \exp(\Delta S_f + \Delta S_m)/R] \exp - (\Delta H_f + \Delta H_m)/RT \quad (14)$$

where the substitution

$$\Delta G = \Delta H - T\Delta S$$

has been made, and K is a constant. Equation 14 can be identified with Equation 10 when

$$D_0 = [K\nu \exp(\Delta S_f + \Delta S_m)/R]$$

and

$$Q = \Delta H = \Delta H_f + \Delta H_m .$$

As shown in Table 1, the energies of formation of both oxides are almost identical suggesting that the energies of formation of cation vacancies in the two materials are probably also nearly the same. The differences in Equations 11 and 12 would seem therefore to arise only from differences in the quantities ν , ΔS_m , and ΔH_m in the two materials.

The two values of ΔH indicate that more energy is required to carry the erbium ion through the saddle point

configuration than is required for the yttrium ion. Since the amount of lattice strain at the saddle point should be about equal for the two ions, or possibly even slightly smaller for the smaller erbium ion, the larger enthalpy of activation for erbium most probably reflects an effect related to the greater mass of the ion. If the values for ΔS_m are nearly the same in the two materials, as seems likely, then a larger ΔH would result in a larger free energy of activation ΔG . The quantity $\exp(-\Delta G/RT)$ represents the probability that any given oscillation of the diffusing species about its equilibrium position will possess enough energy to carry it through the saddle point configuration. Therefore, the experimental results indicate that, for the more massive erbium ion, the probability at a given temperature that the ion will obtain the necessary jump energy from the lattice is less than for the lighter yttrium ion. Alternately, it may be said that it is necessary to transfer more energy from the lattice to the erbium ion in order to enable it to undergo a diffusion jump than is necessary for the lighter yttrium ion.

An interpretation of the observed greater frequency factor for erbium than yttrium self-diffusion is more difficult. It should be realized at the outset that the value of

D_0 is so sensitive to small errors in the individual values of D that the error in this quantity is usually of the same order of magnitude as the quantity itself. Indeed, tabulated values of D_0 for identical systems measured by different investigators differ by as much as four orders of magnitude (38). Following the approach of Zener (44), which has given moderate success in describing some metal systems (4, pp. 62-65), the activation entropy for diffusion by a vacancy mechanism may be approximated by

$$\Delta S \simeq \lambda \beta \frac{\Delta H}{T_m} \quad (15)$$

where λ is a constant characteristic of structure, T_m is the absolute melting temperature of the material and β is defined as

$$\beta \equiv - \frac{d(\mu/\mu_0)}{d(T/T_m)} \quad (16)$$

In this expression, μ is an appropriate elastic modulus for the lattice at temperature T , and μ_0 is the value of the same modulus at absolute zero. Some data on bulk modulus of polycrystalline rare earth sesquioxides have been given by Marlowe and Wilder (97), by Manning et al. (98) and by Manning*. These data indicate that the value of β for both

*Manning, W. R., Ames, Iowa. Bulk moduli of rare earth oxides. Private communication. 1968.

oxides is essentially the same. Using the experimentally-determined values of ΔH and known values of T_m for both oxides, and realizing that λ is the same for both, it can be shown that

$$\Delta S_m^{(Er_2O_3)} \simeq \frac{1}{3} \Delta S_f + \Delta S_m^{(Y_2O_3)}. \quad (16)$$

Further, if ΔS_f is of the same order of magnitude as $\Delta S_m^{(Y_2O_3)}$, then

$$\Delta S_m^{(Er_2O_3)} \simeq \frac{4}{3} \Delta S_m^{(Y_2O_3)}. \quad (17)$$

If, for the moment, the value of ν is assumed the same for the two materials, the ratios of the measured frequency factors would be

$$\frac{D_o^{(Er_2O_3)}}{D_o^{(Y_2O_3)}} \simeq \frac{\exp(\Delta S_m^{(Er_2O_3)}/R)}{\exp(\Delta S_m^{(Y_2O_3)}/R)} \simeq \exp \frac{1}{3} (\Delta S_m^{(Y_2O_3)}/R).$$

This ratio is measured as approximately 10^2 (Equations 11 and 12). Evaluation of $\Delta S_m^{(Y_2O_3)}$ by this relationship leads to a value of approximately $13.9(R)$. This is much too large to be realistic and would lead to a value of ν approximately six orders of magnitude too low (4, p. 64).

