TRANSPORT PHENOMENA IN ALUMINUM OXIDE

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The sign of the current carriers determined from thermoelectric electromotive force measurements on aluminum oxide (Al₂O₃) by Pappis and Kingery was incorrectly reported by the original authors (in ref. 3 of this report). The sign for the current carriers at 1500° C and an oxygen pressure of 1 atmosphere should be negative, and that for current carriers at 1500° C and an oxygen pressure of 10⁻¹⁰ atmosphere should be positive.

The electrical conductivity data of Pappis and Kingery for Al₂O₃ exposed to oxygen pressures of both 10⁻⁵ and 10⁻¹⁰ atmosphere show breaks at temperatures of approximately 1630° C, above the temperatures at which thermoelectric electromotive force measurements were made. Since the magnitudes of the activation energies above the breaks are in reasonable agreement with the intrinsic activation energy for oxide ion diffusion, the author of the subject report still believes that the upper portions of these particular conductivity data are controlled by intrinsic oxygen-ion motion, as indicated in the report. The change from positive-ion control at lower temperatures to negative-ion control at higher temperatures could result from slight losses of oxygen from the samples.

Corrected versions of figures 3 and 4 are attached. In the original version of figure 3, the conductivity data calculated from diffusion data were all inadvertently plotted too large by a factor of 100.

Some variations occur in the values of activation energies listed as 2.57 and 2.85 electron volts. Actual overlap in value is noted. Nevertheless, there are two different processes occurring.

Even though modifications are required in the report where the data of Pappis and Kingery are referred to, the conclusions do not require modification.
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SUMMARY

The results of available electrical conductivity determinations and self-diffusion measurements for aluminum oxide were reevaluated in terms of ionic mechanisms of transport. Four activation energies were found: 5.9, 2.6, 2.9, and 0.66 electron volts. These activation energies seem to be those, respectively, for intrinsic oxygen-ion motion, extrinsic oxygen-ion motion, intrinsic aluminum-ion motion, and extrinsic aluminum-ion motion. The conductivity of the polycrystalline aluminum oxide specimens used in this study is larger than previously reported data for aluminum oxide single crystals. The results for aluminum oxide are compared with those for magnesium oxide and appear to be consistent.

INTRODUCTION

As in the case of magnesium oxide, the results of a number of studies of transport phenomena in aluminum oxide are in the literature. These studies include measurements of self-diffusion coefficients as well as of electrical conductivity. Conductivity results obtained by different investigators vary by several orders of magnitude, and many different activation energies have been reported. As was the case with magnesium oxide (ref. 1), however, the author took a large fraction of the reported data and obtained a consistent picture based upon ionic conduction in aluminum oxide. The sources of major difficulty in interpreting the experimental results will be discussed in the hope of preventing similar problems in the interpretation of transport phenomena in other cases.

Besides being of great interest in view of the many practical applications for aluminum oxide, a proper interpretation of the transport phenomena in aluminum oxide is of great importance in terms of fundamentals. Aluminum oxide, like magnesium oxide, is a good example of an oxide with truly ionic bonding. These two ionic oxides are the ones on which most of the experiments were performed. Results obtained with these oxides should give some idea as to what to expect with other ionic oxides.

The physical and chemical properties of aluminum oxide make fundamental studies carried out on it somewhat simpler experimentally than those with magnesium oxide. Its considerably lower melting point allows studies to be con-
ducted much more simply at moderately high relative temperatures; its lower chemical reactivity simplifies the problems associated with maintaining pure materials and clean surfaces.

Because of the large quantity of experimental data already available, little additional experimentation was needed in order to complete the interpretation. The author's experimental work was intended to fill the need for electrical conductivity data measured in a suitable atmosphere where positive ion conductivity is expected to predominate.

EXPERIMENTAL PROCEDURES

The polycrystalline specimens used for this conductivity study consisted of disks of Triangle RR aluminum oxide, which were approximately 26.5 millimeters in diameter and 1.7 millimeters thick. This material is stated by the manufacturer to be silica free and to be no less than 99.7 percent aluminum oxide (Al2O3). The bulk density of these disks was 3.7 grams per cubic centimeter. (The theoretical density for Al2O3 is 3.97 g/cu cm.) Slight surface irregularities on the disks were removed with a rotating diamond wheel.

