

Electrical Conductivity of Alumina/Aluminum Composites Synthesized by Directed Metal Oxidation

Hari Venugopalan, Kanishka Tankala, and Tarasankar DebRoy

Department of Materials Science and Engineering, The Pennsylvania State University, University Park, Pennsylvania 16802

Electrical conductivities of Al₂O₃/Al composite synthesized by directed oxidation of an aluminum alloy, and sintered Al₂O₃-4% MgO are measured. The high conductivity of the Al₂O₃/Al composite compared to sintered Al₂O₃-4% MgO is shown as proof of the presence of continuous metal channels in the composite. Furthermore, the conductivity data are used to determine the activation energy for the diffusion of the dominant charge carrier in the oxide matrix.

an interconnected network of aluminum metal. Such measurements can establish the nature of the aluminum metal distribution in the composite. Results of such measurements over a temperature range of 450–1323 K are examined in this paper. The data are compared with the measured values of electrical conductivity of a sintered Al₂O₃-4% MgO pellet to seek improved understanding of the distribution of aluminum in the composite.

I. Introduction

THE directed oxidation of molten aluminum alloys by a gaseous oxidant can be used to produce alumina-matrix composites.¹ Additions of elements such as magnesium and silicon to the alloy are often used to accelerate the oxidation.¹ Under appropriate conditions, a rapid reaction of the molten alloy with the oxidant to form α -aluminum oxide occurs, and the reaction product grows outward from the original metal surface. The resulting material is a ceramic/metal composite comprising a three-dimensionally interconnected ceramic reaction product and some metal.² In the case of Al-Mg alloys, most of the Mg in the alloy is found in a layer of MgAl₂O₄ at the surface where the composite growth is initiated.²

Although the understanding of the mechanism of the oxide matrix composite growth is still evolving, it has been suggested that the reaction is sustained by the wicking of liquid metal along interconnected microscopic channels in the reaction product.³ Indeed, the composite growth in some cases can be explained by the wicking hypothesis. However, there are important exceptions. It was shown recently⁴ that the presence of zinc in the alloy improves the growth rate significantly, although zinc does not improve wicking. The results indicate that, in addition to wicking, transport of ions and electrons through the composite layer is important in some cases.

The presence of continuous metal channels is the basis for wicking to occur. If ionic transport in the oxide matrix is important, continuous metal channels can provide a pathway for the transport of electrons and maintain electrical neutrality during composite growth. The presence of narrow channels of alloy in selected microscopic sections in the oxide composite has been presented as "evidence" of the wicking process.² However, the observation of a few alloy channels in an arbitrarily selected microscopic section does not really constitute a rigorous proof that the narrow metal channels extend from the bulk liquid metal at the bottom all the way through the ceramic oxide matrix to the top of the oxide layer.

The electrical conductivity of an oxide matrix composite containing a random dispersion of aluminum metal would be significantly different from that of an oxide matrix containing

II. Experimental Procedure

Cylindrical-shaped pellets of a Al₂O₃/Al composite and sintered Al₂O₃-4% MgO were prepared for electrical conductivity measurements. The Al₂O₃/Al composite was prepared by directed oxidation of a 5056 aluminum alloy for 48 h at 1273 K in air. The Al₂O₃-MgO pellet was prepared by sintering a mixture of fine powders, 110 μ m average particle size, of 96 wt% Al₂O₃ and 4 wt% MgO at 1673 K for 48 h in an argon atmosphere. Sample dimensions of the Al₂O₃/Al and sintered Al₂O₃-4% MgO pellets are presented in Table I.

Figure 1 shows the experimental setup used for measuring the electrical conductivity of the pellets, using the two electrode method. The setup consisted of an electrical conductivity cell, vertical tube furnace, and an electrical conductivity measurement unit (Quad Tech RLC Digibridge Model 1689 M). The conductivity cell consisted of a gas-tight alumina chamber with gas flow, thermocouple, and electrical feedthroughs. The pellet was placed between the platinum foils as shown in Fig. 1. Platinum paint was applied on the flat surfaces of the sample to achieve good contact with the electrodes. Resistance measurements were made as a function of temperature by heating the samples in argon at atmospheric pressure and a gas flow rate of 500 sccm. A Pt-Pt10%Rh thermocouple placed in close proximity to the sample was used to measure the sample temperature. The RLC Digibridge was operated at low test frequency, 12 Hz, to improve the accuracy of the readings. Furthermore, the resistance measurements were made during the time interval when no current was flowing to the furnace, to minimize inductive effects on the measured impedance.