If, on the other hand, the value of ΔS_f is considered much smaller than either ΔS_m , then Equation 16 would reduce to

$$\Delta S_m^{(Er_2O_3)} \simeq \Delta S_m^{(Y_2O_3)}.$$

In this case, the ratio of the frequency factors would have to be explained by a difference in ν of two orders of magnitude in the two materials, an occurrence which seems unlikely. The conclusion must be reached that Zener's approach to the calculation of ΔS (Equation 15) does not explain the observed ratio for these materials. In view of its poor performance in the case of bcc metals (4, p. 65), this is not surprising.

It should be emphasized that the difficulty in interpretation arises in explaining the ratio of the measured frequency factors. If the value of the frequency factor for erbium diffusion is taken alone, and a value of $\nu = 10^{13} \text{ sec}^{-1}$ is taken as a reasonable approximation, Equation 13 gives a value of $\Delta S^{(\text{Y2O3})}$ equal to approximately 3.9R. This is comparable to values measured and computed for metal systems (4, p. 64). This result would indicate that the value of D_0 for the yttrium diffusion may be somewhat low.

It has been assumed in the foregoing analysis that cation migration in these materials proceeds by vacancy migration. If this is indeed the case, then the tracer diffusivities measured will not be precisely equal to the vacancy diffusivities because of correlation effects in the tracer jumps. It can be shown (4, pp. 100-106) that for

face-centered cubic arrangement, such as is possessed by the cations in oxides, the ratio of the tracer diffusivity D_t to the vacancy diffusivity, D is

$$\frac{D_t}{D} = f = 0.78145$$

where f is called the correlation coefficient. Because the correlation coefficient is nearly unity for such a structure, no significant change in diffusion rates would be introduced by including correlation effects.

Oxygen Diffusion Studies

Early in the course of the study of the reoxidation of partially-reduced rare earth oxides, it was realized that the process could not be described by a uniformly decaying oxygen concentration gradient such as that used in treating the cation diffusion data. If the oxidation process was stopped at various times prior to completion, the individual particles were observed to have developed an external shell of transparent material around a central opaque black core. This shell was observed to increase in thickness with time at the expense of the opaque core material until the entire particle was transparent. The progressive development of this shell is shown in Fig. 13 which shows particles of

Figure 13. Progressive oxidation of Er_2O_3 particles

Figure 14. Model for oxidizing spherical particle

partially-reduced Er_2O_3 in various stages of reoxidation. At the left in this figure is a reduced particle (opaque black) as prepared by vacuum fusion. On the right is a fully oxidized (transparent pink) particle. The interface between opaque and transparent material is seen to be a sharp one and remains so when viewed at very high magnifications. These observations suggested that the oxidation of partially-reduced rare earth oxides proceeds by diffusion of oxygen through a progressively thickening layer of fully oxidized material with the interface between fully oxidized material and reduced material remaining sharp.

To extract diffusion information from observation of such a process, it is necessary to relate the movement of the interface between oxidized and reduced material to the rate of supply of oxygen to the reduced material at the interface. This relationship can be determined by the methods of Crank (7, pp. 99-120) for dealing with the problem of diffusion with a moving boundary. Previous work by Wirkus et al. (24) has shown that the rate of oxygen penetration into particles of partially-reduced rare earth oxides is not controlled by surface reactions, but rather is diffusion-controlled. For the special case where oxidation proceeds by and is rate-

controlled by diffusion of dissolved gas through an oxidized layer to reduced material, i.e. the so-called tarnishing reaction of Crank (7, p. 117), the coordinate of the moving boundary as a function of time is given by

$$X_1 = \left[\frac{2D_1 c_1(0)t}{A\rho} \right]^{\frac{1}{2}} \quad (18)$$

for a plane boundary and one-dimensional diffusion. In this equation, X_1 is the displacement of the boundary from its initial position after time t ; D_1 is the diffusivity of the dissolved species through the oxidized material; $c_1(0)$ is the concentration of gas dissolved in the oxidized layer at the outside surface; A is the difference in mass fraction of the gaseous component in the oxidized and the reduced compound; and ρ is the density of the oxidized compound assumed to be independent of concentration of dissolved gas. A derivation of this equation is given in the Appendix.

