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Macroscopic Modelling of the Reaction Bonding of Aluminum Oxide

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Abstract

The reaction-bonded aluminum oxide (RBAO) process is a novel method to produce monolithic alumina-based ceramics. In order to gain some insight into the process, a macroscopic model, which considers the interaction of oxygen diffusion and reaction within a porous body, has been developed. The model allows one to predict, to a first approximation, the effects of parameters, such as heat-treatment cycle, atmosphere, and scale — an important consideration for industrial applications. Thermogravimetric (TG) curves predicted by the model show reasonable agreement with experimental data and indicate that the process is controlled by a combination of reaction and diffusion. © 1997 Elsevier Science Limited.

1 Introduction

The reaction-bonded aluminum oxide (RBAO) process utilizes the oxidation reaction of attrition-milled Al/Al_2O_3 powder compacts, heat-treated in air, to make monolithic alumina-based ceramics.[1-5] The process offers significant advantages over conventional ceramic processing, such as low shrinkage and hence, near-net-shape forming, and machinability of green bodies. Furthermore, the resultant microstructure can be highly dense (>99%) and fine-grained (<1 μm), with fired strengths much higher than those of conventionally processed ceramics of the same composition.[6]

Although there has been a significant amount of work done to identify the mechanisms of oxidation for pure aluminum,[7-9] the mechanisms by which the reaction-bonding process proceed are still unclear. A tentative micro-mechanism has been proposed for the reaction-bonding process whereby the oxidation of aluminum proceeds as both a solid/gas and liquid/gas reaction.[2] However, much of the work has been largely qualitative, with limited understanding of the relationships between the processing, structure, and properties of these materials. In the absence of a quantitative understanding of the microscopic mechanisms involved, it is proposed to develop a macroscopic model of the process.

The current work presents a macroscopic model of the RBAO process along with preliminary results from a parametric study of the model. It is expected that the model will help in gaining a better understanding of the reaction-bonding process and allow one to predict the effect of various operating parameters, such as heat-treatment cycle and atmosphere, on the reaction behavior of these materials. The model will also be important for subsequent process optimization and scale-up — an important consideration for industrial applications.

2 Macroscopic Modelling of the Process

The RBAO process has been shown to be a two-stage process with an initial oxidation and volume expansion stage followed by sintering and shrinkage. A clear macroscopic dimensional change occurs during the oxidation stage of the RBAO process. This behavior has been attributed to the presence of particle-separating forces during oxidation of the body, allowing the reacting body to maintain an interconnecting porous network.[10] This behavior is significantly different from the almost zero macroscopic dimensional change associated with the formation of reaction-bonded silicon nitride (RBSN), where the reaction leads to the closure of the porosity. The fact that the RBAO process maintains a porous network allows one to readily describe the process on a macroscopic scale.

A macroscopic model of the pure RBAO process, where $4\ Al + 3\ O_2 \rightarrow 2\ Al_2O_3$, is the only reaction, has been developed. The model considers the interaction of diffusion through a porous body and reaction, while ignoring the microscopic details of the body. The body is assumed to have a uniform initial composition. Assuming a second-order reaction, the reaction rate, r, can be written as:

$$r = kC_{O_2}C_{Al} \tag{1}$$

where C_{O_2} and C_{Al} are the oxygen and aluminum concentrations, respectively. The reaction rate constant, k, is expressed according to the Arrhenius equation as:

$$k = A_o \exp\left(-\frac{E_a}{RT}\right) \tag{2}$$

where A_o is the frequency factor, E_a is the activation energy, R is the gas constant, and T is the absolute temperature. Although the true reaction mechanism is expected to be far more complex,[2,7-9] this approximation will allow us to gain insight into the effects of various parameters.