III. Results and Discussion

In order to understand the distribution of aluminum metal in the Al₂O₃/Al composite, electrical conductivities of Al₂O₃/Al and sintered Al₂O₃-4% MgO were compared. The matrix of the Al₂O₃/Al composite typically has a few percent of spinel² and some magnesium dissolved in the alumina.⁵ Thus, the sintered Al₂O₃-4% MgO pellet is considered to be more representative

F. W. Zok—contributing editor

Table I. Dimensions of Samples Used for Conductivity Measurements

Material	Surface area (cm ²)	Thickness (cm)
Al ₂ O ₃ /Al composite	0.7	0.4
Sintered Al ₂ O ₃ -4% MgO	0.95	0.5

Manuscript No. 193784. Received February 28, 1994; approved July 22, 1994.
Supported by the National Science Foundation, Division of Materials Research, under Grant No. DMR-91118075.

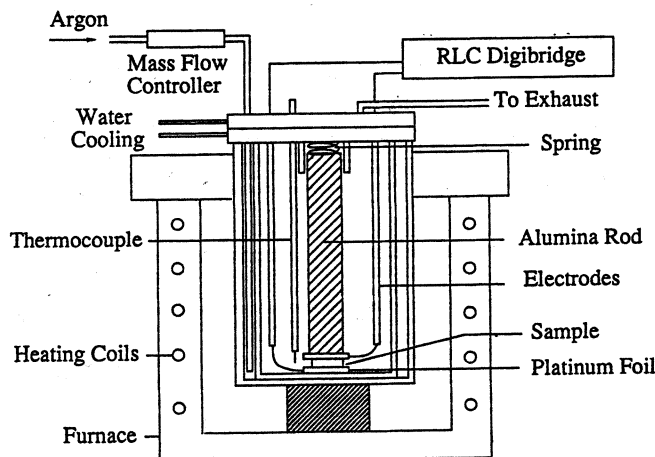


Fig. 1. Schematic diagram of the experimental setup used for electrical conductivity measurements.

of the composite matrix than a pure alumina pellet. The measured conductivities at various temperatures are presented in Fig. 2. The results indicate that the conductivity of the $\text{Al}_2\text{O}_3/\text{Al}$ composite is six to seven orders of magnitude higher than that of sintered $\text{Al}_2\text{O}_3\text{-MgO}$ pellet. The $\text{Al}_2\text{O}_3/\text{Al}$ composite differs from the sintered $\text{Al}_2\text{O}_3\text{-MgO}$ pellet primarily in that the composite has some aluminum metal in it. Thus, the observed higher conductivity of $\text{Al}_2\text{O}_3/\text{Al}$ composite can be attributed to the presence of aluminum, either as a random dispersion, or in the form of interconnected channels, in the alumina matrix.

Assuming the presence of a random dispersion of uniform-sized aluminum spheres, up to 20% by volume, the conductivity of sintered $\text{Al}_2\text{O}_3\text{-4% MgO}$ pellet can be estimated using Maxwell's relation:^{6,7}

$$K_m = \frac{\sigma}{\sigma_m} = \frac{K_d + 2 - 2f(1 - K_d)}{K_d + 2 + f(1 - K_d)} \quad (1)$$

where

$$K_m = \frac{\text{conductivity of the oxide medium with dispersion}}{\text{conductivity of the oxide medium without dispersion}} \quad (2)$$

$$K_d = \frac{\sigma_d}{\sigma_m} = \frac{\text{conductivity of the dispersed phase (aluminum)}}{\text{conductivity of the oxide medium without dispersion}} \quad (3)$$

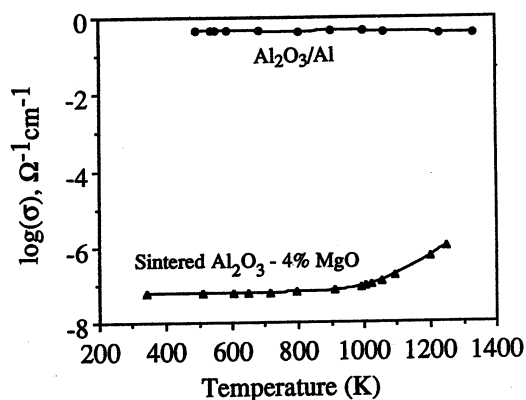


Fig. 2. Electrical conductivity of $\text{Al}_2\text{O}_3/\text{Al}$ composite and sintered $\text{Al}_2\text{O}_3\text{-4% MgO}$ at various temperatures. Measurements were made in argon at 1-atm pressure and a gas flow rate of 500 sccm.