The value of X_1 at any time can be extracted from rate of weight gain of a batch of small particles as follows. The particles are first assumed spherical of radius a , Figure 14. The change in weight after any given time will equal the product of the volume of the oxidized shell and the difference in density between oxidized and reduced material

$$\Delta w = \frac{4}{3} \pi [a^3 - (a - X_1)^3] (\rho - \rho_r) \quad (19)$$

where Δw is the change in weight of a single particle and ρ_r is the density of the reduced oxide. Rearrangement of this equation yields

$$X_1^3 - 3aX_1^2 + 3a^2X_1 - \frac{3\Delta w}{4\pi(\rho - \rho_r)} = 0 \quad (20)$$

This equation can be solved by standard methods for cubics to yield X_1 . Substitution into Equation 18 gives a value for D_1 provided all other quantities are known. Since the process of dissolving oxygen into the crystal structure is not rate-limiting, then the diffusivity yielded is actually the self-diffusion coefficient for oxygen migration by an interstitial mechanism in the defective anion sublattice.

Typical weight change curves for oxidation of the partially reduced oxides are given in Figure 15. The total weight change for oxidation to the stoichiometric oxide is indicated by the horizontal line. The change in weight of the sample for any time period is converted to change in weight of a single particle by the relationship

$$\Delta w = \frac{4\pi a^3 \Delta W \rho_r}{3W_i} \quad (21)$$

where W_i is the initial sample weight, and ΔW is the change in sample weight. The value of the quantity ρ_r can be computed from the lattice parameter and the observation of Miller and

Figure 15. Weight changes during reoxidation of Er_2O_3

Figure 16. Variation in oxidation rates during reoxidation of Er_2O_3

Daane (23) that the oxygen deficiency in these materials is due to oxygen vacancies and not metal interstitials.

Using the constants shown in Table 8, along with Equation 18, values of the product $Dc_1(0)$ were computed.

Table 8. Constants for evaluation of oxygen diffusion rates

Material	a, cm	A	ρ , gm/cm ³	ρ_r , gm/cm ³
Y ₂ O ₃	2.51×10^{-2}	0.2126	5.0308	5.0194
Er ₂ O ₃	2.70×10^{-2}	0.1255	8.6537	8.6494

Some variation in this product was observed when values of ΔW were picked corresponding to different degrees of reoxidation. The variation found during the oxidation of Er₂O₃ at 1141°C is plotted as a function of the ratio ($\Delta W_t / \Delta W_\infty$) in Figure 16. The quantities ΔW_t and ΔW_∞ are, respectively, the change in weight during oxidation for time period t and the change in weight after oxidation for infinite time. The maximum value of the curve occurs approximately one minute after raising the furnace into place, suggesting that the increase in the product $Dc_1(0)$ is probably due to a time lag in reaching thermal equilibrium. The decreasing portion of the curve after approximately 50% of the particle was oxidized is probably due to the lack of sphericity of the individual

particles. At these later times, the irregular shape of the particles, as shown in Figure 13, would cause longer diffusion paths from the surface to the interior in certain directions which would result in an apparent lowering of the diffusion coefficient. The same arguments would lead to apparently high diffusivities in the earliest stages of oxidation, but this effect was probably off-set by the thermal lag. All specimens of both materials exhibited variation curves typified by Figure 16. A value of $(\Delta W_t / \Delta W_\infty)$ of 0.3 was selected as being least likely to be effected by either thermal lag or particle irregularities, and values of the product $Dc_1(0)$ at this fraction reoxidation are tabulated in Tables 9 and 10 and are plotted vs reciprocal temperature in Figure 17. These data are described in least-squares fits to the Arrhenius equation by

$$Dc(0) = 2.16 \times 10^{-6} \exp(19,600 \text{ calories/mole/RT}) \text{ gm/cm-sec} \quad (22)$$

and

$$Dc(0) = 1.76 \times 10^{-5} \exp(30,100 \text{ calories/mole/RT}) \text{ gm/cm-sec} \quad (23)$$

for Y_2O_3 and Er_2O_3 , respectively.