The inert atmosphere furnace, the gas introduction system, and the measuring equipment were the same ones used for the measurements on magnesium oxide (MgO) (ref. 1). Multiple specimens were used in the specimen holder, which has also been described previously (ref. 1). Flowing argon (99.995 percent minimum) was used as the atmosphere for the measurements and was held at approximately 3 pounds per square inch gage. The oxygen content of this argon was approximately 0.001 percent. Having enough oxygen gas present to ensure positive ion motion was important. (Electrical conduction in MgO in this atmosphere occurred by positive-ion motion.)

EXPERIMENTAL RESULTS

The conductivity results for temperatures up to 68 percent of the absolute melting point are presented in figure 1. The logarithm of the product of electrical conductivity and absolute temperature is plotted against the reciprocal of absolute temperature in order to take into account the temperature dependence of the preexponential term of the conductivity equation (cf. ref. 2). The high- and low-temperature activation energies from these data are 2.85 and 0.66 electron volts, respectively. There is no indication of any further changes in slope at the highest experimental temperatures.

The high-temperature activation energy is in reasonable agreement with the value of 2.97 electron volts obtained by Pappis and Kingery (ref. 3) from electrical conductivity measurements conducted on single crystal sapphire in an atmosphere of pure oxygen (O2) gas. Furthermore, as was the case with MgO, the polycrystalline data are slightly less than one order of magnitude larger than the single crystal conductivity data. Thermoelectric electromotive force measurements conducted by Pappis and Kingery (ref. 3) indicated that in 1 atmosphere of O2 conduction in Al2O3 occurred predominantly via positive current carriers.
The energy of formation of Schottky pairs calculated from the author's high- and low-temperature activation energies is 5.48 electron volts.

DISCUSSION

Nature of Conductivity in Aluminum Oxide

The mechanisms of conductivity for $\text{Al}_2\text{O}_3$ suggested by many authors have involved electron and hole migration. The reasons this interpretation need not follow from the experimental data will be discussed subsequently. The most nearly direct approach used to determine the nature of the conductivity is that of potential measurements. Since there is but one such study reported and because of the difficulties involved in obtaining potential measurements, other evidences as to the nature of the conductivity must also be considered.

The author feels that at present the strongest evidence as to the nature of the conductivity of $\text{Al}_2\text{O}_3$ results from a comparison of conductivity data with self-diffusion data. One of the most carefully performed conductivity experiments was that by Heldt and Haase (ref. 4), who measured the conductivity of high-purity $\text{Al}_2\text{O}_3$ specimens in vacuo. Their data are linear over the temper-
The reciprocal of temperature, $\frac{1}{T}$, in kelvin, is plotted against temperature, $T$, in degrees Celsius. The data range from 555°C to 1465°C and are plotted in figure 2. There is no indication of a change in slope even in the highest temperature region.

The activation energy from their data, 2.57 electron volts, is in satisfactory agreement with the activation energy of 2.50 electron volts obtained in the extrinsic region for oxygen-ion ($O^{2-}$) self diffusion in single crystal $Al_2O_3$ by Oishi and Kingery (ref. 5). This agreement would seem to imply that an ionic conductivity mechanism based on $O^{2-}$ motion predominated over that entire temperature range. Extrinsic $O^{2-}$ conductivity would be expected since their conductivity measurements were made in vacuo (ref. 4), where a small loss of oxygen from the samples should have occurred.

Furthermore, with an oxygen pressure of $10^{-10}$ atmosphere, thermoelectric electromotive force measurements conducted on $Al_2O_3$ by Pappis and Kingery (ref. 3) indicated that conduction occurred by negative current carriers. It is of great importance to realize that thermoelectric electromotive force measurements can give the sign of the predominant current carrier but cannot give evidence to determine whether electrons (or holes) or ions are involved. In this regard thermoelectric electromotive force measurements are inferior to Hall coefficient measurements, which can confirm unambiguously the presence of electronic (or hole) conductivity. Although little experimental work has been done with ionic conductors, thermal diffusion, which would produce a thermoelectric electromotive force, has been detected with certain ionic solids (cf. ref. 2). Thermoelectric electromotive forces can thus be produced by processes in which ions move.

To the author's knowledge, Schmalzried has conducted the only study of the potentials of oxygen concentration cells with $Al_2O_3$ (ref. 6).
The experimental cell utilized for his potential measurements consisted of a commercially prepared tube of reasonably high purity Al₂O₃ (Purox), one wall of which was exposed to air, the other to variable oxygen partial pressures obtained by reaction of various mixtures of carbon dioxide - carbon monoxide or carbon dioxide - hydrogen. Schmalzried states that his experimental results indicate the presence of both ionic and electronic (or hole) conduction below 1323° C and electronic conduction above 1323° C. The important thing is that an ionic conductivity mechanism is observed. The fact that he does not find that all the conduction is ionic may result from the experimentally obtained potentials being mixed potentials caused by the chemical reactions of the gaseous components other than O₂ with the Al₂O₃. Further studies with carefully purified argon-oxygen mixtures would be helpful for quantitative evaluation of the percentage of the ionic character of the conductivity.

