

temperature dependent; and (2) because $K_s \neq 1$, the (Ga/Fe) ratio in the melt changes during the run.

It may be assumed that a large crystal has grown throughout the run. The Curie point distribution, and therefore the composition of a single crystal, will vary in much the same way as the bulk of crystallites whose growth cycle was shorter than the run. Such a large crystal was taken, dissected into small cubes, and the Curie point of the volume elements was measured. The crystal was grown using the barium borate flux from a batch calculated to give crystals with a 155° Curie point and the crystal itself had a bulk T_c of 135°. The segments of the crystal varied in Curie point from 87° to 168°. This corresponds to a change in gallium content from $x = 0.32$ to $x = 0.17$ over the crystal giving a change in $4\pi M_s$ of at least 500 across the crystal. The outer layers of the crystal had the highest Curie temperature whereas the core had the lowest. This indicates that the gallium content was highest in the material initially crystallized and was lowest in the material deposited last.

In the case of gradient growth the temperature of operation remained constant. Therefore the melt reaches, and remains in, equilibrium with the nutrient material and the deposit on the crystal is of the same composition as the nutrient although the melt may have a slightly different composition. Figure 3 shows a variation in Curie temperature, for the gradient-grown crystals, of less than 5°, the accuracy of the measurement. If a large crystal is grown and dissected as described here, the Curie points are the same within experimental error. In this case barium borate was used as the flux and again it has a distribution near unity. If a flux with a distribution other than unity were used, however, one would expect the initial deposit to be slightly off composition until the solution adjusted itself into equilibrium with the nutrient. After equilibrium has been reached, deposition of the substituting ion and iron will occur simultaneously with their dissolution from the ceramic nutrient.

IV. Conclusions

In growing homogeneous crystals which exhibit a solid solution range, the concept of the substitution coefficient is

useful. This recognizes that the components may exist as some other specie in the melt phase and may crystallize with different distribution coefficients. The various distribution coefficients are combined into the substitution coefficient which becomes a single growth parameter.

It is possible to grow large substituted YIG crystals from a flux by the slow-cooling method and to cut out sections which have relatively uniform compositions. To grow very large crystals of extremely uniform compositions, however, the gradient method should be used. The gradient method is superior to the slow-cool method because the desired substitution coefficient for the substituting ion can be held constant throughout a run by keeping growth at a constant temperature, by saturating the flux with respect to both the substituting ion and iron, and by keeping an excess of nutrient of the desired composition. This method has also been used successfully for the growth of aluminum garnets, ruby, and emerald with a marked improvement in impurity distribution and will be useful in most flux-growth applications where materials with precise substitutions are to be grown.

Acknowledgments

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Anion Diffusion in α -Cr₂O₃

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Oxygen-18 exchange between gaseous oxygen, held at a pressure of 125 mm Hg in a Pt10Rh chamber, and spheres of α -Cr₂O₃ containing three or less grains was determined from 1100° to 1450°C. Isotope equilibrium on crystal surfaces appears to be quickly established, and the rate-determining factor is self-diffusion conforming to the relation $D = 15.9 \exp(-101,000/RT)$ cm²sec⁻¹. Changing sphere diameters caused no detectable variation in diffusion coefficients. Anions are the much slower diffusing species in this oxide.

I. Introduction

THREE common, interesting, and important oxides possessing the corundum or sapphire structure are α -Al₂O₃, α -Fe₂O₃, and α -Cr₂O₃. Knowledge of cation and anion self-diffu-

sion coefficients in these materials is vital to an understanding of their lattice defects and conduction mechanisms. Careful control of such complex processes as oxide sintering, creep, or high-temperature oxidation of the parent metal is dependent on what is done to the rate-determining species.

