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A new model for diffusion-controlled precipitation reactions using the extended volume concept

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ABSTRACT

In this work a new model for diffusion-controlled precipitation reactions is derived, analysed and tested against a wide range of data. The model incorporates elements of the extended volume concept and combines this with a new treatment of soft impingement of diffusion fields. The model derivation involves an integration over iso-concentration regions in the parent phase in the extended volume, which leads to a single analytical equation describing the relation the fraction transformed, α, and the extended volume fraction, α_{ext}, as: $\alpha = \{\exp(-2\alpha_{ext}) - 1\}/(2\alpha_{ext}) + 1$. The model is compared to a range of new and old data on diffusion-controlled reactions including precipitation reactions and exsolution reactions, showing a very good performance, outperforming classical and recent models. The model allows new interpretation of existing data which, for the first time, show a consistent analysis, in which Avrami constants, n, equal values that are always consistent with transformation theory.

1. Introduction

Diffusion-controlled precipitation reactions are important in a wide variety of commercially important materials. It is important to have an accurate model for the kinetics of the reaction as heat treatment can determine a range of properties. Preferably such a kinetic model should be accurate, transparent, avoid computationally expensive implementations, and lead to analysis methods that are widely applicable. The objective of this work is to derive and test a new model for diffusion-controlled precipitation reactions that meets these criteria.

Diffusion-controlled precipitation reactions can be thought of as being the combination of 4 overlapping processes: nucleation, growth, soft impingement and coarsening. Several attempts at providing a computationally friendly suitable framework for predicting the progress of diffusion-controlled reactions incorporating a treatment of impingement have been published (see e.g. [1–3]), and some less computationally friendly attempts at models have been published more recently [4]. The present paper focuses primarily on the treatment of soft impingement.

One group of existing modelling approaches is based on direct consideration of the diffusion flux at the interface. For instance, the numerical method formulated by Kampmann and Wagner [5], as applied by several authors (e.g. [6–9]), treats the growth of individual spherical particles following the equation:

$$\frac{dR}{dt} = \frac{\frac{-(t)-c_m}{c_p-c_m}}{c}\frac{D}{R} \tag{1}$$

where R is the radius of a growing particle, D is the diffusion constant, c_p is the solute concentration in the precipitate, c_m is the solute concentration at the precipitate/matrix interface that is evaluated by the Gibbs–Thompson relationship [10,11],$\bar{c}(t)$ is the mean concentration of the matrix. A characteristic of this approach is that the interaction of the diffusional growth of the various particles is drastically simplified: a spherical geometry of diffusion field is assumed and interaction is described through a single parameter, the mean concentration $\bar{c}(t)$. We can term this as a mean field approach. Some of the users of KW model have described this treatment of impingement as 'a simple response equation' [12], i.e. it is an approximation for which the accuracy is as yet unproven and it has been suggested that the mean field approach underestimates impingement because it ignores a geometrical component to the impingement process [13]. The contribution of a geometrical component has been investigated in [13,14]. Benefits of the KW approach are that basic capillarity effects can be included and that, in principle and at some computational costs, the numerical scheme can be implemented to

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model different groups of precipitates and (in principle[1]) incorporate coarsening [7,8]. The models described by Svoboda et al. [15,16] applying the thermodynamic extremal principle (first described by Onsager [17]) employ a mean field approach that is equivalent to the KW approach (see [16]).

Other works have adopted the extended volume approach (see e.g. [18–23]). In this approach the fraction transformed, α, is defined as the ratio of the amount of product phase that has formed and the maximum that can form (on completion of the reaction). Alternatively, we can also define α by the level of depletion of the parent phase (often called the matrix) through:

$$\alpha = \frac{\bar{c}(t=0) - \bar{c}(t)}{\bar{c}(t=0) - c_m} \tag{2}$$

(For discussion on definition of α, see Section 4.2). The extended volume is the imaginary 'volume' in which all growing product phases and diffusion fields expand unimpeded by any of the other product phases and their diffusion fields. In this approach the extended volume fraction, α_{ext}, is defined as the fraction transformed in this imaginary extended volume, and thus $\alpha_{ext}(t)$ increases without limit to infinity. Ignoring various effects including capillarity, α_{ext} is generally given by (e.g. [2,20]):

$$\alpha_{ext} = \frac{(kt)^n}{V_o} \tag{3}$$

where t is the time, k is a factor depending on temperature, composition and (semi-) equilibrium concentrations in the two phases, V_o is the reference volume considered, and n is an exponent (alternately referred to as either the reaction exponent or the 'Avrami exponent'). In the early stage of the reaction impingement is negligible and the constants k and V_o describing this imaginary α_{ext} can always be linked to 'real' progress of the reaction by using $\alpha_{ext} = \alpha$. These models then proceed to derive an equation for the 'real' volume transformed through an analysis that defines the relation between the growth of the extended volume and the real volume transformed. The best known model of this type is the classical Johnson–Mehl–Avrami–Kolmogorov (JMAK) model (after [18,21,24,25]), which is an accurate solution for hard impingement, i.e. where impingement is exclusively due to impingement of growing product phases. Although some authors have used it for diffusion-controlled reactions the JMAK method is not designed for diffusion-controlled reactions, and will in general only be valid in the limited range where no impingement occurs.