and f is the volume fraction of the dispersed phase, aluminum in this case. Since the conductivity of aluminum⁸ is 12 orders of magnitude greater than the conductivity of sintered $\text{Al}_2\text{O}_3\text{-MgO}$, i.e., $K_d \gg 1$, Eq. (1) reduces to

$$K_m = (1 + 2f)/(1 - f) \quad (4)$$

It has been reported that alumina matrix composites produced by directed metal oxidation of aluminum alloys contain up to 20 vol% aluminum.² Equation (4) predicts that a random dispersion of 20 vol% aluminum in sintered $\text{Al}_2\text{O}_3\text{-MgO}$ would enhance the conductivity by a factor of 1.75. Thus, a random distribution of aluminum in the composite cannot explain the six to seven orders of magnitude higher conductivity of $\text{Al}_2\text{O}_3/\text{Al}$ composite compared to that of sintered $\text{Al}_2\text{O}_3\text{-MgO}$. The result indicates the presence of high-conductivity aluminum as continuous channels extending through the entire thickness of the $\text{Al}_2\text{O}_3/\text{Al}$ composite. These metal channels provide a low-resistance electrical path in an otherwise high-resistance oxide matrix, resulting in the observed high conductivity of the composite.

Since $\text{Al}_2\text{O}_3/\text{Al}$ composite has continuous aluminum channels, the $\text{Al}_2\text{O}_3/\text{Al}$ composite should have high electrical conductivity. It is observed from Fig. 2 that the measured conductivity of the $\text{Al}_2\text{O}_3/\text{Al}$ composite at 1000 K is $4.3 \times 10^{-1} \Omega^{-1}\text{cm}^{-1}$. The conductivity of liquid aluminum at 1000 K is $4.0 \times 10^4 \Omega^{-1}\text{cm}^{-1}$.⁸ Thus, there is a five orders in magnitude difference in the conductivity of $\text{Al}_2\text{O}_3/\text{Al}$ composite and aluminum. The total sample surface area was used in determining the conductivity of the composite, while most of the current was conducted through only the small area of the metal channels. Assuming the metal channels to be straight extending over the entire thickness of the pellet, a fractional channel area of 1.1×10^{-5} is obtained. Since the estimated area fraction is unrealistically low, the assumptions that the channels are straight and all channels extend over the entire thickness of the $\text{Al}_2\text{O}_3/\text{Al}$ composite must be examined closely. In the composites, the metal is present as tortuous channels, and not all channels extend through the entire thickness of the composite. However, the tortuosity of the channels cannot explain the low area fraction. Therefore, the low conductivity of the composite in comparison with aluminum must be attributed to a composite structure where only a small fraction of the metal channels extend through the entire thickness of the composite.

A comparison of the conductivity of the composite and aluminum metal at 500 K yields a fractional channel area of 2.3×10^{-6} , which is about five times lower than that calculated at 1000 K. This decrease in the fractional channel area with decrease in temperature can be explained on the basis of the large difference in the thermal expansion coefficients of aluminum and alumina. The coefficient of linear thermal expansion of solid and liquid aluminum are $30 \times 10^{-6} \text{K}^{-1}$ and $41 \times 10^{-6} \text{K}^{-1}$,⁹ respectively, while that of alumina is $10 \times 10^{-6} \text{K}^{-1}$.¹⁰ Furthermore, aluminum shrinks by 6% on solidification.⁹ On cooling, this volume shrinkage and the difference in the coefficients of thermal expansion of aluminum and alumina can cause (a) reduction in the cross-sectional area of the channels and (b) discontinuities in the metal channels, reducing the number of channels that extend through the entire thickness of the composite. Although the conductivity of aluminum increases with decrease in temperature, the number and cross-sectional area of the channels decrease, producing two opposing effects on the electrical conductivity of the composite. The observed insensitivity of the conductivity vs temperature data, of the $\text{Al}_2\text{O}_3/\text{Al}$ composite, is consistent with these effects.

