Electrical conductivities of $\text{Al}_2\text{O}_3$/Al composite synthesized by directed oxidation of an aluminum alloy, and sintered $\text{Al}_2\text{O}_3$–4% MgO are measured. The high conductivity of the $\text{Al}_2\text{O}_3$/Al composite compared to sintered $\text{Al}_2\text{O}_3$–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.

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 $\alpha$-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 MgAl$_2$O$_4$ 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.\(^2\) Indeed, the composite growth in some cases can be explained by the wicking hypothesis. However, there are important exceptions. It was shown recently\(^4\) 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.\(^6\) 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 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 $\text{Al}_2\text{O}_3$–4% MgO pellet to seek improved understanding of the distribution of aluminum in the composite.

II. Experimental Procedure

Cylindrical-shaped pellets of a $\text{Al}_2\text{O}_3$/Al composite and sintered $\text{Al}_2\text{O}_3$–4% MgO were prepared for electrical conductivity measurements. The $\text{Al}_2\text{O}_3$/Al composite was prepared by directed oxidation of a 5056 aluminum alloy for 48 h at 1273 K in air. The $\text{Al}_2\text{O}_3$–MgO pellet was prepared by sintering a mixture of fine powders, 110 $\mu$m average particle size, of 96 wt% $\text{Al}_2\text{O}_3$ and 4 wt% MgO at 1673 K for 48 h in an argon atmosphere. Sample dimensions of the $\text{Al}_2\text{O}_3$/Al and sintered $\text{Al}_2\text{O}_3$–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 $\text{Al}_2\text{O}_3$/Al composite, electrical conductivities of $\text{Al}_2\text{O}_3$/Al and sintered $\text{Al}_2\text{O}_3$–4% MgO were compared. The matrix of the $\text{Al}_2\text{O}_3$/Al composite typically has a few percent of spinel and some magnesium dissolved in the alumina.\(^7\) Thus, the sintered $\text{Al}_2\text{O}_3$–4% MgO pellet is considered to be more representative.

| Table I. Dimensions of Samples Used for Conductivity Measurements |
|-------------------------|--------|--------|
| Material                | Surface area (cm$^2$) | Thickness (cm) |
| $\text{Al}_2\text{O}_3$/Al composite | 0.7    | 0.4    |
| Sintered $\text{Al}_2\text{O}_3$–4% MgO | 0.95   | 0.5    |
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 Al₂O₃/Al composite is six to seven orders of magnitude higher than that of sintered Al₂O₃–MgO pellet. The Al₂O₃/Al composite differs from the sintered Al₂O₃–MgO pellet primarily in that the composite has some aluminum metal in it. Thus, the observed higher conductivity of Al₂O₃/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 Al₂O₃–4% MgO pellet can be estimated using Maxwell’s relation: ⁶,⁷

\[
K_m = \frac{\sigma_m}{\sigma_a} = \frac{K_a + 2 - 2f(1 - K_a)}{K_a + 2 + f(1 - K_a)}
\]

where

\[
K_m = \text{conductivity of the oxide medium with dispersion}
\]
\[
K_a = \text{conductivity of the oxide medium without dispersion}
\]
\[
f = \text{volume fraction of the dispersed phase, aluminum in this case. Since the conductivity of aluminum is 12 orders of magnitude greater than the conductivity of sintered Al₂O₃–MgO, i.e., } K_a >> 1, \text{ Eq. (1) reduces to}
\]

\[
K_m = \frac{(1 + 2f)/(1 - f)}
\]

It has been reported that alumina matrix composites produced by directed metal oxidation of aluminum alloys contain up to 20 vol% aluminum. Equations (4) predicts that a random dispersion of 20 vol% aluminum in sintered Al₂O₃–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 Al₂O₃/Al composite compared to that of sintered Al₂O₃–MgO. The result indicates the presence of high-conductivity aluminum as continuous channels extending through the entire thickness of the Al₂O₃/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 Al₂O₃/Al composite has continuous aluminum channels, the Al₂O₃/Al composite should have high electrical conductivity. It is observed from Fig. 2 that the measured conductivity of the Al₂O₃/Al composite at 1000 K is 4.3 × 10⁻¹ Ω⁻¹ cm⁻¹. The conductivity of liquid aluminum at 1000 K is 4.0 × 10⁻¹ Ω⁻¹ cm⁻¹. Thus, there is a five orders of magnitude difference in the conductivity of Al₂O₃/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 × 10⁻³ 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 Al₂O₃/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 × 10⁻⁶ K⁻¹ and 41 × 10⁻⁶ K⁻¹, respectively, while that of alumina is 10 × 10⁻⁶ K⁻¹. Furthermore, aluminum shrinks by 6% on solidification. 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 Al₂O₃/Al composite, is consistent with these effects.

DebRoy et al. 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 Al₂O₃/Al composites precludes the
IV. Conclusions

Electrical conductivities of Al$_2$O$_3$/Al composite and Al$_2$O$_3$-MgO pellets were used to understand the distribution of aluminum metal in the Al$_2$O$_3$/Al composite and the activation energy for the migration of the dominant charge carrier in the alumina matrix. The conductivity of Al$_2$O$_3$/Al composite was found to be six to seven orders of magnitude higher than that of sintered Al$_2$O$_3$-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$_2$O$_3$-4% MgO was found to be 1.36 eV.

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References