Without a knowledge of the concentration of oxygen dissolved in the fully-oxidized material at the outer surface of the particle, it is not possible to extract the values of

Table 9. Oxygen diffusion rates--Er₂O₃

Specimen	Temperature, °C	D _c (O), gm/cm-sec
A	1292	1.13x10 ⁻⁹
B	1217	6.04x10 ⁻¹⁰
C	1164	4.82x10 ⁻¹⁰
D	1141	3.99x10 ⁻¹⁰
E	1125	3.45x10 ⁻¹⁰
F	1060	1.99x10 ⁻¹⁰

Table 10. Oxygen diffusion rates--Y₂O₃

Specimen	Temperature, °C	D _c (O), gm/cm-sec
A	1276	4.00x10 ⁻⁹
B	1242	3.49x10 ⁻⁹
C	1193	2.10x10 ⁻⁹
D	1128	1.92x10 ⁻⁹
E	1064	1.45x10 ⁻⁹

Figure 17. Oxidation rates in Er_2O_3 and Y_2O_3

the diffusion coefficients from Equations 22 and 23. The literature is almost completely lacking in data on the solubilities of oxygen in oxides. Nair et al. (99) have reported some values for $\text{Na}_2\text{O} \cdot 2\text{SiO}_2$, $\text{Na}_2\text{O} \cdot 2\text{B}_2\text{O}_3$ and $\text{Na}_2\text{O} \cdot 2\text{GeO}_2$ glasses. Kozlenko et al. (100) have reported oxygen solubilities in SrO_2 . Of greater applicability to this study, however, is the work of Cohen and Berman (101) on oxygen solubilities in the open structure of various compositions in the UO_2 - ThO_2 system. They found that oxygen solubilities were limited only by the space available in the structure and the ability of the structure to maintain charge neutrality when oxygen was dissolved interstitially. In the case of the defective structure of the sesquioxides of the rare earths, space limitations would predict that a maximum of sixteen atoms of oxygen be dissolved per unit cell. While charge neutrality in the UO_2 - ThO_2 system was preserved by an increase in the oxidation state of uranium, this probably is not the case with the rare earth oxides. Instead, as suggested by Barrett and Barry (27), the solution of oxygen to form negatively-charged interstitials is probably accompanied by generation of positive holes in the valence band of the crystal. In essence, the solution of oxygen interstitially amounts to

the introduction of new electron acceptor levels. Barrett and Barry (27) have suggested that the holes thus generated are quite mobile.

Using the figure of sixteen oxygen atoms dissolved per unit cell as giving the right order of magnitude for the maximum or saturated solubility of oxygen in the fully oxidized material, values of $c_1(0)$ for erbia and yttria are, respectively, 0.3620 and 0.3565 grams oxygen per cubic centimeter of oxide. These values may be used to compute approximate diffusion coefficients from the products $Dc_1(0)$ listed in Tables 9 and 10. These diffusion coefficients are given in Tables 11 and 12, and are fitted to Arrhenius curves in Figure 18. These data are described by

$$D = 4.76 \times 10^{-5} \exp(-30,100 \text{ calories/mole/RT}) \text{ cm}^2/\text{sec} \quad (24)$$

for Er_2O_3 and by

$$D = 6.0 \times 10^{-6} \exp(-19,600 \text{ calories/mole/RT}) \text{ cm}^2/\text{sec} \quad (25)$$

for Y_2O_3 . Included in Figure 18 is an extrapolation of the data of Eyring et al. (26) for oxygen diffusion in Sm_2O_3 in the temperature range 696-900°C as measured by conventional isotope exchange. Sm_2O_3 crystallizes in the B type rare earth oxide structure which possesses the same type of defective anion lattice as does the C type structure. These

Figure 18. Oxygen self-diffusion coefficients in Er_2O_3 and Y_2O_3 .

results indicate that interstitial oxygen diffusion by means of these voids seems to proceed at about the same rate in all materials in which they are present.

The reason for the greater activation energy for oxygen diffusion in Er_2O_3 than in Y_2O_3 is not apparent; however, the 3:2 ratio of these energies in the two materials is the same as is found for cation diffusion described in the preceeding section.