Measurements exist for cation diffusion in polycrystalline α -Al₂O₃,¹ in single crystals² and sintered compacts³ of α -Fe₂O₃, and in sintered^{4,5} and hot-pressed⁶ cylinders of α -Cr₂O₃. Anion diffusion has been determined in single-crystal and polycrystalline α -Al₂O₃⁷ and in sintered samples of α -Fe₂O₃.⁸ Except for a few runs at temperatures too low for quantitative results,⁹ little information concerning anion diffusion in

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$\alpha\text{-Cr}_2\text{O}_3$ has heretofore been available. Hence, the purpose of this investigation was to seek meaningful results for anion diffusion in $\alpha\text{-Cr}_2\text{O}_3$ and to supply an analysis of apparent similarities and differences among the asymmetric corundum oxides.

II. Experimental Procedure

(1) Material

Oxide powder was received from C. K. Williams & Company. Its composition was 99.7 wt% Cr_2O_3 , 0.20 H_2O , 0.05 S, with traces of Fe, Al, Cu, Si, Mg, and slight traces of Ca and Na. This is the highest purity chromium oxide that can be made in the laboratory using commercially available raw materials. Subsequent treatments were ball milling, drying, prepressing, hot-pressing for 15 minutes at 1600°C under 5000 psi, and a stabilizing annealing for 24 hours at 1575°C in dry nitrogen. After surface grinding to cylinders measuring 1.9 cm in diameter by 1.9 cm long, sample densities were taken; they exceeded 98% of the theoretical limit. On polishing cylindrical ends, counts were made of the number of grain-boundary intercepts per unit length of a random line. From these, average grain diameters of 85 to 110 μ were calculated.

The solid cylinders were ground to pass through 80-mesh and remain on 100-mesh sieves. A boron carbide mortar and pestle was used. Most of these particles were then converted to spheres by dropping them through a carbon arc. Carter's¹⁰ powder feeder permitted close control of a slow flow rate. After arcing, the particles were graded to mesh sizes of $-100 +150$ and $-150 +200$. The near-perfect and dense spheres of $\alpha\text{-Cr}_2\text{O}_3$ were selected by again vibrating powder over a slightly inclined plane. Only the best spheres would roll quickly to the bottom. Average sphere diameters for the two grades were 127 and 90 μ , respectively, with a variation of about $\pm 10\%$. A few spheres were mounted and polished and viewed under polarized light; the 127 μ grade contained two or three grains whereas the 90 μ spheres were predominantly single crystals. A small amount of central porosity was noted, but subsequent density determinations revealed nothing lower than 95% of the theoretical limit. Initial surface finish was generally smooth and uniform.

(2) Apparatus

The gaseous-exchange techniques applied, as well as the method of calculating D values, were based primarily on the experience of Haul and co-workers.¹¹ This apparatus differed from one used for low-temperature measurements¹² on glasses in that it had Pt10Rh tubing in the furnace region. A schematic diagram of the apparatus is shown in Fig. 1. Water containing 5.8 at. % ^{18}O was obtained from the Weizmann Institute of Science in Rehovoth, Israel. It was converted to hydrogen and oxygen gas by electrolysis in a thin U-tube containing platinum electrodes. The entire cell was immersed in an ice-filled insulating flask to hinder evaporation. Hydrogen was withdrawn by a mechanical vacuum pump attached to the cathode. Generated oxygen was passed through a gas purifier that transformed residual hydrogen to water vapor; this and any other accumulated moisture were trapped by a flask of dry ice and Dowanol. The reservoir had a calibrated volume of 310 cm^3 ; the manometer was a closed mercury column on which pressures from near zero to 300 mm Hg could be read. Tubular volume between the five middle stopcocks was 10 cm^3 .

The volume of the exchange chamber was calibrated as 380 cm^3 . It consisted of Pyrex glass at the upper end, seven intermediate glasses bonded to Fernico, and 25 cm of end-welded Pt10Rh tubing. During operation, the Fernico seal was cooled by water passing through copper coils. The outer and inner diameters of the noble-metal tubing were 2.86 and 2.70 cm, respectively. A Pt40Rh resistance furnace, whose constant-temperature zone was about 4 cm