It is important to realize that there are a number of electrical conductivity determinations of Al₂O₃ that extend higher than 1323° C with no indication of a change of slope near that temperature. The activation energy below 1323° C seems to indicate conductivity by an O²⁻ mechanism. The mechanism of conductivity is therefore inferred still to be ionic above 1323° C. The data of reference 4 is one of these cases. In summary, the change in mechanism of reference 6 is not supported by the conductivity data.

As is discussed in reference 1, transference number determinations are not very useful in determining the nature of the conductivity in pure compounds such as Al₂O₃ or MgO. The primary difficulty is that the electrode reaction controls what the conductivity mechanism will be. For transference measurements of oxides in an air atmosphere, the cathode reaction should be

\[ 4 \text{e}^- + \text{O}_2 \rightarrow 2 \text{O}^{2-} \]

and the anode reaction should be

\[ 2 \text{O}^{2-} \rightarrow \text{O}_2 + 4 \text{e}^- \]

If the conduction between electrodes then proceeds by O²⁻ migration, there will be no weight changes observable in the anode and the cathode portions of the solid electrolyte caused by solution or deposition of metal. Such results have been obtained with other solid oxides. For example, ceric oxide (CeO₂) solid solutions with lanthanum oxide (La₂O₃), neodymium oxide (Nd₂O₃), and yttrium oxide (Y₂O₃) show negligible weight changes in transference number determinations (ref. 7). Furthermore, the amount of oxygen liberated at the anode for six of the eight compositions studied was the amount corresponding to a transference number for O²⁻ of approximately 1.

Kingery and Meiling also observed no weight changes in their transference measurements on Al₂O₃ conducted in air (ref. 8). This lack of weight change eliminates the possibility of cation motion. Furthermore, no weight changes were encountered when stabilized zirconium oxide (Zr₀.₈₅Ca₀.₁₅O₁₈₅) disks (known anionic conductors) were placed between the Al₂O₃ disks and the electrodes. Since the presence of such disks should have prevented electronic conductivity from occurring in the Al₂O₃, such results would seem to imply that the conductivity was by anions. Kingery and Meiling believed, however, that the O²⁻ conductivity could not be large enough to provide the necessary number of cou-
lombs passed, and therefore they considered the conductivity to be electronic. (Weight changes would be zero for this type of conductivity, also.) Their reasoning for considering $0^{\text{in}}$ transfer to be an insignificant contributor depended upon a comparison at 1500°C of the magnitude of conductivity made in $10^{-5}$ atmosphere of O$_2$ (in the extrinsic range) with the magnitude of conductivity (in the extrinsic range) calculated from diffusion data measured in O$_2$ at 152 torr. Such a comparison may well be misleading for at least two reasons: (1) The results obtained, in the extrinsic range in both cases, will be strongly dependent upon the purity of the sample, both chemically and in dislocation content. (2) The measurements were made under vastly different oxygen pressures. Oxygen-ion conductivity would be expected to be strongly dependent upon oxygen partial pressure. (This situation can be true even if the total ionic conductivity does not vary greatly.) Since a large variation in $0^{\text{in}}$ extrinsic range conductivity, exceeding three orders of magnitude, has been shown to occur with MgO (ref. 1), it is not inconceivable that an equally large variation would occur with Al$_2$O$_3$. (See fig. 3, p. 8, which is discussed in the following subsection.) It is concluded then that the transference number measurements can best be explained on the basis of $0^{\text{in}}$ conductivity.

Reevaluation of Available Conductivity and Diffusion Data on Aluminum Oxide

Ionic mechanisms of conductivity and the related self-diffusion measurements should produce four activation energies, two based upon aluminum-ion (Al$^{+++}$) motion and two based upon $0^{\text{in}}$ motion. A careful examination of the available conductivity and diffusion data for Al$_2$O$_3$ indeed gives evidence for four different values for activation energies, at approximately 5.9, 2.6, 2.9, and 0.7 electron volts. Each of these values is identified and discussed in the order mentioned.