The general equation for n is [20,26]:

$$n = N_{dim} g + B \tag{4}$$

where g is 1 for linear growth or 1/2 for parabolic (diffusion-controlled) growth, B is 0 in the case of site saturation (no nucleation during the transformation), or 1 for continuous nucleation (at constant nucleation rate), N_{dim} is the dimensionality of the growth. For diffusion-controlled growth n is thus taken as 1/2, 1 or $1^1/_2$.

In one extended-volume based model an impingement parameter is introduced, which results in the equation [26–28]:

$$\alpha = 1 - \left(\frac{\alpha_{ext}}{\eta_i} + 1\right)^{-\eta_i} \tag{5}$$

where η_i is the impingement parameter. Through adjusting the impingement parameter this equation can encompass the JMAK model [18,19,21,24,25] (which is obtained for $\eta_i \to \infty$), the lesser known Austin–Rickett [29] equation (which is obtained for $\eta_i = 1$), and a good approximation for the site saturated case of the KW model is obtained for $\eta_i = 5$ [2].

Further, several authors [30–32] have applied approaches in which impingement of diffusion fields is approximated through approximating diffusion profiles (concentration as a function of the distance to the interface) as linear and subsequently assuming that the progress can be divided into two stages: one where no interaction occurs followed by a stage of interaction.

Phase field methods for simulating precipitation (see eg. [13,33,34]) can reveal many details at the level of single precipitates, but are computationally expensive to the extend that simulation of impingement is rarely attempted (see [13,35] for rare examples of a phase field model with impingement).

As would be expected, all these approaches agree in terms of the prediction of the early stage of transformation in that they all predict the total volume of reaction product to grow according to a power law, Eq. (3). Beyond the initial stage, going into the stage where diffusion fields around particles start to interact, predictions of these models start to increasingly diverge.The main aim of the present paper is to show that we can derive a computationally efficient kinetic equation that is realistic both in (i) the treatment of the distribution of nuclei, i.e. by considering stochastically distributed nuclei, and (ii) a diffusion field around each particle with concentration in the parent phase at the interface given by c_m.

2. A new soft impingement model

To derive a new model for diffusion-controlled reactions we start by adopting one of the existing models for nucleation, proceed to calculate the amount the nucleation and initial growth of the phases in the extended volume and, as is done in a range of works [18,26,28], assume that this can be mapped onto Eq. (3), i.e. the parameters of the growth of the extended volume fraction, k and n, are obtained from the nucleation and initial growth model. Initial growth is here defined as the stage at which α is less than ~0.2, we will show below that during this stage impingement is negligible.

In the present model we will define the extended volume as the imaginary volume in which all diffusion caused by the growth of a single nucleus is unimpeded by the other nuclei. (Note that this is different from some other models, notably [13].) The present model focusses on the diffusion fields in the parent phase, and the fraction transformed is thus obtained from the concentrations in the parent phase, through Eq. (2). The amount of transformed phase (the total volume of the growing nuclei) is directly proportional to this and the absolute values can be obtained from a mass balance equation.

The new element of the model is the treatment of impingement. In the kinetic equation we will characterise the diffusion field as follows. We will define the local depletion fraction of the diffusing species, χ, in the parent phase (the phase in which the diffusion occurs) at position $\bar{x}$ and time t as:

$$\chi(\bar{x}, t) = \frac{c(\bar{x}, t) - c_m}{\bar{c}(t=0) - c_m} \tag{6}$$

where $c(t=0)$ is the starting concentration of the diffusing species in the parent phase. For all locations in the parent phase χ is initially 1 and decreases over time to 0. In the extended volume we can now identify the volumes in which the depletion of the matrix has progressed beyond a certain amount, i.e. we can identify $V(\chi_I) = V_{M2} + V_{M1}(\chi < \chi_I)$ as the volume in which the parent phase M1 with starting concentration c_0 has converted to material M2 and depleted M1 with depletion fraction χ_I. We can do this for

[1] In practice this has proved challenging and generally an additional fittable parameter representing the interfacial energy during the coarsening stage has to be introduced (see e.g. [9]).