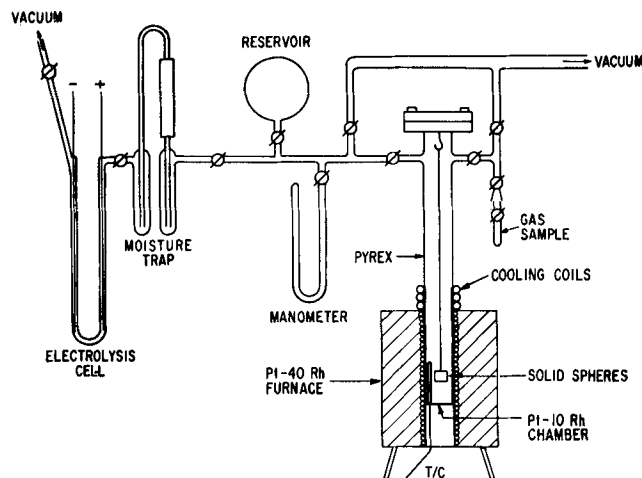


Fig. 1. Gaseous-exchange apparatus.

for the temperature range considered here, was positioned at the lower end of the exchange chamber. A small, closed Pt10Rh tube extended from the chamber bottom to 3 cm above the furnace hot zone for insertion of a Pt-Pt10Rh thermocouple. The upper end of the chamber was sealed with a Neoprene O-ring inside a bolted metal flange. Spheres were contained in an open platinum basket hung from a hook on the metal flange with a platinum wire. The gas-sampling stopcock was half filled with black wax to provide a volume of about 0.1 cm^3 ; this is a negligible amount of the chamber volume.

Oxygen was generated to fill the reservoir to a pressure of about 280 mm Hg. Each batch of spheres was preheated for 15 hours in dry air at the diffusion temperature. The exchange chamber was then evacuated; on establishing thermal equilibrium, oxygen was passed from the reservoir into the chamber to give a constant pressure of 125 mm Hg, and a sample bottle for zero time was taken. Additional gas samples were removed at 2-hour intervals for times up to 32 hours in some cases. The mole fraction of ^{18}O in each bottle was determined with a Consolidated Model 21-620 mass spectrometer. Peaks at mass numbers 32 ($^{16}\text{O}_2$) and 34 ($^{16}\text{O}^{18}\text{O}$) were used. Air contamination was monitored by observing constancy of the 28 ($^{14}\text{N}_2$) peak. Fresh charges of spheres weighing about 0.8 g were used for each D value.

Data were processed by applying the error-function equation

$$(p - p_1)/(p_2 - p_1) = \text{erfc}(\sqrt{Dt}/a\lambda) \quad (1)$$

where p is the mole fraction of ^{18}O in the convection-stirred gas at time t , p_1 is the mole fraction of ^{18}O initially in the oxide (taken as the normal amount of 0.0020), p_2 is the original mole fraction of ^{18}O in gas at zero time, a is sphere radius divided by three, and λ is the ratio of total oxygen g -atoms in gas (n_g) to the total oxygen g -atoms in oxide (n_s). The simple geometric radius was used for a ; n_g was derived from the amount of gas originally in the reservoir and the amount of gas remaining in the rest of the system after expansion to the heated chamber; n_s required accurate determinations of sample weight and a stoichiometric $\alpha\text{-Cr}_2\text{O}_3$ composition was assumed.* The numerical solution of equation (1), where $\text{erfc}(\sqrt{Dt}/a\lambda)$ can also be expressed as $\exp(Dt/a^2\lambda^2)[1 - \text{erf}(\sqrt{Dt}/a\lambda)]$, has been given in several texts (e.g.,

* Although chemical analyses usually find somewhat less than 68.4 wt% chromium, the difference (<0.4 wt%) is negligible.

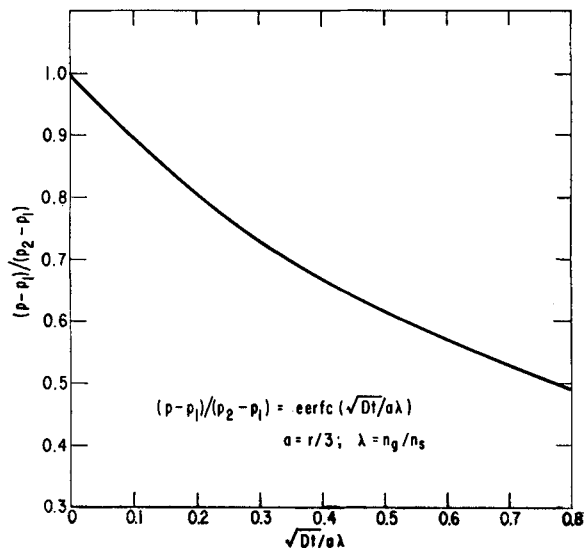


Fig. 2. Plot of relation used to convert changing mole-fraction ratios to $\sqrt{Dt/a\lambda}$.

