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Analysis of nucleation and growth with the model for diffusion-controlled precipitation reactions based on the extended volume concept

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ABSTRACT

Recently (Starink, 2014) a new model for diffusion-controlled precipitation reactions based on the extended volume concept was derived. The model leads to an analytical equation describing the relation between the fraction transformed, α, the reaction time, t, and the reaction exponent, n, as:

$$\alpha = \{\exp(-2(k_1 t)^n) - 1\}/(2(k_1 t)^n) + 1$$

In the present work, new analysis methods are derived which allow determination of the reaction exponent n. The new methods are applied to analysis of nucleation and it is shown that generally during a reaction with growth in 3 dimensions there are only 2 modes: either the nucleation rate in the extended volume is constant or it is negligibly small. A new approach to the interaction of diffusion-controlled growth and nucleation is proposed to rationalise these findings. The exponential decay of the average solute content predicted by the new model is further analysed and compared with a range of experimental data and contrasted with other models. The new model is found to correspond excellently to these solute decay data.

1. Introduction

Diffusion-controlled precipitation reactions can be thought of as the combination of 4 consecutive partially overlapping processes: nucleation, growth, soft impingement and coarsening. Substantial data on diffusion-controlled precipitation reactions has been published and several models have been proposed [1]. Very recently [1] a new model was derived which focusses particularly on the impingement of diffusion fields. A comparison with of over 20 sets of transformation vs time data at a wide range of temperatures (40–1500 °C) showed that the new model accurately fits the data on all reactions, and overall is clearly outperforming all other models. A key factor in the model is that it derives and employs an expanded form of the imaginary extended volume concept (see e.g. [2–6]), through applying an integration of impingement over various extended volumes defined by iso-composition surfaces [1]. Through this approach the new model avoids the over-simplification of soft impingement inherent in mean field approaches such as the Kampmann and Wagner (KW) model [7–11] and the model by Svoboda and co-workers [12–14].

The main aim of the present paper is to show the consequences of this new model for analysis of nucleation, and to derive methods that can be used to analyse the transformation modes of the diffusion-controlled reactions. An ancillary aim is to show, through these analyses, that the new model is correct, and can form the basis for a range of analysis methods.

For the full derivation of the model the reader is referred to [1]. Key elements of the model are that depletion in the extended volume is approximated by linear functions whilst impingement is treated as occurring in a volume (rather than a surface as in the approach by Avrami [2] and Kolmogorov [3,4]). (For details the reader is referred to [1].) Whilst the resulting equations are straightforward (see below), a graphical representation of the model is very difficult and the underlying concepts are challenging. To illustrate the 3 dimensional growth of particles one would need to represent each particle growing in its own 3 dimensional space with each point in 3D space having a time dependent composition. This is not realistically possible. Hence we here attempt to represent 1 dimensional growth. Fig. 1a shows the composition profile of one particle shortly after it nucleated. There is one growth

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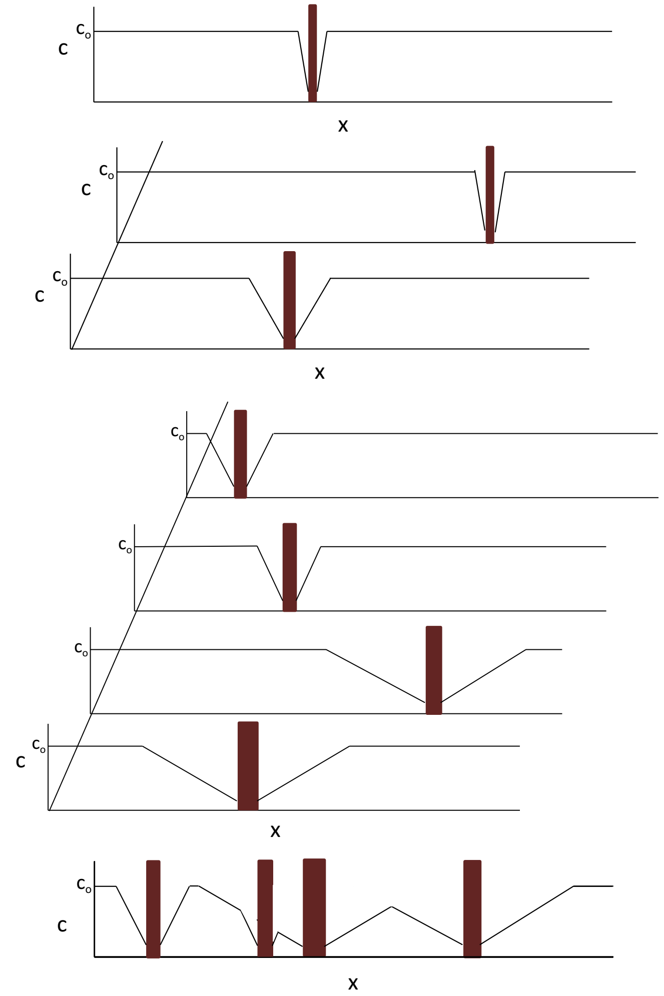

Fig. 1. Schematic illustration of the model for 1 dimensional growth. See text for description. The initial concentration of solute in the alloy is c_o.

dimension: along the x axis. To reflect the assumptions in [1] the composition profile is taken as straight lines. Fig. 1b represents the system in the extended space/volume[1] a short time later; there are now 2 particles that are growing. As we are formulating the model in the extended space/volume, each particle is associated with its own composition profile in the surrounding matrix that is developing independent of diffusion fields around other particles. Thus in the extended space/volume each particle grows in its own space, which is reflected in Fig. 1b and c by a set of graphs each reflecting one particle.

