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A thermokinetic description of nanoscale grain growth: Analysis of the activation energy effect

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Abstract

The inhibition of grain growth by solute segregation in nanoscale materials has often been described using kinetic models (e.g. Acta Mater 1999;47:2143) or thermokinetic models (e.g. Acta Mater 2009;57:1466), in which constant activation energy and a negligible effect of solute segregation on activation energy were assumed. In this paper, an intact thermokinetic model for nanoscale grain growth was developed by incorporating mixed effects of activation energy and grain boundary (GB) energy. By application of the model to nanoscale grain growth in Ni–P, Pb–Zr, Fe–Zr and Ru–Al alloys, the validity of the present model was confirmed, in combination with verification of the initial condition of GB segregation. On this basis, the increase of activation energy and the decrease of GB energy are interrelated and thus the kinetics and the thermodynamics of normal grain growth are linked. Based on a comparison of three characteristic velocities V_{TK}, V_{GE} and V_{AE} of GB derived from the present thermokinetic model, grain boundary energy model and activation energy model, a mechanism of controlled nanoscale grain growth was proposed, which indicated a transition from a kinetic-controlled to a thermodynamic-controlled process.

Keywords: Grain boundary energy; Activation energy; Grain growth; Solute segregation

1. Introduction

Recently, nanocrystalline (NC) materials (grain size < 100 nm) have generated great interest due to their unique physical, mechanical and chemical properties [1–3]. However, the increased energy associated with the increase of grain boundary (GB) area makes NC materials unstable, even at low temperatures. In order to extend the useful temperature range for processing and applications, NC materials must be stabilized against grain growth. GB segregation is a promising approach to inhibit grain growth, and has been widely demonstrated in various NC materials [4–7]. So far, the two kinds of models proposed are solute drag (kinetic mechanisms) [8–13] and reduction in GB energy, σ_b (thermodynamic mechanisms) [14–19].

It is well known that the presence of solute segregation in GB regions may give rise to a significant drag force on GB migration. The theory of solute drag has well been developed, after successive contributions from Lücke and Detert [20], Cahn [9] and Hillert and Sundman [21]. In Cahn's model [9], at the low velocity extreme the apparent mobility (M_{app}) of GB motion with solute drag can be given as:

$$\frac{1}{M_{app}} = \frac{1}{M_{IM}} + \frac{1}{M_{DS}} \tag{1}$$

with M_{IM} as the intrinsic mobility induced by pure metals and M_{SD} as the solute-drag mobility induced by solute drag. Obviously, M_{app} was lower than M_{IM} and the GB velocity was decreased due to solute drag. However, the

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solute drag model of Cahn did not provide a description for a stabilized grain size. Based on the kinetic mechanism, the case where a drag term is independent of the grain size was considered by Burke [22]. Michels et al. [11] introduced a grain-size-dependent drag term to stabilize the grain size of the NC materials. However, considering the integrated effect of the drag term due to GB concentration and rate of GB migration according to the solute drag theory of Cahn [9], Rabkin [12] verified that the solute drag effect could not restrain the normal grain growth, i.e. the stabilized grain size cannot be determined by this model.

Thermodynamically, σ_b reduces with increasing solute excess at GBs according to the Gibbs adsorption theorem [14]. On this basis, further thermodynamic treatments from Weissmüller [15], Kirchheim et al. [16,17] and Krill et al. [18,19] were given. Kirchheim [23,24] extended the Gibbs adsorption isotherm and Wagner's definition of excess solute to other crystalline defects (e.g. dislocations and vacancies), and then claimed that solute segregation to dislocations and vacancies also reduce their formation energies. Accordingly, a metastable equilibrium with certain grain size (D^*) could be attained when σ_b reduced to zero. Some reasonable agreements between the predictions of thermodynamic analysis and the experimental observations have been shown in Refs. [16–19]. However, the kinetic process was omitted in all the above thermodynamic treatments. Therefore, departing from Borisov's equation [25], Chen et al. [26] derived a thermokinetic model for the evolution of grain size by the incorporation of reduced σ_b into the parabolic law to predict the evolution of grain size. Subsequently, the initial GB excess, Γ_b, was analyzed by Gong et al. [27] applying a similar model.