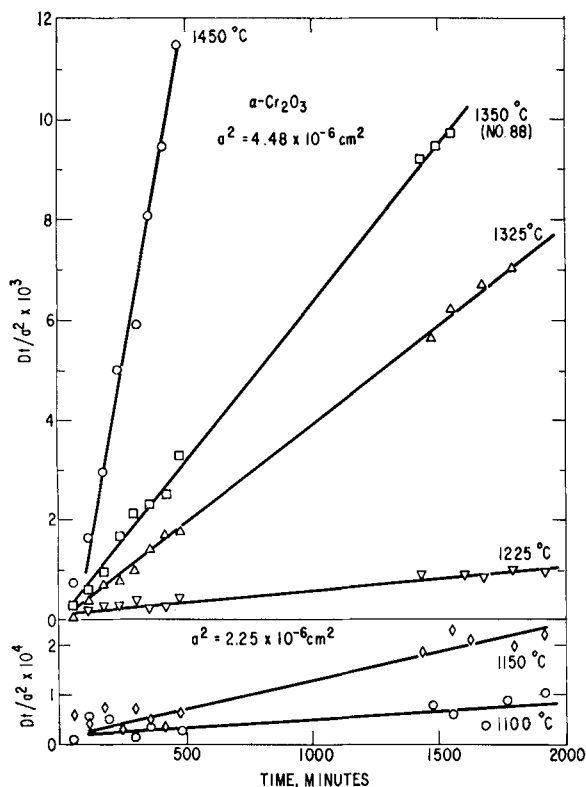


Fig. 3. Representative data for several temperatures, using two sphere sizes, plotted as Dt/a^2 vs. diffusion time.

Crank¹³). Figure 2 shows its curvature through the range where data were obtained. Beyond $\sqrt{Dt/a\lambda} = 1.8$, the relation becomes less rigorous. Derived Dt/a^2 values were plotted versus time, and slopes were taken from the best straight lines describing the data for a determination of anion diffusion coefficients at various temperatures.

III. Results

Experimental points from a few runs are plotted in Fig. 3. Exchange times were extended over a 2-day interval for



Fig. 4. (A) Spheres of 90μ α - Cr_2O_3 after 1100°C diffusion annealing; (B) 127μ α - Cr_2O_3 spheres after diffusion at 1450°C . ($\times 55$.)

temperatures to 1350°C . With some overlap to check internal consistency, the smaller diameter spheres were used for lower temperatures. Blank runs performed at 1100° , 1250° , and 1400°C disclosed no detectable exchange with nonsample surfaces. One attempt at detecting exchange in 90μ spheres held for 2 days at 1050°C was unsuccessful as was an earlier study⁹ with more primitive apparatus. The small spheres tended to become faceted with increasing time and temperature of oxygen exposure. Figure 4(A) shows the 90μ spheres after 47 hours in air and oxygen at 1100°C ; Fig. 4(B) shows the 127μ spheres after 23 hours at 1450°C . With the latter, sintering was starting to occur and higher temperature runs were not attempted. Chromium oxide volatilizes¹⁴ in oxygen atmospheres, but use of very dry oxygen reduced volatilization rates to lower levels than previously found.⁹ For the sample held at 1450°C , weight loss was only 0.0012 g from an initial weight of 0.7795 g (less than 0.2%). The facets may exercise some influence on assumed boundary conditions but the ^{18}O penetration extends well within each sphere and no apparent deviations were found in a mass spectrometer study.