As time progresses, the diffusion fields around each particle become wider. Fig. 1c shows the system in the extended volume at a later time; there are now 4 particles that are growing. Fig. 1d shows the composition profile in the real space, with composition profiles determined from the transformation from extended to real space (as described in [1]). Whilst the straight line approximation for the composition profiles have introduced an approximation in the model, the resulting composition profile (Fig. 1d) is complex and realistic. It is seen that the model avoids simplifications that have been used in selected other models: particles are randomly distributed (they are not in equidistant arrays) and there is no mean field concentration assumption used in approximating interaction.

In the new model, the fraction transformed, α, is calculated on the basis of the average amount of solute in the parent phase, $\bar{c}(t)$, i.e. it is calculated as

$$\alpha = \frac{c_o - \bar{c}(t)}{c_o - c_m} \tag{1}$$

where c_m is the solute concentration at the precipitate/matrix interface. The results can be described by just 3 basic equations:

$$\alpha = \frac{\exp(-2\alpha_{\text{ext}}) - 1}{2\alpha_{\text{ext}}} + 1 \tag{2}$$

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

where α is the fraction of material that is transformed, α_{ext} is the extended volume fraction, k is a factor depending on temperature, t is the time, V_o is the reference volume considered, and n is an exponent (generally referred to as either the reaction exponent or the 'Avrami exponent'). The general equation for n is [15–18]:

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

where g is $\frac{1}{2}$ for diffusion-controlled (parabolic) growth, B is 0 in the case where nucleation ceases very early in the reaction, or 1 for continuous nucleation (at constant nucleation rate in the extended volume), N_{dim} is the dimensionality of the growth. For diffusion-controlled growth n is thus taken as $\frac{1}{2}$, 1 or $1\frac{1}{2}$.

2. Methods for direct determination of *n*

2.1. Plot slope method

The main equation in the Johnson–Mehl–Avrami–Kolmogorov (JMAK) model (after [2,3,19], see also [16,20]), $\alpha = 1 - \exp(-\alpha_{\text{ext}})$, can be readily inverted to express α_{ext} in terms of α. This allows calculation of α_{ext} from data on α and allows plotting $\ln \alpha_{\text{ext}}(\alpha)$ vs $\ln t$. This is the oft employed plot of $\ln t$ vs $\ln(-\ln(1-\alpha))$ (sometimes referred to as an 'Avrami plot'), which allows determination of n from the slope. (Expressions for selected other models can also be inverted [17,21–23].) This 'Avrami plot' method has been applied extensively throughout many works and the n values thus obtained have been extensively discussed in these works. It would appear to be an attractive method, because comparison of n determined from the slope of the plot with Eq. (4) provides information on dimensionality of the growth and nucleation. Even though this is clearly incorrect for diffusion-controlled reactions for all but very small values of α, plotting of $\ln t$ vs $\ln(-\ln(1-\alpha))$ has been applied for these reactions. To rectify this situation, and provide a correct means for determination of n for diffusion-controlled reactions, we will here provide a correct expression for deriving n from slopes of plots for the case of diffusion-controlled reactions.

The new model (Eqs. (2)–(4)) does not allow inverting the main expression (Eq. (2)) to provide a simple expression for $\alpha_{\text{ext}}(\alpha)$. However, it is possible to derive highly accurate approximations for this purpose. Through trial and error it was found that a suitable approximation is

$$\ln \alpha_{\text{ext}}(\alpha) \cong 0.48 \ln(((1-\alpha)^{1.8} - 1)/-1.8) + 0.525 \ln(((1-\alpha)^{-1.8} - 1)/1.8) \tag{5}$$

Analysis of this equation shows that it allows approximation of the local slope of an $\ln \alpha_{\text{ext}}(\alpha)$ vs $\ln t$ plot (which equals n) to within 2.3% for α between 0 and 0.9 (and to within 5% for α between 0 and 0.97)[2]. The average slope for α between 0.02 and 0.8 equals n to within 0.3%, and the average slope for α between 0.02 and 0.97 equals n to within 0.6%. These levels of variation are generally less than errors and uncertainties introduced by experimental factors, and hence the above approximation can be used to analyse experimental data without adding to experimental errors.

2.2. Time range methods

Whilst the plot slope method in the previous section is in many cases the most accurate and detailed method available for determining n, also faster methods based on transformation time ratios are possible. These methods are possible because, just like in the JMAK method, for each pair of fraction transformed the

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[1] The basic concept of and terminology 'extended volume' derives from the JMAK model [2–4]. In this paragraph and Fig. 1 the extended 'volume' is illustrated for one dimension. In this paragraph the 'volume' is thus a 1 dimensional 'space'.

[2] A plot of $\ln t$ vs $\ln(\alpha/[1-\alpha])$ is also interesting as the slope equals n at $\alpha = 0$ and $\alpha = 1$. But in rises to 1.23 n at $\alpha = 0.7$ and hence is less suitable for determination of n.