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Letter

Thermodynamic state and kinetic process: Analysis of grain boundary excess in nano-scale grain growth

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ABSTRACT

Derivation for grain boundary (GB) energy at thermodynamic equilibrium is reviewed. On this basis, the evolution of GB excess and bulk concentration with grain growth, and the relation between thermodynamic state and kinetic process have been discussed, for nanocrystalline materials. A concise description for the stop of grain growth is given in terms of thermodynamic and kinetic analysis.

1. Introduction

Nanocrystalline (NC) materials have been widely studied for their excellent physical and chemical properties [1,2]. It is an important aspect to maintain the stabilities of the nanocrystalline materials in their application. Inhibiting grain growth by grain boundary (GB) segregation, as a promising approach, has been demonstrated in various nanocrystalline materials [3–13]. Two kinds of models have been proposed: the kinetic one in which the force due to solute drag stops grain growth [3–7], and the thermodynamic one in which the driving force, i.e., GB energy is suppressed [8–13]. It is commonly recognized that the two models have different physical origins.

Recently, several models have been proposed to establish relations between thermodynamic and kinetic models [14–20]. Particularly, Li et al. [20] incorporate the thermodynamic relation for GB energy into the ideal grain-growth law, and derive equations with the same forms as Burke's and Michel's models [3,4]. On this basis, they claim that the velocity-independent or velocity-dependent drag force is physically equal to the reduced driving force due to decreased GB energy [20]. As far as we think, the relation between drag force and decreased GB energy depends on how to describe the evolution of GB excess and bulk concentration during the grain growth and the relation between thermodynamic state and kinetic process. In the following, we will first review the derivation for GB energy at thermodynamic equilibrium, and then discuss the above mentioned evolution and relation.

2. The theoretical background

In 1992, Weissmüller [8] first presented a concept for the stabilization of NC solids against grain growth by GB segregation. Later, an analogous analytical treatment was derived by Kirchheim [9] on the basis of Gibbs adsorption equation [21],

$$\sigma_b = \sigma_0 - \Gamma_{b0}\left[RT\ln x_g + \Delta H_{seg}\right] \tag{1}$$

where σ_b and σ_0 are the GB energy for alloy and pure solvent, x_g the bulk concentration, Γ_{b0} the solute excess of GB monolayer available for segregation at saturation, and ΔH_{seg} the enthalpy change of segregation per mole solute. In Eq. (1), it is assumed that the GBs are always saturated by solute atoms segregated. This equation is generally used to describe [9], (i) at a fixed temperatures, the GB energy decreases with increasing x_g, (ii) at different temperatures, different grain sizes with saturated GBs are ascribed to different x_g. In combination with Mclean's model for equilibrium GB segregation, Liu and Kirchheim also derived an analytical model for GB energy as [10],

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

where $\Gamma_b\,(\le\Gamma_{b0})$ is the solute excess at GBs, V_m is the molar volume of the alloy, x_0 is the total solute content and x_0-$3\Gamma_b V_m/D$ (D the grain size) is equal to x_g. Only if the GBs are saturated as grain

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growth stops, the grain size at metastable equilibrium ($\sigma_b = 0$) can be expressed as [10],

$$D^* = \frac{3\Gamma_{b0}V_m}{x_0 - \exp((\sigma_0 - \Gamma_{b0}\Delta H_{seg})/\Gamma_{b0}RT)} \quad (3)$$

Generally, Γ_b and D approach infinitely to Γ_{b0} and D^*, which are ideal values. Eq. (3) can also be written as,

$$D^* = \frac{3\Gamma_{b0}V_m}{x_0 - x_\alpha} \quad (4)$$

where x_α, the ideal bulk concentration at metastable equilibrium, is given as,

$$x_\alpha = \exp((\sigma_0 - \Gamma_{b0}\Delta H_{seg})/\Gamma_{b0}RT) \quad (5)$$

Eq. (5) infers that, at a fixed temperature, x_α and Γ_{b0} at metastable equilibrium are fixed, and independent of the total solute content. As compared to Eq. (1), Eq. (4) can be adopted to describe the decrease or increase of grain size with increasing or decreasing x_0, at a fixed temperature [10]. Using a more general statistical (atomistic) treatment in the Fowler–Guggenheim approximation, Beke et al. [15] also obtained an analogical analytical relation for the temperature dependence of the segregation stabilized boundary fraction (or grain size).

From Eqs. (2) to (5), it can be known that, the ideal metastable equilibrium ($\sigma_b = 0$) corresponds to the ideal values of Γ_{b0} and D^*, when the GBs are really saturated. This implies that, the stop of grain growth could possibly correspond to unsaturated GBs, i.e., $\Gamma_b < \Gamma_{b0}$, $D < D^*$ and $x_g \neq x_\alpha$. In our previous works [10,13,16,22], however, we mainly concentrate on the final metastable equilibrium and assume that, for any x_g and Γ_b, the state of $\sigma_b = 0$ could be satisfied with saturated GBs. That is to say, the evolution of x_g and Γ_b and its effect on the GB energy upon growth is neglected. In fact, both x_g and Γ_b change with the increasing grain size. It is a central problem to describe their change with the increasing grain size in the nanocrystalline stability studies.

