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Original Article

A NEW GAS–SOLID REACTION MODEL FOR VOLOXIDATION PROCESS WITH SPALLATION

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ABSTRACT

A new methodology, the crack–spallation model, has been developed to analyze gas–solid reactions dominated by crack growth inside of the solid reactant and spallation phenomena. The new model physically represents three processes of the reaction progress: (1) diffusion of gas reactant through pores; (2) growth of product particle in pores; and (3) crack and spallation of solid reactant. The validation of this method has been conducted by comparison of results obtained in an experiment for oxidation of UO₂ and the shrinking core model. The reaction progress evaluated by the crack–spallation model shows better agreement with the experimental data than that evaluated by the shrinking core model. To understand the trigger point during the reaction progress, a detailed analysis has been conducted. A parametric study also has been performed to determine mass diffusivities of the gas reactant and volume increase constants of the product particles. This method can be appropriately applied to the gas–solid reaction based on the crack and spallation phenomena such as the voloxidation process.

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1. Introduction

One well-known methodology to analyze gas–solid reactions is the shrinking core model (SCM) [1]. An approximated solution of this model is widely explained in standard textbooks [2,3], as follows. In the SCM, the gas reacts with the reactant material at the surface, and the reaction zone moves inward of the reactant, as shown in Fig. 1. In other words, the unreacted solid sequentially shrinks. The completely reacted solid remains at its original locations, and is called “ash.” It is assumed that (1) all particles are identical and do not vary during the reaction and (2) the densities of particles and solid reactant are similar. Then, for a simple gas–solid reaction defined as



where A is the gas reactant, B is the solid reactant, C is the solid product, and b and c are stoichiometric coefficients, the governing equation for the one-dimensional diffusion of the gas reactant into the solid reactant is

$$\frac{\partial C_A}{\partial t} = D_e \left(\frac{\partial^2 C_A}{\partial r^2} + \frac{N}{r} \frac{\partial C_A}{\partial r} \right), \quad (2)$$

where C_A is the molar concentration of A , t is the time, D_e is the effective mass diffusivity, N is the geometry factor ($N = 0$, rectangular coordinate; $N = 1$, cylindrical coordinate; and $N = 2$, spherical coordinate), and r is the spatial coordinate (r should be replaced by x for the rectangular coordinate). The governing equation can be solved by applying the quasi-steady-state approximation. To show how much the reactant material has been reacted, a parameter, X_B , is defined as

$$X_B(t) = 1 - \left(\frac{R(t)}{R_0} \right)^{N+1}, \quad (3)$$

where R is the radius of unreacted solid material and R_0 is the initial radius of the solid reactant. With appropriate boundary and initial conditions for a cylindrical solid reactant, the analytical solution can be derived as

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$$t = \frac{\rho_{Bm} R_0}{b C_{Ag}} \left[\frac{1}{2 k_{Ag}} X_B + \frac{R_0}{4 D_e} \{X_B + (1 - X_B) \ln(1 - X_B)\} + \frac{1}{k_{As}} \{1 - (1 - X_B)^{1/2}\} \right], \quad (4)$$

where ρ_{Bm} is the molar density of the solid reactant, C_{Ag} is the molar concentration of the gas reactant in the bulk gas, k_{Ag} is the mass transfer coefficient of the gas reactant between the gas film and the ash layer, and k_{As} is the rate constant for a first-order surface reaction at the solid reactant surface.

Many researchers have attempted further expansion and modification of the SCM. The Johnson–Mehl equation has been applied to the chemical reaction resistance term in Eq. (4) [4]. The particle size distribution of the solid material has been coupled with the SCM [5]. The varying of the ash zone size during the reaction time has been mathematically applied by modifying the SCM [6]. Shi et al. [7] modified the SCM to study methane hydrates in a dry-water droplet. Comparisons of the SCM applying the assumption of quasi-static diffusion against without that also have been conducted [8]. These SCM-based methods basically assume that chemical reaction and loss of solid reactant occur on the solid surface.