CONCLUSIONS

1. The cation tracer self-diffusion coefficients in fully-dense polycrystalline material can be described for yttria in the temperature range 1400-1670°C as

$$D = 1.65 \times 10^{-2} \exp(-69,200/RT) \text{ cm}^2/\text{sec}$$

and for erbia in the temperature range 1400-1700°C as

$$D = 1.48 \exp(-102,200/RT) \text{ cm}^2/\text{sec}.$$

2. The reoxidation of partially-reduced rare earth oxides proceeds by formation of a fully-oxidized shell on the surface followed by, and limited by, diffusion of oxygen through the fully-oxidized material to a sharp interface with the reduced interior.

3. Based on a saturation value of sixteen interstitial oxygen ions per unit cell, the oxygen self-diffusion coefficients in single crystals of these materials can be described for yttria in the temperature range 1064-1276°C as

$$D = 6.0 \times 10^{-6} \exp(-19,600/RT) \text{ cm}^2/\text{sec}$$

and for erbia in the temperature range 1060-1292°C as

$$D = 4.76 \times 10^{-5} \exp(-30,100/RT) \text{ cm}^2/\text{sec}.$$

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APPENDIX

Diffusion with a Moving Boundary (7, pp. 111-118)

Consider two media that may be moving relative to one another but at any time are sharing an interface perpendicular to the X-axis. Position in medium 1 is specified by a coordinate in the x_1 system stationary with respect to medium 1. Position in medium 2 is similarly specified with respect to a coordinate system x_2 stationary with respect to medium 2. The interface at time t is given by the plane $x_1 = X_1$, $x_2 = X_2$ which is initially at $x_1 = x_2 = 0$. Medium 1 occupies part of space $X_1 < x_1 < \infty$; medium 2 occupies part of space $-\infty < x_2 < X_2$. In both media there is a substance moving by diffusion relative to x_1 and x_2 and being transferred from one medium to the other. The concentration of substance at time t is given by c_1 at x_1 and c_2 at x_2 . In the two media, the concentration distributions as a function of time are given by

$$\frac{\partial c_1}{\partial t} = D_1 \frac{\partial^2 c_1}{\partial x_1^2} \quad (A-1)$$

and

$$\frac{\partial c_2}{\partial t} = D_2 \frac{\partial^2 c_2}{\partial x_2^2} . \quad (A-2)$$

At any time the concentrations at either side of the

interface, i.e., $c_1(X_1)$ and $c_2(X_2)$, are assumed to be related by

$$c_2(X_2) = Qc_1(X_1) + R \quad (A-3)$$

where Q and R are constants. Conservation of the diffusing species at the interface requires that

$$D_1 \left(\frac{\partial c_1}{\partial x_1} \right)_{x_1=X_1} - D_2 \left(\frac{\partial c_2}{\partial x_2} \right)_{x_2=X_2} + c_1(X_1) \left(\frac{dX_1}{dt} \right) - c_2(X_2) \left(\frac{dX_2}{dt} \right) = 0. \quad (A-4)$$

Further, it is assumed that

$$X_2 = PX_1 \quad (A-5)$$

where P is a constant.

For the initial and boundary conditions

$$c_1 = c(\infty) \quad x_1 > 0, \quad t = 0$$

$$c_1 = c_1(0) \quad x_1 = 0, \quad t > 0$$

a solution for Equation A-1 in an infinite medium is

$$\frac{c_1(\infty) - c_1}{c_1(\infty) - c_1(0)} = 1 - \operatorname{erf} \left\{ \frac{x_1}{\sqrt{4D_1t}} \right\}. \quad (A-6)$$

For the initial and boundary conditions

$$c_2 = c_2(-\infty) \quad x_2 < 0, \quad t = 0$$

$$c_2 = c_2(0) \quad x_2 = 0, \quad t > 0$$

a solution for Equation A-2 is

$$\frac{c_2(-\infty) - c_2}{c_2(-\infty) - c_2(0)} = 1 + \operatorname{erf} \left\{ \frac{x_2}{\sqrt{4D_2t}} \right\} . \quad (\text{A-7})$$

The fact that Equations A-6 and A-7 are derived for infinite media does not prevent their use for bounded media provided that within the boundaries, at all times, the concentrations are the same as those for an infinite or unbounded medium.