Only material balances are considered in this analysis. Thus, the sample is assumed to be isothermal with its temperature being that of the furnace. Future work will allow for deviations of the sample temperature from that of the furnace by considering the energy balance. A flat slab of thickness 2 L is assumed. The material balance on the reacting gaseous component (continuity equation for O_2) contains a term arising from the vapor diffusion through the pore system and a reaction term:

$$D_{e,O_2}\frac{\partial^2 C_{O_2}}{\partial z^2} = 3r \tag{3}$$

where D_{e,O_2} is the effective diffusivity of oxygen, and z is the position in the reacting body. Although this is a transient process, the accumulation of the reacting gaseous component has been neglected. The continuity equation for the reacting metal, Al, is:

$$\frac{\partial C_{Al}}{\partial t} = -4r \tag{4}$$

where t is the time. The effective diffusivity, D_{e,O_2}, is given as follows:

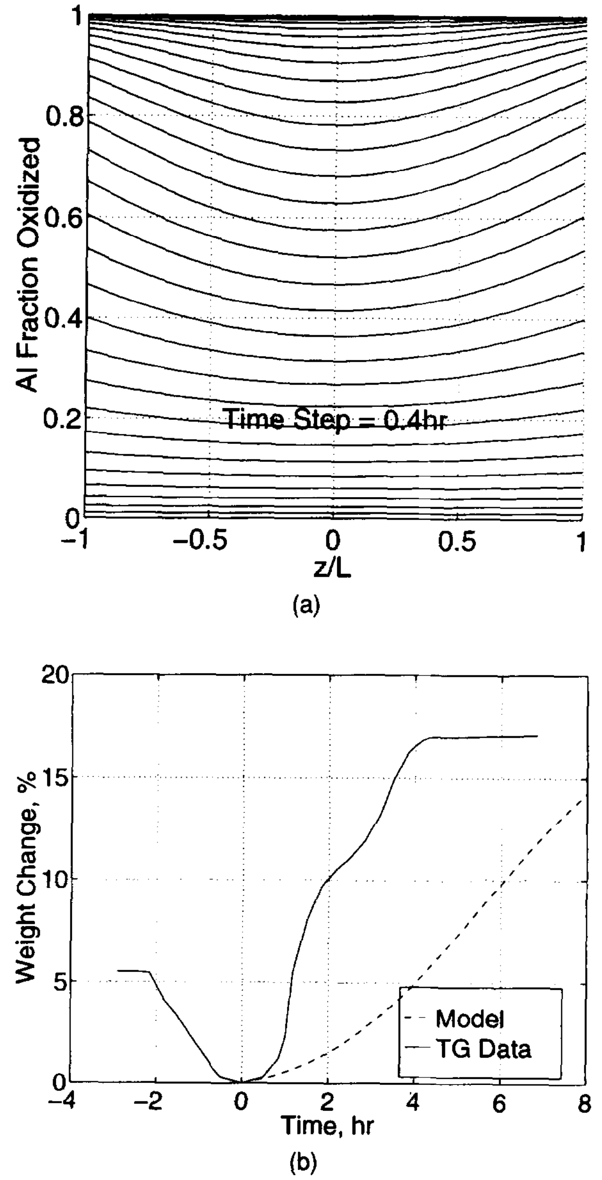
$$D_{e,O_2} = \frac{D_{O_2}\varepsilon_s}{\tau} \tag{5}$$

where ε_s is the internal void fraction, τ is the tortuosity, which includes both the effect of altered diffusion path length as well as changing cross-sectional areas in constrictions, and D_{O_2} is the Knudsen diffusivity, which is a function of the temperature and pore radius (r_p).

The solution to these equations using standard initial, $C_{Al}(z,0) = C_{Al,o}$, and boundary, $C_{O_2}(\pm L,t) = C_{O_2,s}$ $(= p_{O_2,s}/RT)$ and $(\partial C_{O_2}/\partial z)\,(0,t) = 0$, conditions gives the concentrations of the gas and metal as a function of time and position in the body. $C_{Al,o}$ is the initial aluminum concentration in the body, $p_{O_2,s}$ is the partial pressure of oxygen at the surface of the body, and $C_{O_2,s}$ is the oxygen concentration at the surface of the body. One can then calculate the conversion profile of Al as a function of time and position in the body and thermogravimetric (TG) curves, which indicate the overall weight gain of the sample as a function of time.

