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Letter

A thermokinetic description of nano-scale grain growth under dynamic grain boundary segregation condition

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ABSTRACT

Under the dynamic grain boundary (GB) segregation state, an important thermokinetic transition stage between solute segregation and precipitation was considered. The thermokinetic model for nano-scale grain growth was extended by incorporating mixed effects of GB energy, activation energy and Zener drag. The application of the model in Fe–Cr and Nano-Fe alloys showed that formation of precipitation could accelerate the increase of GB energy and decrease of activation energy and finally induce to the second grain growth and second stabilization.

1. Introduction

For the nanocrystalline (NC) materials (grain size <100 nm), the increased energy associated with the increase of grain boundary (GB) area makes NC materials unstable, even at low temperatures [1,2]. So far, two kinds of stabilized models have been proposed, kinetic model induced by solute drag or Zener drag [3–5] and thermodynamic model induced by reduction in GB energy, σ_b [6–14].

The presence of solute segregation in GB regions may give rise to a significant drag force on GB migration or reduction of GB energy. Accordingly, a metastable equilibrium with certain grain size (D_1^*) could be described by thermodynamic models from Weissmüller [10], Kirchheim [11], Kirchheim and Liu [12] and Krill et al. [6]. The case above is a metastable rather than stable equilibrium because the formation of precipitation from saturated GBs is kinetically hindered [11]. As for the strong segregated system, it is so easy to form a saturated GB to accommodate the additional solute atoms. If the nominal impurity concentration in the alloy slightly exceeds the corresponding solubility limit, the excess impurity atoms leaving the GB should cause the nucleation of the particles of impurity-rich phase [13,14]. Gibbs [9] has derived the following well-known Gibbs adsorption isotherm for surfaces and GBs,

$$d\sigma_b = -\Gamma_b d\mu_b; \quad \frac{d\sigma_b}{d\ln X_\alpha} = -\Gamma_b RT \tag{1}$$

with σ_b as the GB energy, Γ_b the solute excess of the GB, μ_b the chemical potential of the solute, X_α the concentration of the matrix. Eq. (1) predicts that σ_b is reduced for a positive excess Γ_b and an increasing chemical potential μ_b [9,11]. However, with the onset of precipitation, the chemical potential may be reduced, leading to an increasing GB energy and therefore providing the driving force for rapid grain growth [13]. Unfortunately, the important stage of continuous solute segregation and formation of precipitation, i.e., dynamic GB segregation state at $D > D_1^*$, have been omitted, which have been observed in lots of experiments [15–17].

In this paper, it was aimed to derive a thermokinetic model applicable for the grain growth accompanying the formation of precipitation in GBs under dynamic GB segregation condition. The effects of σ_b and Q_D induced by precipitation on nano-scale grain growth were discussed.

2. Model derivations

2.1. GB energy model

Based on the concept for stabilization of NC solids of Weissmüller [10], an analogous analytical treatment was derived

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by Kirchheim [11] and Liu and Kirchheim [12] on the basis of Gibbs adsorption Eq. [9],

$$\sigma_b = \sigma_0 - \Gamma_{b0}\left[RT\ln\left(x_0 - \frac{3\Gamma_b V_m}{D}\right) + \Delta H_{seg}\right] \tag{2}$$

where σ_0 is the GB energy of pure solvent, x_0 the total solute content, σ_{b0} the saturated GB excess, V_m the molar volume of the alloy and ΔH_{seg} the enthalpy change of segregation per mole solute. As for a closed system at constant pressure and constant temperature, the change of Gibbs free energy, for a polycrystal can be written as [9],

$$dG = \sigma_b\, da \tag{3}$$

with a as the GB area. As shown by Eq. (3), whenever the GB energy σ_b is positive, grain growth will reduce the free energy of the system, independent of $\sigma_b < \sigma_{b0}$ or $\sigma_b = \sigma_{b0}$. Since systems with $\sigma_b < 0$ are not thermodynamically stable (i.e., negative σ_b means that the GB is more stable arrangement of atoms than regular crystal lattice and then, indeed, the material should have a tendency to contain only GBs), the only case where grain growth can be suppressed is where $\sigma_b = 0$ [9,12]. For the cases of $\sigma_b < \sigma_{b0}$ (unsaturated GB segregation condition) or $\sigma_b = \sigma_{b0}$ (saturated GB segregation condition), grain growth occurs inevitably when $\sigma_b > 0$ (see Eqs. (1)–(3)). In combination of the Taylor expansion, Eq. (2) could be further extended as,