The D values obtained from the best straight lines through the data points are listed in Table I and are plotted in Fig. 5 as $\log D$ versus $1/T$. Samples 71, 111, 37, 121, and 41 were 90μ spheres; all others were 127μ spheres. At 1150° and 1200°C differences in their D values lie within experimental error; use of both sizes provides comparable results. Application of the method of least squares to the data of Table I yielded the equation:

Table I. Summary of α -Cr₂O₃ Anion-Diffusion Data

Sample No.	Temp. (°C)	D (cm ² sec ⁻¹)
116	1450	2.21×10^{-12}
114	1400	9.40×10^{-13}
88	1350	4.71×10^{-13}
112	1350	3.44×10^{-13}
120	1325	2.90×10^{-13}
41	1300	2.38×10^{-13}
121	1275	7.12×10^{-14}
85	1250	6.88×10^{-14}
123	1225	3.49×10^{-14}
37	1200	1.70×10^{-14}
36	1200	1.54×10^{-14}
125	1175	1.11×10^{-14}
80	1150	5.30×10^{-15}
111	1150	4.29×10^{-15}
71	1100	1.20×10^{-15}

$$D = 15.9 \frac{+28.6}{-10.2} \exp[(-100.8 \pm 1.6) \times 10^3/RT] \text{ cm}^2\text{sec}^{-1} \quad (2)$$

Assuming no error in temperature control and measurement, a probable error in log D of $\pm 25\%$ and the above indicated errors in the preexponential D_0 and activation energy Q were calculated from data scatter about the least-squares line in a manner prescribed by Worthing and Geffner.¹⁵ Passage of other straight lines through the same family of data could yield variations in D_0 of \pm a factor of 4 and in Q of about ± 10 kcal mole⁻¹. No indication of curvature to higher D values (extrinsic diffusion) was noted on decreasing temperature to 1100°C. Apparatus limitations prevented a meaningful survey of the variation in anion diffusion with a large change in oxygen partial pressure.

IV. Discussion

Use of solid α -Cr₂O₃ spheres does not permit the same high sensitivity and precision found in the earlier study of oxygen diffusion in fibers of calcium-aluminoborate and calcium-aluminosilicate glasses.¹² Fibers can be drawn to considerably smaller diameters; a larger sample can be used; ¹⁸O constitutes a greater weight fraction of the glass compositions than it does in α -Cr₂O₃. These factors and longer exposure times made it possible to obtain D values near 10^{-17} cm² sec⁻¹ rather than the lower limit of 10^{-15} cm² sec⁻¹ found here. Diffusion annealings were not conducted above 1450°C because the sample from that temperature (Fig. 4(B)) was starting to show signs of excessive volatilization and partial sintering.

Calculated diffusion coefficients could be affected by errors in determining a , n_0 , n_s , t , T , p_2 , p , and oxygen pressure in the exchange chamber. The variability in a has been discussed. Since two different particle sizes caused no significant changes in the Arrhenius plot of Fig. 5, there appears to be little increased diffusion from the additional grain boundaries in the 127 μ material. Similarly, if a surface-exchange reaction in any way controls overall diffusion coefficients, the two different surface areas would test this feature. Similar to the findings of Boreskov and Popovskii,¹⁶ transfer of adsorbed oxygen into the lattice of α -Cr₂O₃ seems to be a relatively fast process and is not the exchange limiting factor. This can be observed from the linear Dt/a^2 versus time data of Fig. 3, although a large amount of scatter does occur at low temperatures during the first day's sampling.

The n_0 term depends on measurements of manometer gas pressure and on the calibration of system volumes; the n_s term depends on the sample weight and chemical composition. Any errors from these sources are so small (less than 0.5%) that they can be neglected. Time was digitally indicated with a reset timer; including stopcock manipulation, this is known to within ± 0.5 minute. Temperature accuracy with secondary-calibrated Pt-Pt10Rh thermocouples from 1100° to

