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ScienceDirect
Acta Materialia 59 (2011) 3276–3286
Acta MATERIALIA
www.elsevier.com/locate/actamat

Kinetics of solid-state transformation subjected to anisotropic effect: Model and application

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Received 9 January 2011; accepted 1 February 2011
Available online 2 March 2011

Abstract

In the present work, a growing particle subjected to anisotropic effect, if not influenced by other particles, is assumed to be an isotropically growing particle with constant volume. Accordingly, how to describe the anisotropic growth just becomes how to solve the blocking effect arising from the anisotropic growth. Following the statistical description of Johnson–Mehl–Avrami–Kolmogorov kinetics, the blocking effect was investigated further. Consequently, a series of analytical models for solid-state transformation, where a particle undergoes 1-scale blocking, k-scale blocking and infinite-scale blocking, were developed. On this basis, it was analytically proved for the first time that the classical phenomenological equation accounting for the anisotropic effect ($f = 1 - [1 + (\xi - 1)x_e]^{-1/\xi-1}$) corresponds to an extreme case where a particle encounters infinite-scale blocking. From the model analysis, the anisotropic effect on the transformation depends on two factors: the non-blocking factor γ and the blocking scale k. From the model calculations, the Avrami exponent, subjected to the anisotropic effect, changes as a function of the transformed fraction, whereas the effective activation energy is not affected by the anisotropic effect. The present models were adopted to describe isothermal crystallization of amorphous $Fe_{33}Zr_{67}$ ribbons; good agreement with the published results was achieved.

Keywords: Extended fraction; Anisotropic growth; Blocking effects; Probability

1. Introduction

In studies of phase transformations involving nucleation and growth, the classical Johnson–Mehl–Avrami–Kolmogorov (JMAK) equation [1–5] often plays an important role. This equation provides an expression for the fraction of material transformed as a function of time $f(t)$ in terms of the nucleation and growth rates. It is known that the JMAK formula is exact, provided the conditions imposed in the original derivations are not violated, such as: isothermal transformation, either pure site saturation at time $t = 0$ or pure continuous nucleation; high driving force (large undercooling or superheating); and randomly dispersed nuclei which grow isotropically [6–11]. In these cases, the kinetic parameters, the Avrami exponent n, the effective activation energy Q and the pre-exponential factor K_0 all hold constant with respect to time and temperature.

Recently, a modular model for transformation kinetics [8–16] was proposed which includes, but is not restricted to, the classical JMAK description [11,12]. The model recognizes three mechanisms, i.e. nucleation, growth and impingement of growing new-phase particles, and is applicable to both isothermal and non-isothermal transformations. By choosing suitable nucleation and growth mechanisms, in particular a mixture of nucleation modes (e.g. the mixture of pre-existing nuclei and continuous nucleation), the model even leads to analytical formulations for the degree of transformation which exhibit the framework of the JMAK equation but with time-dependent kinetic parameters $n(t)$, $Q(t)$, $K_0(t)$ (isothermal transformation) or temperature-dependent kinetic parameters $n(T)$, $Q(T)$, $K_0(T)$ (isochronal transformation) [13–15]. This implies that a transformation can still be considered

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doi:10.1016/j.actamat.2011.02.001

"iso-kinetic" in the sense that the prevailing transformation mechanism does not change throughout the transformation process, in spite of the change in n and Q with transformation. In this modular model, the effects due to anisotropic growth and non-random nuclei distribution have also been considered as two contrary modes for impingement [11,12], which merely modify the relation between the transformed fraction f and the extended fraction x_e, applying the phenomenological factors for impingement. However, the calculation of x_e still follows the essential JMAK-like restrictions, e.g. randomly dispersed nuclei and isotropic growth.

Under practical conditions, unfortunately, the JMAK-like restrictions are often violated. For example, the transient nucleation [17,18], the spatially correlated nucleation [19,20], the necessarily associated size-dependent growth [21,22] or the non-parallel anisotropic growth with blocking up to all relevant orders [23,24] all lead to deviations from the JMAK-like kinetics. On this basis, some extensions based on JMAK-like theory have been made, especially in the cases subjected to the anisotropic effect.

