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EXPANDING SPHERICAL SHELL KINETIC MODEL FOR DIFFUSION-CONTROLLED SOLID-STATE REACTIONS

W. RICHARD OTT AND BARRY K. SPERONELLO*
Department of Ceramics, Rutgers University, New Brunswick, New Jersey (U.S.A.)
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ABSTRACT

A reaction kinetic model has been derived for a solid-state diffusion-controlled reaction in a system of spherical particles of A isolated in a matrix of B. This model is analogous to the Ginstling–Brounsthein model except that the diffusion of A is the rate-controlling step. The model, therefore, resulting in an expanding spherical shell of product AB, is

$$1 + \frac{2x}{3} - (1 + x)^{2/3} = Kt$$

where t = time, x = fraction reacted, K = reaction rate constant.

INTRODUCTION

Traditional solid-state reaction kinetic studies have examined reactions with one phase (A) completely surrounded by particles of the second phase (B). Phase B then diffuses into the spheres of A giving the traditional contracting spherical shell models described by Hulbert[1] in his review. This paper develops a model to describe an expanding spherical shell of reaction product. Particles of A are completely surrounded by the B material. The A material diffuses out to form the reaction product layer AB. When the reaction is completed a hole remains the size of the original A particle (R_1).

This model is of particular interest in the area of ceramics because of the extensive use of silica and alumina. Small additions of alkali or alkaline earth materials are isolated in the matrix and diffuse out into the silica or alumina.

THE MODEL

The derivation of solid-state reaction kinetic models requires a number of assumptions. These include: (1) an additive reaction, (2) undirectional bulk diffusion,

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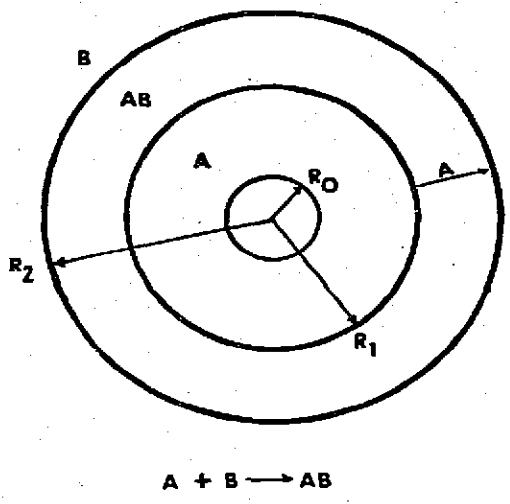
* Present address: Engelhard Minerals and Chemicals Co., Menlo Park, NJ, U.S.A.



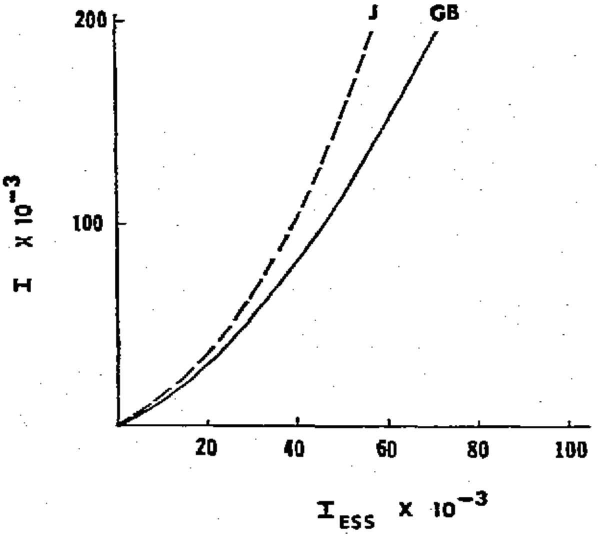


Fig. 1. The model geometry, where R_1 = the original radius of A, R_0 = the instantaneous radius of the void (assumed spherical at the center) at time t, R_2 = the instantaneous outer radius of the AB product layer.

Fig. 2. A comparison of the expanding spherical shell model with the Jander and Ginstling–Brounsthein models.

(3) uniform particle size of A, (4) the product phase is not miscible with the reactant phase, (5) the ratio of the volume of the product layer to the volume of material reacted is unity, (6) the activity of the reactants remains constant on both sides of the reaction interface, and (7) the diffusion coefficient of the species being transported is not a function of time. These are discussed in greater detail by Hulbert[1]. Additionally, it is assumed that a continuous product layer is formed about the particles.

The A material diffuses out through the AB layer reacting with the B material at the B–AB interface. As a result a void is created in the A cavity (Fig. 1).

The quantity of A present at time t is

$$Q_A = \frac{4}{3}\pi R_1^3 - \frac{4}{3}\pi R_0^3 \tag{1}$$

Barrer's[2] equation for the rate of change of Q_A is

$$\frac{dQ_A}{dt} = \frac{-4\pi k R_2 R_1}{(R_2 - R_1)} \tag{2}$$

where k is a constant.