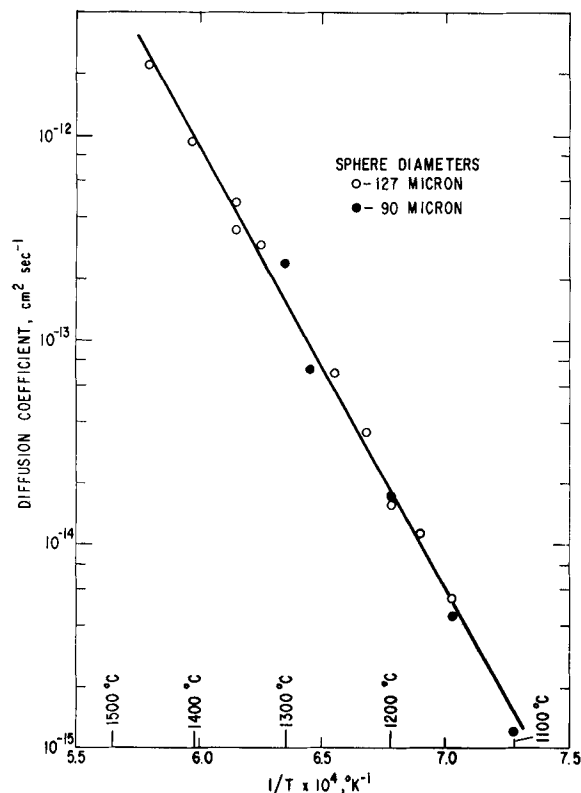


Fig. 5. Arrhenius plot of self-diffusion data for oxygen in α -Cr₂O₃ under a partial pressure of 125 mm Hg.

1450°C is about $\pm 2^\circ$, and long-time control fluctuated within $\pm 5^\circ$. The zero-time mole fraction of ¹⁸O, p_0 , varied from 0.0580 by ± 0.0009 ; this $\pm 1.5\%$ error probably applies to p at time t . Oxygen pressure in the exchange chamber was measured as 125 ± 2 mm Hg. The widest range in reproducibility for two runs with the same size spheres was 37% from the low value at 1350°C; overall scatter about the least-squares line of equation (2) indicates somewhat less uncertainty.

One method of comparing cation and anion diffusion in the corundum oxides is to plot their least-squares lines as a function of reciprocal reduced temperature, T_m/T , where T_m is melting temperature and T varies through only the experimental temperature range. Since some disagreement still exists about the exact T_m of each oxide, the abscissa of Fig. 6 was constructed from values listed in the Handbook of Chemistry and Physics¹⁷ i.e., 2015°C for α -Al₂O₃, 1565°C for α -Fe₂O₃, and 1990°C for α -Cr₂O₃. Other preferred T_m 's would shift the lines to the right or left, but the shift would not be great. In review, the confidence that might be placed in these relations can be assessed. The work concerned with the diffusion of ²⁶Al in densely sintered (200 μ grain size) α -Al₂O₃ under an air atmosphere¹ appears to have been carefully done. Lindner³ measured the diffusion of ⁵⁹Fe in sintered α -Fe₂O₃ tablets under air, and some confirmation of his data was provided by Himmel *et al.*² The latter group reported three points for ⁵⁵Fe in large, natural hematite crystals under 1 atm of oxygen and found no dependence on crystallographic direction. Lindner and Åkerström⁴ also conducted a preliminary six-point investigation of the diffusion of ⁵¹Cr in sintered α -Cr₂O₃, but they gave no details about sample purities, densities, or annealing atmospheres. Hagel and Seybolt⁶ found higher D values for ⁵¹Cr in hot-pressed α -Cr₂O₃ which had been annealed under nitrogen to avoid volatilization; by using sintered samples of 93.7% theoretical density, the low data of Lindner and Åkerström could be approached. Presumably at higher temperatures