DeRoy *et al.*⁴ have shown that, in some cases, the rate of oxidation in the growth stage of aluminum oxide-based composites synthesized by directed metal oxidation of Al alloys is influenced by the rate of transport of ions through the oxide matrix. The determination of the activation energy of this process and the nature of the dominant charge carrier in the oxide matrix is therefore of interest. The presence of continuous aluminum channels in the $\text{Al}_2\text{O}_3/\text{Al}$ composites precludes the

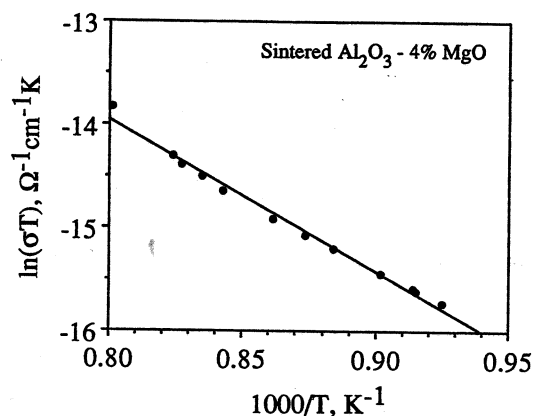


Fig. 3. Arrhenius plot of $\ln(\sigma T)$ vs $1000/T$ for determination of the activation energy for the diffusion of the dominant charge carrier in sintered Al_2O_3 -4% MgO .

determination of the dominant charge carrier in the oxide matrix from the measured electrical conductivity of the composite. Since the matrix in the $\text{Al}_2\text{O}_3/\text{Al}$ composite is similar in chemical composition to the sintered Al_2O_3 -4% MgO pellet, the nature of the charge carrier in the alumina matrix can be examined using the electrical conductivity data for sintered Al_2O_3 -4% MgO presented in Fig. 2. Conductivity data of sintered Al_2O_3 -4% MgO , in the temperature range 1080 to 1250 K, were used to determine the activation energy for the diffusion of the dominant charge carrier. At lower temperatures, because of the very low bulk conductivity of Al_2O_3 -4% MgO , surface and/or gas phase conduction can result in inaccurate bulk conductivities.¹¹ Hence, meaningful activation energy data cannot be derived from the conductivities at temperatures lower than 1000 K. Figure 3 is a plot of $\ln \sigma T$ vs $1000/T$, commonly used to determine the activation energy for the diffusion of the dominant charge carrier.¹² An activation energy of 1.36 eV for the diffusion of the dominant charge carrier in Al_2O_3 -4% MgO is obtained from the slope of the line in Fig. 3. The measured activation energy of 1.36 eV is in fair agreement with a value of 1.6 eV obtained by Yee and Kroger¹³ for a MgO -doped polycrystalline Al_2O_3 sample.

Yee and Kroger¹³ have shown that, in the temperature range of interest and for $p_{\text{O}_2} < 10^{-4}$ atm, the transference number of ions, i.e., the ratio of the ionic conductivity and the total conductivity, is close to unity. Hence, this activation energy would correspond to the activation energy of diffusion of an ionic species. The magnesium in sintered Al_2O_3 -4% MgO would be in saturated solid solution in alumina, and hence extrinsic ionic defects would be expected to dominate. Therefore, the observed activation energy represents the migration energy of the dominant extrinsic defect in sintered Al_2O_3 -4% MgO . Several investigators¹⁴⁻²² have attempted to identify the nature of the dominant extrinsic defect in acceptor (Mg , Fe) dominated Al_2O_3 . However, there is significant controversy as to whether aluminum ion interstitials¹⁵⁻¹⁸ or oxygen ion vacancies¹⁹⁻²² are the dominant extrinsic defects. The activation energy measured in this study could represent migration energy of either aluminum ion interstitials or oxygen ion vacancies.

IV. Conclusions

Electrical conductivities of $\text{Al}_2\text{O}_3/\text{Al}$ composite and Al_2O_3 - MgO pellets were used to understand the distribution of aluminum metal in the $\text{Al}_2\text{O}_3/\text{Al}$ composite and the activation energy for the migration of the dominant charge carrier in the alumina matrix. The conductivity of $\text{Al}_2\text{O}_3/\text{Al}$ composite was found to be six to seven orders of magnitude higher than that of sintered Al_2O_3 -4% MgO . A small fraction of the aluminum channels extend over the entire thickness of the composite. Activation energy of migration of the dominant charge carrier in the sintered Al_2O_3 -4% MgO was found to be 1.36 eV.

Acknowledgments: The authors wish to thank Drs. R. Roy and E. Brevail for their interest in the work and Mr. R. Biswas for his help in preparing the samples for electrical conductivity measurements.

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