However, according to experimental studies, for example, considering the oxidation behavior of UO₂ pellets [9], a gas–solid reaction can progress mainly by cracks growing and spallation of a solid reactant because of volume changes from the transformation of reactants into product in pores and grain boundaries of the solid reactant. Therefore, the SCM method, based on the demonstration of a gas film within the bulk gas, the diffusion of the gas through the ash layer, and shrinking of the reactant material by the surface chemical reaction, cannot physically describe the crack and spallation mechanism for this type of gas–solid reaction. In this study, a new kinetic model for gas–solid reactions has been proposed to demonstrate reactions dominated by crack and spallation rather than surface chemistry.

2. Kinetic model

2.1. Crack–spallation model

To begin with, let us consider a simple gas–solid reaction as described in Eq. (1). If the reaction progress is dominated by cracks and spallation from the growth of the product particle in the pores, the reaction process can be illustrated as shown in Fig. 2. In this model, we assume that (1) the spherical pores are uniformly distributed in the media with identical physical features, for example, the physical shape and size; (2) cracks and spallation occur at pore locations when the product particle size is larger than the pores; (3) pores have enough space to generate and grow particles; (4) product particles are spherical and grow one-dimensionally; (5) the reaction progress by surface chemistry is

much slower than that by cracks and spallation; (6) the chemical reaction time for spalled solid reactants is not considered, because it could be negligible compared with the whole reaction progress time because of the dramatic increase of the surface area; (7) the diffusion process is one-dimensional; (8) the diffusivity is constant in the solid reactant during the entire reacting time; (9) there is a sufficient amount of gas reactant around the solid reactant; and (10) the spalled reactant does not affect the diffusion of the gas reactant into the solid reactant.

There are three main processes for this model. The first process is the diffusion of gas reactant through pores, which are assumed to include all kinds of porous spaces such as cracks, fractures, grain boundaries, and porous vacancies in the solid reactant. Then, the diffused gas in the solid reactant starts to react with the solid reactant, as shown in Fig. 2b. This is the second process, which is the growth of product particles in pores. Because the amount of solid reactant is sufficient to react with the gas reactant, the dominant factor for the control of the gas–solid reaction in the pores is the concentration of diffused gas reactant in those pores. Finally, as illustrated in Fig. 2d, when the size of the product particles becomes greater than the size of the pores, the part of the solid reactant including that pores starts to crack and spall out.

2.2. Computation methodology

First, the diffusion process is solved by numerical calculation of the diffusion equation shown in Eq. (2). At the beginning of this process, there are no products, C (solid), inside of the solid reactant because of the lack of diffusing gases at this point. This initial condition is represented as

$$C_A(r < R_0, t = 0) = 0. \quad (5)$$

The boundary condition shown in Eq. (6) is that the molar concentration of gas reactant, C_A , at the surface of the solid reactant at a certain time, t , is equal to that in the air, C_{Ag} :

$$C_A(r = R, t) = C_{Ag}. \quad (6)$$

The growth process is governed by the concentration of gas reactant in the pores, as explained in the previous section. After the diffusing of the gas reactant into the solid reactant, the generation of solid product particles begins. The produced solid particles inside the pores sequentially grow by continuous gas–solid chemical reaction. For this growth model, it is assumed that the volumetric growth rate of the product is modeled as a linear function of the gas concentration in the pores:

$$\frac{dV}{dt} = k C_A, \quad (7)$$

where V is the volume of the product in each pore and k is a constant. Then, the equation can be rewritten as

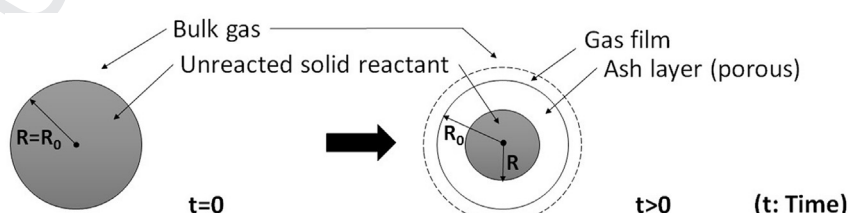


Fig. 1. Configuration of the SCM for an isothermal spherical reactant [3]. SCM, shrinking core model.

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