3 Results

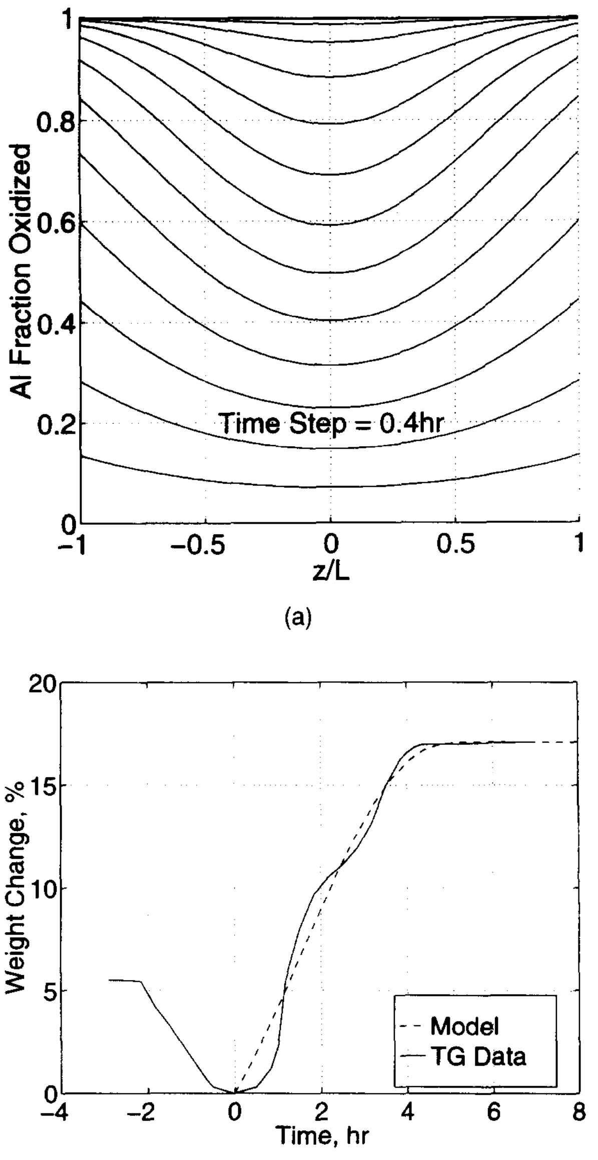
Figures 1–3 show the effect of the frequency factor, A_0, on the aluminum conversion profile and the overall weight gain of the sample. The values for the frequency factor have been arbitrarily assumed in order to illustrate reaction and



(a)

(b)

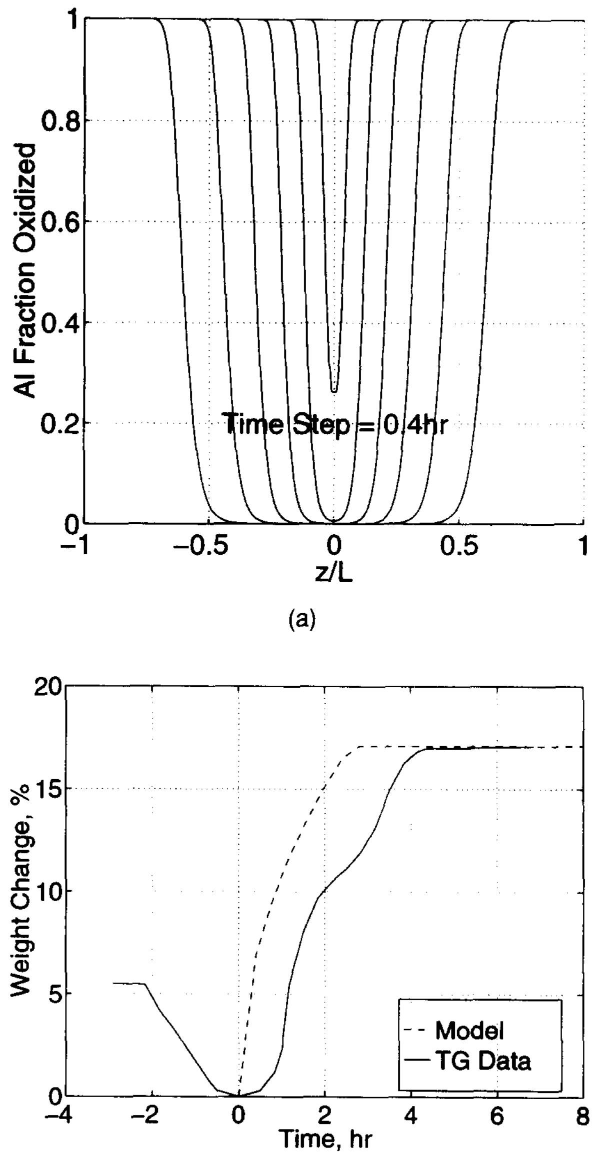
Fig. 1. RBAO model at a frequency factor, A_0, of 25. Reaction-controlled case. (a) Progression of the aluminum conversion profile with time. (b) Percentage weight change of the body with time.