$$\sigma_b = \left|\sigma_1 \times \left(1 - \frac{D_1^*}{D}\right)\right| \tag{4}$$

where D_1^* is the metastable equilibrium grain size, expressed as $-\sigma_2/\sigma_1$. σ_1 and σ_2, as the GB energy parameters, could be expressed as,

$$\sigma_1 = \begin{cases} \sigma_0 - \Gamma_{b0}\left[RT\left(\ln x_0 - \frac{V_m\rho}{2}\right) + \Delta H_{seg}\right], & \Gamma_b/\Gamma_{b0} < 1, \\ \sigma_0 - \Gamma_{b0}\left[RT(\ln x_0) + \Delta H_{seg}\right], & \Gamma_b/\Gamma_{b0} = 1 \end{cases}$$
$$\text{and}\quad \sigma_2 1 = \begin{cases} 3\Gamma_{b0}RTV_m\Delta\rho, & \Gamma_b/\Gamma_{b0} < 1, \\ 3\Gamma_{b0}^2 RTV_m/x_0, & \Gamma_b/\Gamma_{b0} = 1. \end{cases} \tag{5}$$

where Δ is the GB thickness and ρ the average density. It is indicated that σ_b is positive in Eq. (4). When $D \leqslant D_1^*$, $\sigma_b = \sigma_1 \times (1 - D^*/D)$; when $D > D_1^*$, $\sigma_b = \sigma_1 \times (D_1^*/D - 1)$. That is to say, with the onset of precipitation, grain size D and GB energy σ_b increase from D_1^* and "0" value again, respectively.

2.2. Activation energy model

Borisov et al. [18] derived the following expression for GB energy,

$$\sigma_b = \left(\frac{RT}{\alpha a_0^2 N_A}\right) m_a \left[\ln\left(\frac{\delta \frac{D_D}{D_L}}{a_0\lambda^\alpha}\right) - \ln m_a\right] \tag{6}$$

where $\lambda \approx 1$ [18], $\alpha = 1$ is for the interstitial mechanism, and $\alpha = 2$ for the vacancy mechanism, a_0 the average inter-atomic distance, $\delta(=m_a a_0)$ the GB width, m_a the number of atomic layer forming the GB, N_A as Avogadro's number. D_D $(=D_0 exp(-Q_D/RT))$ and D_L $(=D_0 exp(-Q_L/RT)$ with Q_L as lattice diffusion activation energy) are diffusion coefficients for lattice and interface, respectively. Assuming Mono-atomic layer ($m_a = 1$) [18], Γ_{b0} $(=1/(\alpha a_0^2 N_A))$ [19] and combining Eqs. (4) and (6), GB activation energy Q_D can be expressed as,

$$Q_D = \begin{cases} Q_1 + Q_2\frac{1}{D}, & D \leqslant D_1^* \\ Q_1' + Q_2'\frac{1}{D}, & D > D_1^* \end{cases} \tag{7}$$

where Q_1, Q_2 [20], Q_1', Q_2' are the activation energy parameters and Q_1' and Q_2' are expressed as,

$$Q_1' = \begin{cases} Q_L + \frac{\sigma_0}{\Gamma_{b0}} - RT\left(\ln x_0 - \frac{V_m\rho}{2}\right) + \Delta H_{seg}, & \Gamma_b/\Gamma_{b0} < 1, \\ Q_L + \frac{\sigma_0}{\Gamma_{b0}} - RT(\ln x_0) + \Delta H_{seg}, & \Gamma_b/\Gamma_{b0} = 1 \end{cases} \tag{8a}$$

$$Q_2' = \begin{cases} -\frac{\sigma_0}{\Gamma_{b0}} + RT\left(\ln x_0 - \frac{V_m\rho}{2}\right) - \Delta H_{seg}, & \Gamma_b/\Gamma_{b0} < 1 \\ -\frac{\sigma_0}{\Gamma_{b0}} + RT(\ln x_0) - \Delta H_{seg}, & \Gamma_b/\Gamma_{b0} = 1 \end{cases} \tag{8b}$$

Thus, semi-empirical expressions for the activation energy have been proposed. Obviously, when $D \leqslant D_1^*$, Q_D increases with the increase of D, and then tends to Q_L $(D \to D_1^*)$; when $D > D_1^*$, Q_D decreases with the increase of D from Q_L.