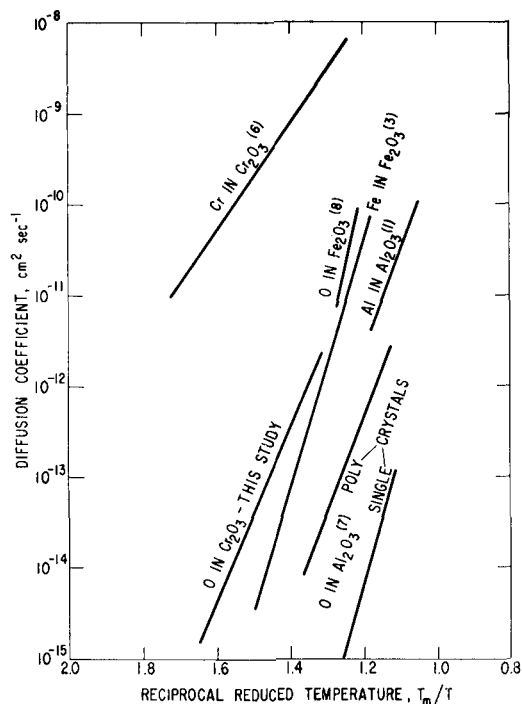


Fig. 6. Comparison of cation and anion self-diffusion in the corundum oxides as a function of reciprocal reduced temperature. Reference numbers show source of information.

some sintering continues during the long diffusion runs to give high apparent activation energies. Conductivity studies on other than sound hot-pressed or well-sintered oxides frequently show the same effect. Ignatov *et al.*⁵ document that $D_0 = 4.29 \times 10^{-8} \text{ cm}^2 \text{ sec}^{-1}$ and $Q = 22.0 \text{ kcal mole}^{-1}$ for cation diffusion in $\alpha\text{-Cr}_2\text{O}_3$ between 900° and 1200°C under oxygen at 10^{-2} mm Hg ; their relation intersects the Hagel-Seybolt data and goes to a higher level below 1000°C in a manner suggestive of grain-boundary diffusion or extrinsic behavior.

Oishi and Kingery⁷ studied anion diffusion in single crystals and polycrystals of $\alpha\text{-Al}_2\text{O}_3$. Most of their D values were obtained from the $^{18}\text{O}/^{16}\text{O}$ ratio in solid particles after annealing for a known time under an oxygen pressure of 152 mm Hg; the scatter is quite high. Diffusion in crushed powder containing many 20 to 30 μ grains was almost two orders of magnitude greater than in pieces of single crystals. This difference was attributed to fast diffusion along grain boundaries, but surface irregularities and initial equilibration may have played a role. The short line for anion diffusion in $\alpha\text{-Fe}_2\text{O}_3$,⁸ where D_0 possesses the abnormally high value of $10^{11} \text{ cm}^2 \text{ sec}^{-1}$, was constructed from only three points. Extrapolation to temperatures below about 1100°C shows that cations in $\alpha\text{-Fe}_2\text{O}_3$ now become the faster diffusing species. This inference is contrary to the findings of Davies, Simnad, and Birchenall¹⁸ who placed radioactive silver markers on the surface of Fe_3O_4 ; after partial reaction to $\alpha\text{-Fe}_2\text{O}_3$ in oxygen, the silver could not be found. They concluded that the silver had volatilized during oxidation and that the $\alpha\text{-Fe}_2\text{O}_3$ had grown by the inward diffusion of oxygen ions. In another check it was assumed that cations are the rate-controlling species for growth of $\alpha\text{-Fe}_2\text{O}_3$ (using Lindner's data); Himmel *et al.* noted a discrepancy of two orders of magnitude between the calculated and experimentally determined rate constants for the oxidation of magnetite. Of all these measurements, perhaps the one for low anion diffusion in $\alpha\text{-Fe}_2\text{O}_3$ would bear most careful reconsideration. Extrapolation of the line for cation diffusion in $\alpha\text{-Al}_2\text{O}_3$ shows that anion diffusion may become rate controlling for oxidation at low temperatures. Doherty and Davis¹⁹ have observed,

from transmission electron microscopy, the initial growth of an amorphous film on oxidized aluminum by outward transport of cations, but the outer crystalline layer appears to grow by the inward transport of anions.