(a)

(b)

Fig. 2. RBAO model at a frequency factor, A_0, of 330. (a) Progression of the aluminum conversion profile with time. (b) Percentage weight change of the body with time.



(a)

(b)

Fig. 3. RBAO model at a frequency factor, A_0, of 150,000. Diffusion controlled case. (a) Progression of the aluminum conversion profile with time. (b) Percentage weight change of the body with time.

diffusion control of the process. The following parameters and corresponding values were used in the computations: $L = 0{\cdot}003$ m, $C_{Al,o} = 17{\cdot}98$ kmol m^{-3}, $p_{O_2,s} = 21278$ Pa, $E_a = 52$ kJmol^{-1}, $r_p = 30$ nm, $\varepsilon_s = 0{\cdot}4$, $\tau = 3{\cdot}0$. The values of the parameters describing the body geometry, L, the body composition, $C_{Al,o}$, and the atmosphere, $p_{O_2,s}$, correspond to the conditions under which the experimental TG data was taken.[2] The differences in geometry between the sample and the model have been taken into account. The pore system of RBAO compacts has been characterized in the literature.[2,5] It has been shown that the median pore radius and overall porosity increase during the oxidation stage of the process. This supports the idea that the body is able to maintain an interconnecting porous network due to the presence of particle-separating forces. The tortuosity, τ, which describes the tortuous nature of the pore system, including the effect of altered diffusion path length as well as changing cross-sectional areas in constrictions, usually ranges between 2 and 6, averaging about 3.[11] The average value, 3, is assumed for the tortuosity. The values of the other parameters describing the porous network, r_p and ε_s, are approximate values from the literature.[2,5] The values of the frequency factor used in Figs 1, 2, and 3 are 25, 330, and 150,000, respectively. Part (a) of each figure shows the progression of the Al conversion profile with time as a function of the dimensionless coordinate, z/L, of the body. The Al conversion profile corresponds directly to the composition gradient that develops across the sample during oxidation. The Al conversion profile, and thus the composition gradient, depends critically on the rate of reaction relative to the rate of gas phase diffusion. Part (b) of each figure shows the percentage weight change of the body as a function of time. Since the model is unable to describe the evaporation of fugitive species in the TG data and we are only concerned with the reaction, the process is modelled from the onset of the oxidation reaction, which corresponds to a temperature of ~380°C. The experimental TG data presented in part (b) of the figures are from the literature.[2] The heating rate for the region under consideration is $1°\text{C min}^{-1}$.

It can be seen from Fig. 1(a) that at a low value of the frequency factor (25) the aluminum is uniformly consumed throughout the body. This indicates that the rate of reaction is slow relative to the rate of gas phase diffusion. That is, the process is reaction controlled. Figure 1(b) shows that the percentage weight change predicted by the model proceeds at a much slower rate than the experimental data.

Figure 2(a) shows that at a moderate value of the frequency factor (330) a more pronounced Al conversion profile develops across the body. The process in this case is controlled by a combination of reaction and diffusion. Figure 2(b) shows that the percentage weight change predicted by the model is in reasonable agreement with the experimental data.

