

### 2-2.1.2 Chemical Reaction between Solids

The simplest system involves the reaction between two solid phases, A and B, to produce a solid solution C, A and B are commonly elements for metallic systems, while for ceramics they are commonly crystalline compounds. After the initiation of the reaction, A and B are separated by the solid reaction product C (Fig. 2. 3). Further reaction involves the transport of atoms, ions, or molecules by several possible mechanisms through the phase boundaries and the reaction product. Reactions between mixed powders are technologically important for powder synthesis. However, the study of reaction mechanisms is greatly facilitated by the use of single crystals because of the simplified geometry and boundary conditions.

The spinel formation reaction  $AO + B_2O_3 = AB_2O_4$  is one of the most widely studied reactions. Figure 2. 4 shows a few of the possible reaction mechanisms. Included are: (1) mechanisms (Fig. 2.4a and b) in which  $O_2$  molecules are transported through the gaseous phase and electro neutrality is maintained by electron transport through the product layer, (2) mechanism (Fig. 2.4c) involving counter diffusion of the cations with the oxygen ions remaining essentially stationary, and (3) mechanisms (Fig. 2.4d and e) in which  $O^{2-}$  ions diffuse through the product layer.

In practice, the diffusion coefficients of the ions differ widely. For example, in spinels, diffusion of the large  $O^{2-}$  ions is rather slow when compared to cationic diffusion so that the mechanisms in Fig. 2.14d and e can be eliminated. Furthermore, if ideal contact occurs at the phase boundaries so that transport of  $O_2$  molecules is slow, then the mechanisms in Fig. 14a and b are unimportant. Under these conditions, the most likely mechanism is the counter diffusion of cations (mechanism Fig. 2.4c), where the flux of the cations is coupled to maintain electro neutrality. When the rate of product formation is controlled by diffusion through the product layer, the product thickness is observed to follow a parabolic growth law:

$$x^2 = Kt \quad (2.11)$$

Where  $K$  is a rate constant that obeys the Arrhenius relation.

Several investigations have reported a parabolic growth rate for the reaction layer, which is usually taken to mean that the reaction is diffusion controlled. The reaction between ZnO and Fe<sub>2</sub>O<sub>3</sub> to form ZnFe<sub>2</sub>O<sub>4</sub> is reported to occur by the counter diffusion mechanism in which the cations migrate in opposite directions and the oxygen ions remain essentially stationary. The reaction is reported to occur by a solid state mechanism in which the diffusion of zinc ions through the product layer controls the rate. However, as described below for reactions between powders, the reaction kinetics can also be described by a gas–solid reaction between ZnO vapor and Al<sub>2</sub>O<sub>3</sub>.

For powder reactions (Fig. 2.5), a complete description of the reaction kinetics must take into account several parameters, thereby making the analysis very complicated. Simplified assumptions are commonly made in the derivation of kinetic equations. For isothermal reaction conditions, a frequently used equation has been derived by Jander. In the derivation, it is assumed that equalized spheres of reactant A are embedded in a quasi-continuous medium of reactant B and that the reaction product forms coherently and uniformly on the A particles. The volume of unreacted material at time  $t$  is

$$V = \frac{4}{3}\pi(r-y)^3 \quad (2.12)$$

Where  $r$  is the initial radius of the spherical particles of reactant A and  $y$  is the thickness of the reaction layer. The volume of unreacted material is also given by

$$V = \frac{4}{3}\pi r^3(1-\alpha) \quad (2.13)$$

Where  $\alpha$  is the fraction of the volume that has already reacted. Combining Eqs. (2.12) and (2.13),