In regard to chromium oxidation, many features (e.g. a porous consumption zone at the metal-oxide interface, marker coverage, rate reduction by lower valence additions, and conduction by electron holes) provide strong evidence for scale growth via the outward diffusion of cations. Caplan *et al.*²⁰ found, however, that electropolished samples oxidize rapidly with much blistering, wrinkling, and multilayered ballooning. They believe that these effects result from development of compressive stresses during film thickening. Their explanation involves a counterflux of diffusing anions; this supposedly promotes formation of new oxide *within* the scale. The anion-diffusion data found here are so much lower than the cation data (by three to four orders of magnitude) that it seems highly unlikely that anions play much of a role in oxide growth. Other sources of poor scale adherence, such as contamination during stress-relief annealing or the presence of an intermediate oxide caused by electropolishing, should receive more attention.

Sintering is another rate process in which these relative diffusion coefficients are helpful to a mechanistic understanding. Coble²¹ found that apparent diffusion coefficients calculated from the shrinkage of $\alpha\text{-Fe}_2\text{O}_3$ compacts, assuming Kingery and Berg's sintering model,²² agree with Lindner's extrapolated cation diffusion data within a factor of two. This agreement has often been used to show that initial sintering of $\alpha\text{-Fe}_2\text{O}_3$ takes place by a volume-diffusion mechanism where the rate-controlling species are cations. With $\alpha\text{-Al}_2\text{O}_3$, the situation is more confusing since the apparent diffusion coefficients from sintering data are two orders of magnitude above those for anion diffusion; they still lie slightly below those for cation diffusion. Paladino and Coble²³ have suggested that the cations actually may be rate controlling because of greatly enhanced grain-boundary diffusion for anions. The arguments are unresolvable from the information obtained to date. It seems that a more careful study of the sintering kinetics of $\alpha\text{-Cr}_2\text{O}_3$, where cation and anion diffusion coefficients differ greatly, should be more straightforward.

V. Summary

Hot-pressed compacts of high-purity $\alpha\text{-Cr}_2\text{O}_3$ from an earlier cation-diffusion study were crushed and re-formed into small spheres of uniform diameter. By using a modified Haul-type apparatus constructed of Pt10Rh the exchange of ^{18}O (at a pressure of 125 mm Hg) with the spheres' ^{16}O was determined for equilibrium temperatures of 1100° to 1450°C. Anion self-diffusion conforms to the least-squares equation

$$D = 15.9 \exp(-101,000/RT) \text{ cm}^2 \text{ sec}^{-1}$$

These diffusion coefficients range from 10^{-15} to $2 \times 10^{-12} \text{ cm}^2 \text{ sec}^{-1}$ and are four to three orders of magnitude smaller than the values for cation diffusion at comparable temperatures. From this wide difference, it would be expected that the rate of chromium oxidation is controlled by the faster moving cations and that sintering is controlled by the slower moving anions. The situation is less certain in $\alpha\text{-Fe}_2\text{O}_3$ and $\alpha\text{-Al}_2\text{O}_3$.

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Phase Relations in the System Boron Oxide-Silica

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The suggested phase diagrams for the system B₂O₃-SiO₂ as drawn from the findings of previous investigators are presented. These diagrams show the wide controversy regarding this system. The principal difficulties in obtaining reliable equilibrium data are the volatilization of B₂O₃, the hydration of B₂O₃-rich glasses, and the great viscosity of B₂O₃-SiO₂ melts. In this investigation firings were made in sealed platinum capsules. Where necessary, they were opened and studied under xylene to eliminate hydration. Phases were identified by optical and X-ray methods. The liquidus was obtained by determination of the temperatures at which the stable phases of SiO₂ completely dissolved in the borosilicate melts. The criteria used for equilibrium are discussed.

I. Introduction

THE system B₂O₃-SiO₂ is not only one of the basic glass systems but is also of interest in many ceramic and mineralogic studies. Although extensive work has been done on vari-

ous compositions in the binary system B₂O₃-SiO₂, its phase diagram has not previously been accurately established. This is not to the discredit of the many investigators who have done work on the system, since it would be difficult to select a binary system more fraught with experimental difficulties. The principal difficulties involved in obtaining reliable equilibrium data are the volatilization of B₂O₃ at elevated temperatures, the rapid hydration of the B₂O₃-rich materials, and the high viscosity of borosilicate melts. Add to these the many

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