This equation assumes the concentration gradient is fixed by the activity of the diffusing species at each interface and the thickness of the diffusion layer. The radii of R_0, R_1 and R_2 can be related by the equation

$$R_2^3 = R_0^3 + R_1^3 \tag{3}$$

Allowing x to equal the fraction of A reacted at time t

$$\frac{4}{3}\pi R_0^3 = x\left(\frac{4}{3}\pi R_1^3\right) \tag{4}$$

or

$$R_0 = R_1(x)^{1/3} \tag{5}$$

Differentiating eqn. (1) with respect to time and setting it equal to eqn. (2) gives

$$-4\pi k_1 R_0^2 \frac{\mathrm{d}R_0}{\mathrm{d}t} = \frac{-4\pi k R_2 R_1}{(R_2 - R_1)} \tag{6}$$

Substituting eqn. (3) and integrating gives

$$\frac{R_0^3}{3R_1} - \frac{1}{2}(R_0^3 + R_1^3)^{2/3} = kt + C \tag{7}$$

Substituting eqn. (5) and evaluating the integration constant gives the equation for the expanding spherical shell model

$$1 + \frac{2x}{3} - (1 + x)^{2/3} = Kt \tag{8}$$

where K is the reaction rate constant and is equal to $(kD\Delta C)/R_1^2$.

The similarity to the Ginstling–Brounsthein[3] model is obvious. To determine if the models were significantly different the two functions of x are plotted against one another. The deviation from linearity for both the Jander[4] and Ginstling–Brounsthein models is obvious in Fig. 2, indicating the uniqueness of the expanding spherical shell model.

EXPERIMENTAL DATA

Large (−40, +60 mesh) particles of potassium carbonate were dispersed in a matrix of fine silica (−200, +325 mesh). Eight times the required stoichiometric quantity of silica was found to isolate the particles of K_2CO_3 and no surface diffusion was apparent. The reaction

$$K_2CO_3 + SiO_2 \rightarrow K_2O \cdot SiO_2 + CO_2\uparrow$$

was monitored using thermal analysis. The procedure has been previously described[5] and the reaction is known to be diffusion controlled[6].

Figure 3 shows that from 675 to 750 °C a reasonably linear relation exists for the data. This indicates the applicability of the model. The slope is the reaction rate constant.

The K_2CO_3 particle size was varied to further test the model. It was found that while the rate constant varied with the square of the carbonate particle radius the data did not pass through the origin. Microstructural examination indicated that the

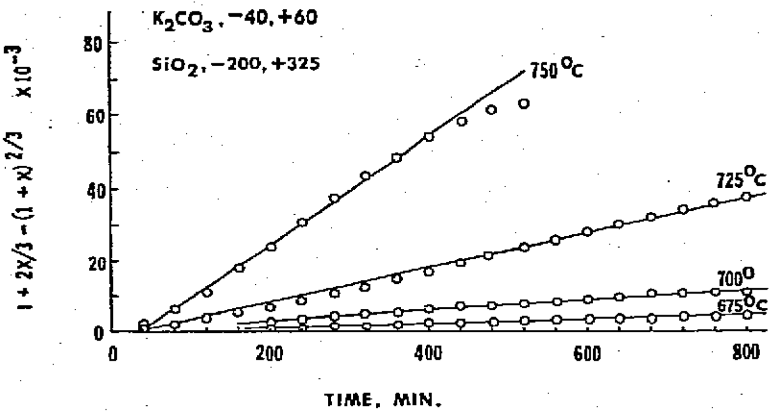


Fig. 3. Expanding spherical shell model applied to the potassium carbonate–silica reaction data.

carbonate particles densified during the reaction cycle and vapor-phase transport provided the carbonate to the potassium-silicate reaction layer. However, since this was a polycrystalline matrix some collapse into the void space occurred; destroying the linear relationship through the origin between the rate constant and the inverse square of the potassium carbonate particle size.

Similar experiments using the reaction between ZnO and Al_2O_3 resulted in a better fit with the expanding spherical shell boundary conditions. Branson[7] concluded that this reaction is controlled by the diffusion of zinc ions or atoms through the $ZnAl_2O_4$ product layer. Kellogg[8] reported that the gaseous species in equilibrium with ZnO are zinc vapor and oxygen, and that the vapor pressure of zinc in air at 1050 to 1150°C would be significant (10^{-13}–10^{-6} atm).

Pellets were pressed from a powder of coarse (−100, +200 mesh) ZnO dispersed in a 10-fold excess of fine (−325 mesh) Al_2O_3. The pellets were reacted isothermally at either 1040 or 1150°C by inserting them into the hot zone of a horizontal tube furnace and removing two every 30 min. The reaction was carried to completion for four pellets. Scanning electron photomicrographs were taken of polished sections through each pellet. The average inner and outer radii of the spherical $ZnAl_2O_3$ product shell at each pair of time–temperature conditions were calculated from the diameters of the circular section of randomly dispersed spheres cut by the polishing plane. The formula for determining the size of uniform spheres cut by random plane surfaces was used

$$1/R = \frac{4}{\pi n} [\Sigma_1^n (1/\mathrm{d}n)]$$

where R is the respective inner or outer radius, n is the number of spherical shells measured at each set of conditions, and dn is the diameter of the respective inner or outer circular cross-section measured on the photomicrograph. The fraction reacted, x, at any time was calculated from the formula