Evidence for the value of 5.9 electron volts comes from $0^{\text{in}}$ diffusion data, electrical conductivity data, sintering studies conducted on Al$_2$O$_3$ spheres, and, surprisingly, also from Al$^{+++}$ self-diffusion experiments. The data of reference 5 for $0^{\text{in}}$ diffusion in Al$_2$O$_3$ single crystal and polycrystalline samples show a relatively large scatter, and different activation energies are reported therein for the intrinsic range for these two types of samples. It is hard to decide in certain cases whether the datum point represents intrinsic or extrinsic behavior. The results from a least-squares evaluation of the single crystal data is strongly dependent upon which points are included and which are neglected. The activation energy values from such analyses range from 5.0 to 6.5 electron volts. The value obtained in reference 5 seems to be based solely upon the data for spheres, although we know of no reason for disregarding the results obtained on grain samples. In the reevaluation of the single crystal data an attempt was made to weight equally all reported experimental points that appear to be in the intrinsic range. The resulting line has an equal number of these points on each side, and the sum of the distances of points from the line has been minimized. Moreover, we feel that both sets of data, single crystal and polycrystalline, show the same activation energy. Furthermore, the reevaluated value for the activation energy, 5.87 electron volts, may be a reasonable one, since it is in excellent agreement not only with the high-temperature activation energy for conductivity of single crystal Al$_2$O$_3$ (5.8 eV, as determined

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in ref. 3) but also with the activation energy of 5.85 electron volts obtained from the sintering studies of Kuczynski, Abernethy, and Allan on Al₂O₃ spheres (ref. 9).

An activation energy of 5.9 electron volts would not be expected from the Al⁺⁺⁺ tracer diffusion results. Yet, examination of these data (ref. 10) reveals that, within the limits of experimental error, the diffusion activation energy resulting from the aluminum tracer measurements is the same as that resulting from the oxygen tracer measurements. In addition, the values for the diffusion coefficients in the two cases are very nearly equal. This unexpected result could indicate that both sets of measurements are controlled by the same process - O⁺⁺⁺ motion. By comparison with the results for MgO, the measured activation energy is far too large to represent Al⁺⁺⁺ diffusion. Furthermore, it would not be expected to be equal to the activation energy for O⁺⁺⁺ motion. The fact that the Al⁺⁺⁺ diffusion runs were made in an air atmosphere may in some way have been responsible for the results obtained. Impurities in the radioactive Al₂O₃ samples could also have played a part.

The data for extrinsic O⁺⁺⁺ motion, which yield an activation energy of approximately 2.6 electron volts, were discussed in the previous subsection.

Figure 3 contains much of the data thus far discussed in this subsection. A number of sets of data in which O⁺⁺⁺ motion seems to be the controlling mechanism are plotted in that figure. Other sets of electrical conductivity data for polycrystalline Al₂O₃ that appear in the literature could also be included if space permitted. The Nernst-Einstein equation, with an assumed value for the transference number of 1, was used to convert diffusion data to conductivity data, so that both types could be plotted in the same figure. The values for activation energies for all these data are approximately 5.87 electron volts for the intrinsic range and 2.57 electron volts for the extrinsic range. Reasonable estimates of the possible variation in these values would be ±0.15 electron volt for the intrinsic data and ±0.07 electron volt for the extrinsic data. The energy of formation of Schottky pairs calculated from these activation energies is 5.49 electron volts. This value is in excellent agreement with the value of 5.48 electron volts from the conductivity data, which the author interprets as conductivity predominantly by Al⁺⁺⁺.

The two activation energies so far discussed are based upon both conductivity and diffusion data. For the remaining two, 2.9 and 0.7 electron volts, there are just conductivity data available. Since the value of 2.9 electron volts is not markedly different from the one of 2.6 electron volts discussed previously, it is important to show that the two do not really represent the same process. Conclusive evidence comes from thermoelectric electromotive force measurements of reference 3, which have been mentioned previously, since they show that the sign of the current carrier differs in the two cases. Positive current carriers were indicated for the process with an activation energy of approximately 2.9 electron volts and negative current carriers for the case of 2.6 electron volts. Additional evidence comes from a consideration of possible variation in the values themselves. Reasonable estimates for the two cases, 2.57±0.07 and 2.85±0.12, indicate that they would not overlap in actual value.
Figure 3. Oxygen-ion conductivity in aluminum oxide.
Conductivity data for the cases representing Al^{+++} motion are presented in figure 4. As mentioned previously, the high- and the low-temperature activation energies from the measurements of the present investigation were 2.85 and 0.66 electron volts, respectively. The values of the preexponentials from the two portions of the data indicate that the former represents the intrinsic case. Presumably, therefore, since the atmosphere in which the measurements were made is unchanged, the value of 0.66 electron volt represents extrinsic Al^{+++} motion.