Now, consider that the movement of one or both media relative to the boundary is due only to transfer of diffusing substance across the interface. The necessary conditions are that two of the quantities $c_1(\infty)$, $c_1(0)$, $c_1(X_1)$, $c_2(-\infty)$, $c_2(0)$ are known and that the magnitudes of X_1 and X_2 are at all times proportional to the amount of diffusing substance which has crossed the interface. Thus,

$$\frac{dX_1}{dt} = S \left\{ D_1 \left(\frac{\partial c_1}{\partial x_1} \right)_{x_1=X_1} + c_1(X_1) \frac{dX_1}{dt} \right\} \quad (\text{A-8})$$

where S is the constant ratio of the magnitude of X_1 to the amount of diffusing substance which has crossed the interface in the direction of decreasing x . A similar expression for (dX_2/dt) will not be needed.

Substitution of Equations A-3, A-5, and A-6 into A-8 gives

$$\frac{dX_1}{dt} \left\{ \frac{1}{S} - c_1(X_1) \right\} = \left\{ c_1(\infty) - c_1(0) \right\} \left(\frac{D_1}{\pi t} \right)^{\frac{1}{2}} \exp(-X_1^2/4D_1t). \quad (\text{A-9})$$

Also, from Equation A-6, with $x_1 = X_1$ and $c_1 = c_1(X_1)$

$$c_1(X_1) = c_1(0) + \left\{ c_1(\infty) - c_1(0) \right\} \operatorname{erf} \left\{ \frac{X_1}{\sqrt{4D_1t}} \right\}. \quad (\text{A-10})$$

Equations A-9 and A-10 can be satisfied for all values of t if, and only if, the quantity $X_1/t^{\frac{1}{2}}$ is a constant. Thus, let

$$X_1 = 2\alpha(D_1t)^{\frac{1}{2}} \quad (\text{A-11})$$

which gives for Equations A-9 and A-10, respectively,

$$c_1(\infty) - c_1(0) = \pi^{\frac{1}{2}}\alpha \left\{ \frac{1}{S} - c_1(X_1) \right\} \exp(\alpha^2) \quad (\text{A-12})$$

and

$$c_1(X_1) = c_1(0) + \left\{ c_1(\infty) - c_1(0) \right\} \operatorname{erf}\alpha. \quad (\text{A-13})$$

As a special case, consider the formation of a fully oxidized layer on the surface of a reduced compound by reaction with a gas. The reaction proceeds at the interface after diffusion of the dissolved gas through the full-oxidized layer. At the interface, $c_1(X_1)$ is assumed to be zero, i.e., the oxidation reaction at the interface is assumed to be so rapid that the process is limited by the rate of supply due to diffusion. The outer surface of the oxidized layer is assumed to remain constantly saturated with gas.

The fully-oxidized layer is labeled medium 1. Let A be the mass fraction of the oxygen in the fully-oxidized compound, ρ the density of the oxidized compound (assumed independent of concentration of dissolved gas), and c_1 the concentration of the dissolved gas (mass of gas per unit volume of oxidized compound) at a distance x_1 beneath the exterior surface of the oxidized layer. From Equation A-8,

$$S = - \frac{1}{A\rho}$$

Furthermore, since $c_1(X_1) = 0$, $c_1(0)$, the saturated concentration of gas at the outer surface of the oxidized layer, is, from Equations A-12 and A-13,

$$\frac{c_1(0)}{A\rho} = \pi^{\frac{1}{2}} \alpha \exp(\alpha^2) \operatorname{erfc} \alpha \quad (\text{A-15})$$

and

$$X_1 = 2\alpha(D_1 t)^{\frac{1}{2}} \quad (\text{A-16})$$

where D_1 is the diffusion coefficient of the dissolved gas in the oxidized layer. In the special case where $c_1(0) \ll A\rho$, combining Equations A-15 and A-16 gives

$$X_1 = \left[\frac{2D_1 c_1(0)t}{A\rho} \right]^{\frac{1}{2}}. \quad (\text{A-17})$$

This equation allows calculation of the product $D_1 c_1(0)$ from the value of the oxidized layer thickness at any time.