$$y = r[1-(1-\alpha)]^{1/3} \quad (2.14)$$

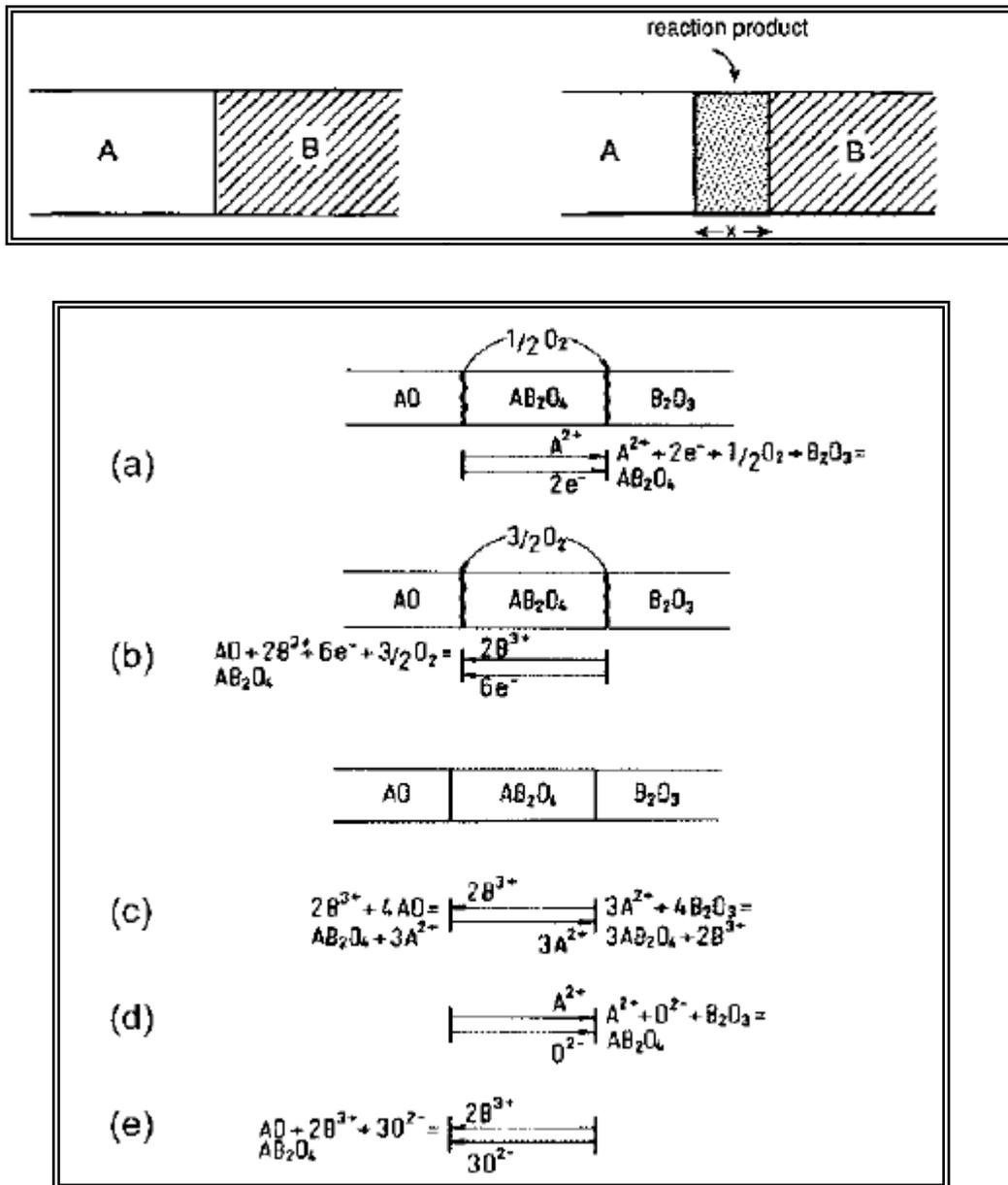


FIGURE 2.4 Reaction mechanisms and corresponding net phase boundary reactions for the spinel formation reaction  $\text{AO} + \text{B}_2\text{O}_3 = \text{AB}_2\text{O}_4$ .