Although cation conductivity would be expected to predominate in Al_{2}O_{3} on the basis of ion size, far fewer cases of conductivity representing Al^{+++} motion have been reported than cases representing O^{=} motion. In this respect, Al_{2}O_{3} is very much like MgO, for which, also, the data from most studies indicate O^{=} motion.

In summary, an evaluation of diffusion and electrical conductivity data for Al_{2}O_{3} shows the presence of four activation energies, 5.87, 2.57, 2.85, and 0.66 electron volts. These activation energies seem to be the ones, respectively for intrinsic O^{=} motion, extrinsic O^{=} motion, intrinsic Al^{+++} motion, and extrinsic Al^{+++} motion.

Comparison of Aluminum Oxide with Magnesium Oxide

Both oxides are good examples of the truly ionic oxides. The MgO conductivity data have previously been evaluated (ref. 1). They possess features that can be satisfactorily explained by ionic mechanisms of conductivity. Aluminum
oxide might therefore be expected to behave similarly. At this point, a comparison of the values of intrinsic activation energy $Q$ ratios with ionic radius $r$ ratios for the ions is of interest.

For $\text{Al}_2\text{O}_3$,

$$\frac{Q_0}{Q_{\text{Al}^{+++}}} = \frac{5.87}{2.85} = 2.06$$

For $\text{MgO}$,

$$\frac{Q_0}{Q_{\text{Mg}^{++}}} = \frac{5.22}{3.50} = 1.49$$

For $\text{Al}_2\text{O}_3$,

$$\frac{r_0}{r_{\text{Al}^{+++}}} = \frac{1.40}{0.57} = 2.46$$

For $\text{MgO}$,

$$\frac{r_0}{r_{\text{Mg}^{++}}} = \frac{1.40}{0.78} = 1.79$$

$$\left(\frac{\text{Q ratio}}{\text{MgO}}\right)_{\text{Al}_2\text{O}_3} = \frac{2.06}{1.49} = 1.38$$

$$\left(\frac{\text{Radius ratio}}{\text{MgO}}\right)_{\text{Al}_2\text{O}_3} = \frac{2.46}{1.79} = 1.37$$

Such results seem to imply that the same mechanism of diffusion applies with both oxides. Furthermore, since the activation energy increases with the size of the ion, apparently the positive ions are not being polarized to an appreciable extent. Although the theoretical basis of this effect based upon fundamental diffusion theory is not obvious, it is important to note that this same phenomenon also occurs with certain of the chlorides for which the necessary data are available. It does not seem to occur with two ionic solids when only one of them has a close-packed lattice.

CONCLUSIONS

With activation energies as guides, an attempt was made to determine the current carriers for the conductivity process in aluminum oxide. Aluminum oxide conductivity data possess features that can be satisfactorily explained by ionic
mechanisms of conductivity. While the oxygen self-diffusion data for aluminum oxide showed some scatter and while aluminum-ion diffusion-controlled tracer data were not available, the available data all lead to a consistent picture. The mechanism of conduction in single crystals and polycrystals appears to be the same. Many features previously observed with magnesium oxide likewise appeared in the aluminum oxide data. Among these features should be mentioned the relatively large variation of the preexponential term, especially between single crystal and polycrystalline specimens, but with no change in activation energy. A thorough understanding of the causes of this phenomenon is not yet available. As was the case with magnesium oxide, most of the literature conductivity data seems to be for conductivity controlled by oxygen-ion transport.

The values for the activation energies for aluminum oxide appear to be the following: 5.9 electron volts for intrinsic oxygen-ion motion, 2.6 electron volts for extrinsic oxygen-ion motion, 2.9 electron volts for intrinsic aluminum-ion motion, and 0.66 electron volt for extrinsic aluminum-ion motion.

Lewis Research Center,
National Aeronautics and Space Administration,
Cleveland, Ohio, February 19, 1965.

REFERENCES


"The aeronautical and space activities of the United States shall be conducted so as to contribute ... to the expansion of human knowledge of phenomena in the atmosphere and space. The Administration shall provide for the widest practicable and appropriate dissemination of information concerning its activities and the results thereof."

—National Aeronautics and Space Act of 1958

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