Calculation of transformation kinetics involving anisotropic particles is a much more challenging problem than that for isotropic particles. Up to now, two approaches have been proposed to deal with the anisotropic effect. One approach is the phenomenological extension of JMAK-like formulation by adding (one or more) new variables which provide freedom to improve the agreement where anisotropic growth occurs [11,12,25–27]; this approach changes only the relation between f and x_e, but does not change x_e itself (e.g. the modular model mentioned above, or see Section 2.2). The other approach is, according to the physical essence of anisotropic effect, devoted to deriving an analytical description with physically realistic variables (e.g. the growth rate anisotropy g_r and the orientation ϕ) [28–34]; this approach does reduce x_e.

Furthermore, computer modeling and simulations have also been used to analyze the anisotropic effect. Shepilov and co-workers performed computer simulations to investigate the growth of randomly distributed and oriented ellipsoidal particles in two-dimensional (2D) [35] and three-dimensional (3D) [23] spaces, where the mutual blocking of growing particles in the first and the second order was studied. In the first-order treatment, the possibility that a third particle hinders the blocker in blocking the aggressor (second-order blocking) was not accounted for. Subsequently, with the Monte Carlo method, Pusztai and Gránásy [24] and Kooi [36,37] also studied the mutual blocking of anisotropically growing particles up to all relevant orders, and Kooi proposed an analytical model to describe the blocking effect. On the basis of Kooi's model, the deviations from JMAK-like kinetics due to the anisotropic effect were investigated further by Liu and Yang [38].

Actually, a proper analytical treatment in the spirit of JMAK-like theory has not yet been developed to describe such transformation. In the present work, a statistical analysis for the blocking effect arising from the anisotropic growth is performed. Analytical models for solid-state transformation, where the particle undergoes 1-scale blocking, k-scale blocking and infinite-scale blocking, are developed. In Section 2, a theoretical background essential for the current models is summarized. In Section 3, a philosophical description of the statistical analysis and a derivation of the current models are presented. In Section 4, first, new expressions for the Avrami exponent n_{new} and effective activation energy Q_{new} subjected to the anisotropic effect are obtained and discussed; then the present model calculation, which illustrates the contributions of non-blocking factor γ and blocking scale k (see Sections 3 and 4) to the anisotropic effect, is discussed; and finally, the model fit to crystallization of amorphous $Fe_{33}Zr_{67}$ ribbons at 663 K is performed. Several brief concluding remarks are summarized in Section 5.

2. Theoretical background

2.1. JMAK kinetics

In the JMAK description, nucleation and the growth are modeled as two statistical processes. The original derivation of the JMAK equation rests on calculating the probability that a randomly chosen point in space (e.g. the origin point O) will have remained untransformed by a given time t. The probability that a particle nucleated at time τ will grow to the origin point O at time t is expressed as [5]

$$I = \dot{N}(\tau)\mathrm{d}\tau Y(\tau, t) \tag{1}$$

where $\dot{N}$ is the steady-state nucleation rate per unit volume, $\dot{N}(\tau)\mathrm{d}\tau$ is the probability for a particle nucleated in the time interval $[\tau, \tau + \mathrm{d}\tau]$ per unit volume, and $Y(\tau, t)$ is the volume of a particle at time t when it was nucleated at time τ. Accordingly, $q(t)$, the probability of the random point O untransformed at time t, can be obtained, from Eq. (1), as [5,23]

$$q(t) = \exp\left(-\int_0^t \dot{N}(\tau)Y(\tau, t)\mathrm{d}\tau\right) \tag{2}$$

And thus, the JMAK equation describing the temporal evolution of transformed fraction follows

$$f(t) = 1 - \exp[-x_e(t)] \tag{3}$$

where the extended fraction x_e obeys

$$x_e = \int_0^t \dot{N}(\tau)Y(\tau, t)\mathrm{d}\tau \tag{4}$$

As such, the probability that a particle nucleated at time τ will transform the origin point O at time t corresponds to the differential form of x_e (i.e. $\mathrm{d}x_e$). For the sake of generalization, $\mathrm{d}x_e$, defined herein as a comprehensive probability factor, i.e. the increment of x_e incorporating all the prevalent modes of nucleation and growth, will be used to derive the current models (see Sections 2.3 and 3).