All the above models were developed assuming constant activation energy Q_D, which was only valid for pure materials. As shown in Eq. (1), the apparent GB mobility M_{app} was a mixture of M_{IM} and M_{SD}. The increase of grain growth activation energy with increasing temperature or solute additives was thought to be closely related to the accumulation of solute in GBs during grain growth, which has been observed in lots of experiments [28–30]. Borisov et al. [25] have related the increased atomic mobility in GB diffusion to the decreased GB energy in a semi-empirical equation. Detailed measurements of solute segregation were also determined experimentally and by computer simulation in NC Ni–W alloys [31–34], and linking the thermodynamic and kinetic approaches, a threshold value for σ_b, which should substantially stabilize the NC structure, was determined [33]. In other words, not only the GB energy but also the activation energy in GB diffusion was altered by the presence of solute segregation. Therefore, a question arises: how to combine the effects of Q_D and σ_b to model the nanoscale grain growth.

In the present work, we aimed to answer the above question. The paper is arranged as follows. A concise review for the theoretical development of parabolic law is given in Section 2.1 and a GB energy model of grain growth based on initial GB segregation condition is given in Section 2.2. Departing from Borisov's equation, an activation energy model of grain growth is proposed in Section 2.3. By incorporating the above models, a thermokinetic model for the evolution of grain size is derived in Sections 2.4 and 2.5. Applications of the present models are described in Section 3, i.e. interpreting the saturated grain size (Section 3.1) and describing the grain size evolution (Sections 3.2 and 3.3). Then, the validity of the present model and the effects of Q_D and σ_b on nanoscale grain growth are discussed in Sections 4.1–4.3. Finally, the controlling mechanism of grain growth is proposed in Section 4.4. This paper is concluded in Section 5.

2. Model derivations

2.1. Parabolic kinetics of grain growth

More than 50 years ago, following the formalism of absolute reaction rate theory, a relation was developed by Burke and Turnbull [8] for the rate of GB migration, V (i.e. dD/dt). Considering the energy of transferring an atom across an interface from one grain to another under a driving force ΔP, in order for an atom to break away from its parent grain, it must acquire, by thermal activation, an activation energy of Q_D. Based on the reaction rate theory, in which boundary movement is controlled by single atom movements, the rate of GB migration can be given as [8]:

$$V = v\lambda\left[\exp\left(-\frac{Q_D}{RT}\right) - \exp\left(-\frac{(Q_D + \Delta P)}{RT}\right)\right] \tag{2}$$

with v as the jump frequency, and λ the spacing of atoms in the GB. If $\Delta P \ll RT$ and ΔP ($\approx \sigma_b/D$) for a curvature-induced process is assumed, then

$$V = \frac{v\lambda}{RT}\exp\left(-\frac{Q_D}{RT}\right)\frac{\sigma_b}{D} \tag{3}$$

Let $M_0 = v\lambda/RT$ [35]:

$$\frac{dD}{dt} = M_0\frac{\sigma_b}{D}\exp\left(-\frac{Q_D}{RT}\right) \tag{4}$$

The classical parabolic model is precisely applicable to high-purity, single-phase materials. As for a practical mixture, both Q_D and σ_b are functions of state variables such as temperature T and concentration x_0 [19]. This implies that Q_D should be increased in contrast with reduced σ_b upon solute segregation. Approximately, a single grain growth process can be according to Eq. (4), separated as several domains [36]:

$$\begin{aligned}\int_{D_0}^{D_s} DdD &= \int_{D_0}^{D_1} DdD + \cdots + \int_{D_{s-1}}^{D_s} DdD \\ &= M_0\left\{\int_0^{t_1}\left[\sigma_{b1}\exp\left(-\frac{Q_{D1}}{RT}\right)\right]dt + \cdots \right. \\ &\quad \left. + \int_{t_{s-1}}^{t_s}\left[\sigma_{bS}\exp\left(-\frac{Q_{DS}}{RT}\right)\right]dt\right\}\end{aligned} \tag{5}$$