$$x_t = \frac{V_t}{V_f} = \frac{R_t^3 - R_1^3}{R_f^3 - R_1^3}$$

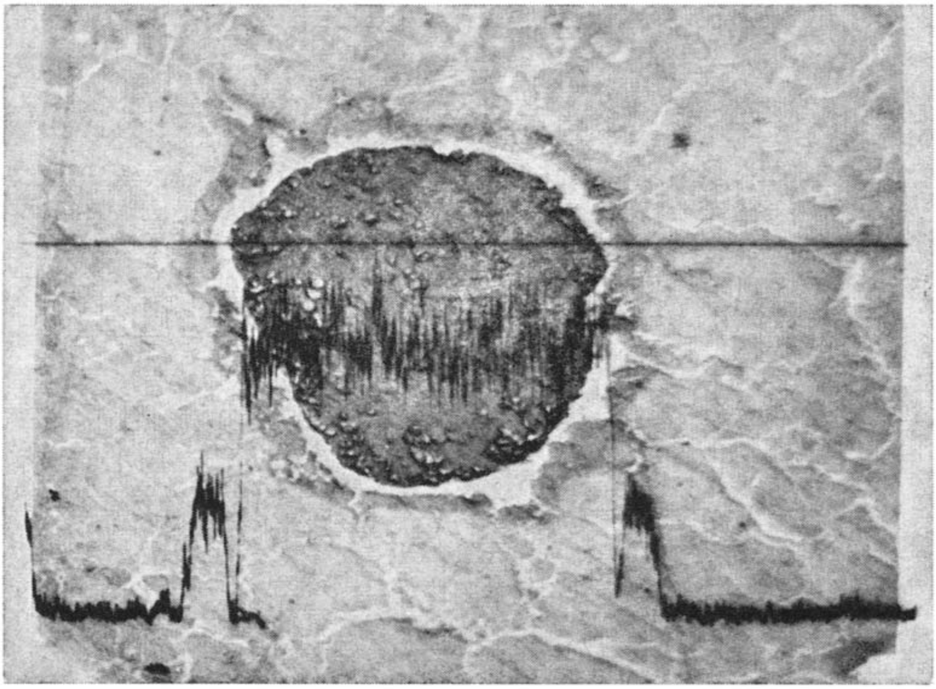


Fig. 4. Scanning electron microscopy and X-ray microanalysis data for ZnO diffusing into an alumina matrix.

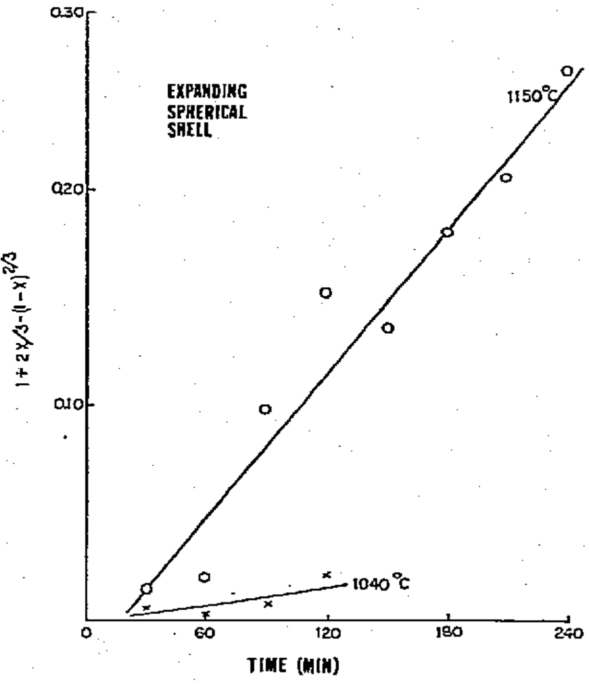


Fig. 5. Expanding spherical shell model applied to the zinc oxide–aluminum oxide reaction data.

where V_t is the average volume of $ZnAl_2O_4$ in a shell at time t, V_f is the average volume of $ZnAl_2O_3$ in a shell when all ZnO is consumed, R_1 is the average inner radius of the $ZnAl_2O_3$ shells, R_t is the average outer radius of a shell at time t, and R_f is the average outer-radius of the shells when all ZnO is consumed.

Fig. 4 is a scanning electron photomicrograph with qualitative X-ray fluorescence data for Zn concentration superimposed. It clearly shows the uniform growth of a $ZnAl_2O_3$ product layer despite the distance between the ZnO and $ZnAl_2O_3$ surfaces. Vapor transport once again supplied the reactant phase to the product layer.

Figure 5 shows that the expanding spherical shell model yields a straight line for the fraction reacted data in the $ZnO–Al_2O_3$ system at 1040 and 1150°C.

CONCLUSION

An expanding spherical shell model has been derived for diffusion controlled reactions. This model,

$$1 + \frac{2x}{3} - (1 + x)^{2/3} = Kt$$

was tested and found to be valid for the reactions between potassium carbonate and silica and zinc oxide and aluminum oxide.

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