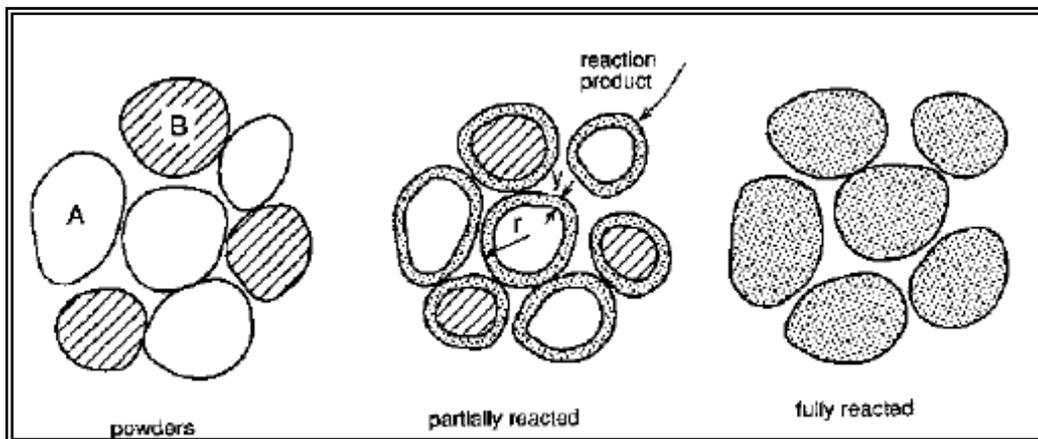


FIGURE 2.5 Schematic of solid-state reaction in mixed powders.

Assuming that  $y$  grows according to the parabolic relationship given by Eq. (2.11), then the reaction rate is

$$\left[1 - (1 - \alpha)^{1/3}\right]^2 = \frac{Kt}{r^2} \quad (2.15)$$

Equation (2.15), referred to as the *Jander equation*, suffers from two oversimplifications that limit its applicability and the range over which it adequately predicts reaction rates. First, the parabolic growth law assumed for the thickness of the reaction layer is valid for one-dimension reaction across a planar boundary and not for a system with spherical geometry. At best, it is expected to be valid only for the initial stages of the powder reaction when  $y \ll r$ . Second, any change in molar volume between the reactant and the product is neglected. Derived the following equation:

$$\left[1 + (Z - 1)\alpha\right]^{2/3} + (Z - 1)(1 - \alpha)^{2/3} = Z + (1 - Z)\frac{Kt}{r^2} \quad (2.16)$$

Where  $Z$  is the volume of the reaction product formed from unit volume of the reactant A. Equation (2.16), referred to as the *Carter equation*. For a solid-state diffusion mechanism, the growth of the reaction product in powder systems occurs at the contact points and for nearly equal-sized spheres; the number of contact points is small. Nevertheless, for many systems, the Jander equation and the Carter equation give a good description of the reaction kinetics for at least the initial stages of the reaction. It appears that rapid surface diffusion provides a uniform supply of one of the reactants over the other. Alternatively, if the vapor pressure of one of the reactants is high enough [e.g., ZnO in Eq. (2.4)], condensation on the surface of the other reactant can also provide a uniform supply of the other reactant. In this case, the powder reaction can be better described as a gas–solid reaction rather than a solid-state reaction.

In practical systems, solid state reaction in powder systems depends on several parameters. They include the chemical nature of the reactants and the product; the size, size distribution, and shape of the particles; the relative sizes of the reactant particles in the mixture; the uniformity of the mixing, the reaction atmosphere; the temperature; and the time. The reaction rate will decrease with

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an increase in particle size of the reactants because, on average, the diffusion distances will increase. For coherent reaction layers and nearly spherical particles, the dependence of the reaction kinetics on particle size is given by Eq. (2.15) or Eq. (2.16). The reaction rate will increase with temperature according to the Arrhenius relation. Commonly, the homogeneity of mixing is one of the most important parameters. It influences the diffusion distance between the reactants and the relative number of contacts between the reactant particles, and thus the ability to produce homogeneous, single-phase powders.

Powder preparation by solid-state reactions generally has an advantage in terms of production cost, but as outlined earlier, the powder quality is also an important consideration for advanced ceramics. The powders are normally agglomerated and a grinding step is almost always required to produce powders with better characteristics. Grinding in ball mills leads to the contamination of the powder with impurities. Incomplete reactions, especially in poorly mixed powders, may produce undesirable phases. Furthermore, the particle shape of ground powders is usually difficult to control.