2.3. Drag force from second-phase precipitation

The drag effect of second phase particles was first theoretically investigated by Zener [5]. There seems to be general agreement that the maximum pinning force (F_p) exerted by a single particle of radius (r) on a GB is given by [7],

$$F_P = \pi\sigma_b r \tag{9}$$

If the number of interacting particles per unit area of the GB is set equal to n_a $(=3f/4\pi r^2$ [21]), the resulting retardation pressure (P_z) becomes,

$$P_Z = k\sigma_b\frac{f}{r} \tag{10}$$

where $k = 3/4$. It is shown that the retarding force depends both on r and f.

2.4. Incorporation of GB energy, activation energy and drag term to parabolic law

Following the formalism of absolute reaction rate theory, a relation was developed by Burke and Turnbull [4] for the rate of GB migration, V (i.e., dD/dt). If the second phase precipitation forms, the effective driving force is defined as the numerical difference between driving force of boundary migration P_G $(=\sigma_b/D)$ and P_Z (Eq. (10)). The parabolic model can be rewritten as,

$$\frac{dD}{dt} = M_0|\sigma_b|\left(\frac{1}{D} - \frac{1}{D_2^*}\right)\exp\left(-\frac{Q_D}{RT}\right) \tag{11}$$

where pre-exponential factor M_0 was determined as 0.8 mol m/J s [20]. $D_2^*(=r/(k \times f))$ is the limiting grain size. Both Q_D and σ_b are functions of state variables such as temperature T and concentration x_0 [6]. A substitution of Eqs. (4), (7), and (10) into Eq. (11) leads to,

$$\frac{dD}{dt} = M_0\sigma_1\left(\frac{D_1^*}{D} - 1\right)\left(\frac{1}{D} - \frac{1}{D_2^*}\right)\exp\left(-\frac{Q_1' + Q_2'\frac{D_1^*}{D}}{RT}\right) \tag{12}$$

Assumption of $\exp\left(\frac{Q_2'D_1^*}{RT}\frac{1}{D}\right) \approx 1 + \sum_{i=1}^{n}\frac{1}{i!}\left(\frac{Q_2'D_1^*}{RT}\frac{1}{D}\right)^i$, in combination with $i = 2$, leads to an evolution of grain size with time,

$$\begin{Bmatrix} \frac{1}{2}\left[(D - D_1^*)^2 - (D_{02} - D_1^*)^2\right] \\ + \left[(D_1^*)^2 + \frac{Q_2'(D_1^*)^2}{RT} + \frac{1}{2}\left(\frac{Q_2'D_1^*}{RT}\right)^2\right]\ln\left(\frac{D - D_1^*}{D_{02} - D_1^*}\right) \\ + \left[\frac{Q_2'D_1^*}{RT} + 2D_1^*\right](D - D_{02}) \end{Bmatrix}$$
$$- \begin{Bmatrix} \frac{1}{2}\left[(D - D_2^*)^2 - (D_{02} - D_2^*)^2\right] \\ + \left[(D_1^*)^2 + \frac{Q_2'D_1^*D_2^*}{RT} + \frac{1}{2}\left(\frac{Q_2'D_1^*}{RT}\right)^2\right]\ln\left(\frac{D - D_2^*}{D_{02} - D_2^*}\right) \\ + \left[\frac{Q_2'D_1^*}{RT} + 2D_2^*\right](D - D_{02}) \end{Bmatrix}$$
$$= \sigma_1 M_0 D_2^*(D_1^* - D_2^*)\exp\left(-\frac{Q_1'}{RT}\right)t \tag{13}$$