Figure 3(a) shows that at a high value of the frequency factor (150,000) the reaction occurs in an external layer leaving an internal unreacted core that shrinks as the reaction progresses. In general, a steep composition gradient, as seen in Fig. 3(a), indicates a high rate of reaction relative to the rate of gas phase diffusion. A high reaction rate promotes an instantaneous reaction of the gas as it penetrates into the body, thus producing a steep gradient between reacted and unreacted regions. This type of behavior has been observed at Lehigh as well as in the literature.[1] The percentage weight change of the body as a function of time for a frequency factor of 150,000 is shown in Fig. 3(b). The reaction is seen to proceed at a much faster rate than the experimental data.

4 Summary

A macroscopic model has been developed which shows reasonable agreement with the experimental data in the literature. The model indicates that the process is controlled by a combination of reaction and diffusion. Although the model is preliminary in nature, it is evident that the RBAO process may be described, to a first approximation, by a simple macroscopic model, shedding light on the controlling mechanisms of the process.

In order to further develop the model, various input parameters, such as the effective oxygen diffusivity and reaction constants, need to be experimentally determined. The model will also be extended to allow for deviations of the sample temperature from that of the furnace by considering the energy balance. The model will then be used to predict the effect of various process parameters, such as sample size, porosity, pore size (compaction pressure), oxygen partial pressure, and heating cycle, on the reaction behavior of the system.

Acknowledgement

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Appendix A

A1 Derivation of the continuity equation for oxygen

Considering a thin section of the slab, width Δz, perpendicular to the direction of oxygen flux through the body, one can write the material balance for oxygen as follows:

$$\text{In} - \text{Out} + \text{Generation} - \text{Consumption} = \text{Accumulation}$$

$$A_t N_{O_2}(z) - A_t N_{O_2}(z + \Delta z) + 0 - A_t \Delta z(-r_{O_2}) = A_t \Delta z \varepsilon_s \frac{\partial C_{O_2}}{\partial t} \quad \text{(A1)}$$

where N_{O_2} is the flux of oxygen, A_t is the transfer area of the oxygen flux, r_{O_2} is the rate of oxygen consumption, ε_s is the internal void fraction, C_{O_2} is the oxygen concentration, and t is the time. Assuming quasi-steady state, the accumulation term can be taken to be zero. The equation then reduces to:

$$N_{O_2}(z) - N_{O_2}(z + \Delta z) = -\Delta z r_{O_2} \quad \text{(A2)}$$

Rearranging and taking the limit as $\Delta z \to 0$, one obtains:

$$\frac{\partial N_{O_2}}{\partial z} = r_{O_2} \quad \text{(A3)}$$

The flux of oxygen through the pore system is given by Fick's Law:

$$N_{O_2} = -D_{e,O_2} \frac{\partial C_{O_2}}{\partial z} \quad \text{(A4)}$$

where D_{e,O_2}, the effective diffusivity of oxygen, is used to account for complex pore structures.

Inserting Fick's Law, eqn (A4), into eqn (A3) and using the stoichiometry of the reaction to relate the rate of oxygen consumption, r_{O_2}, to the overall reaction rate, r, one obtains the continuity equation for oxygen:

$$D_{e,O_2} \frac{\partial^2 C_{O_2}}{\partial z^2} = 3r \quad \text{(A5)}$$

A2 Derivation of the continuity equation for aluminum

Considering a thin section of the slab, width Δz, perpendicular to the direction of oxygen flux through the body, one can write the material balance for aluminum as follows:

$$\text{In} - \text{Out} + \text{Generation} - \text{Consumption} = \text{Accumulation}$$

$$0 - 0 + 0 - A_t \Delta z r_{Al} = -A_t \Delta z \frac{\partial C_{Al}}{\partial t} \quad \text{(A6)}$$

Simplifying and using the stoichiometry of the reaction to relate the rate of aluminum consumption, r_{Al}, to the overall reaction rate, r, one obtains the continuity equation for aluminum:

$$\frac{\partial C_{Al}}{\partial t} = -4r \quad \text{(A7)}$$