3. Thermodynamic and kinetic analysis of grain growth

The increase of GB excess due to solute segregation has been found in many experiments, such as segregation of Fe atoms to Y GBs verified by lattice parameter variation [23], continuous P-segregation in the Ni GBs directly proved with tomographic atom probe (TAP) [24] as well as grain growth in NC Pd–Zr alloys [12]. It has also been found experimentally that Γ_b always increases due to solute segregation during the grain growth, while x_g could either increases (in NC Ni–W [25]) or decreases (in NC Ni–P [24], Ni–Hf [26]), or even maintains constant during this process. For grain growth in NC Fe–Ag system [22], Ag atoms are continuously segregated to the GBs as D increases. However, during isothermal grain growth of NC $Fe_{75}Si_{25}$ alloy, it has been observed that the lattice parameter changes rapidly at the beginning and then maintains an almost constant value [27]. So, the real evolution of x_g with grain growth should be *in situ* measured in the experiment.

In order to describe the above evolution of x_g and Γ_b with the grain sizes, the assumption $\Gamma_b = \beta D^n$ with β as constant and n growth exponent will be introduced into the following considerations. As shown in Fig. 1, if $n = 1$, Γ_b changes linearly with D, and x_g keeps constant, i.e., $x_g \equiv x_\alpha$; if $n > 1$ or $n < 1$, x_g decreases or increases continuously and approaches infinitely x_α, while Γ_b approaches Γ_{b0} as grain growth stops. Incorporating the above relation, a detailed study of Eq. (2) shows that, if possible, decreasing the bulk concentration from x_g to x_α equals to decreasing the second term at the right-hand side of Eq. (2). Since x_α corresponds to the saturated GBs with zero GB energy (i.e., σ_b approaches zero), σ_0 must be according to Eq. (2) negative if $x_g > x_\alpha$.[1] As is well known, negative GB energy indicates a physically unstable (unrealistic) state, i.e., grain size decreases upon grain growth. Therefore, for general grain growth including evolution of x_g and Γ_b, Eq. (2) should be rewritten as,

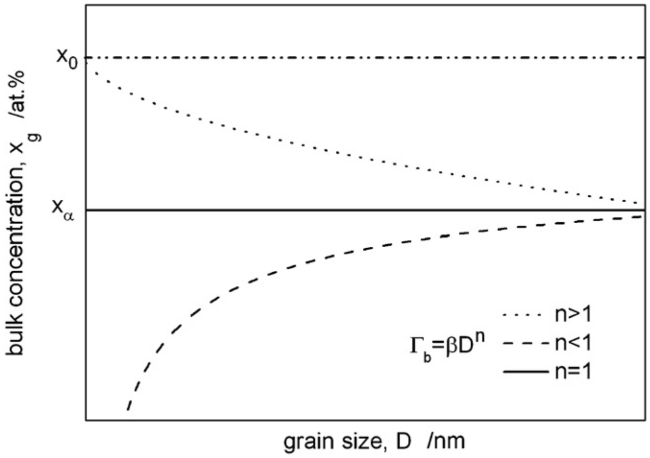

Fig. 1. Bulk concentration x_g as function of grain size D. Regarding x_g (=x_0-3$\Gamma_b V_m/D$), the relation between x_g, x_0 and x_α could be described by assuming $\Gamma_b = \beta D^n$ with β a constant, n growth exponent. If $n = 1$, $x_g \equiv x_\alpha$; if $n > 1$ or $n < 1$, x_g decreases or increases continuously and approaches infinitely x_α.

$$\sigma_b = \left|\sigma_0 - \Gamma_{b0}(RT\ln x_g + \Delta H_{seg})\right| \quad (6)$$

Actually, Eq. (6) embeds a kinetic process of grain growth accompanied with solute segregation (i.e., $\Gamma_b \rightarrow \Gamma_{b0}$) and decreased GB energy, as well as the stop of grain growth, although it cannot describe quantitatively the relation between thermodynamic state and kinetic process. Fortunately, the combination of Γ_b (=$\delta\rho x_b$, with δ, ρ, x_b as the density, thickness and concentration of the GB), McLean's equation and a simple mass conservation equation ($x_0 = x_b f + x_g(1-f)$, with f as the fraction of GB volume) leads to the evolution of Γ_b with grain size quantitatively [19],

$$\frac{\Gamma_b}{\Gamma_{b0}-\Gamma_b} = \frac{x_0 - (D^3-(D-\delta)^3/D^3)(\Gamma_b/\delta\rho)}{1-x_0+(D^3-(D-\delta)^3/D^3)(\Gamma_b/\delta\rho-1)}\exp\left(\frac{\Delta H_{seg}}{RT}\right) \quad (7)$$

The above equation gives out the change of Γ_b with grain size from the viewpoint of thermodynamics, namely, the change of the parameters describing the grain growth process is implied in the above thermodynamic relationships. As shown in Fig. 2, Γ_b increases gradually with increasing grain size and infinitely approaches Γ_{b0} at metastable equilibrium. For an alloy with fixed x_0, if x_α is reached from x_g as grain growth stops ($D = D^*$) with saturated GBs, then Γ_b approaches Γ_{b0} at the metastable equilibrium (Figs. 1 and 2). But this is far from enough to describe the NC grain growth, and the real kinetic process should also be considered. In the following, the stop of grain growth will be concisely described, in terms of thermodynamic and kinetic analysis on the basis of Eq. (2) or (6).

Thermodynamically, Eqs. (2) and (3) serve for the final state of metastable equilibrium, but it also infers possible unsaturated GBs, i.e., different x_0 leads to different Γ_b, and in turn, different D, as grain growth stops. From Figs. 1 and 2, x_g (=x_0-3$\Gamma_b V_m/D$) decreases or increases with grain growth; only if Γ_{b0} and x_α are reached, the real metastable equilibrium indicated by zero GB energy being obtained. So Eq. (2) can be physically reasonable to adopted to

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[1] On the other hand, if $x_g < x_\alpha$, then increasing the bulk concentration from x_g to x_α equals to increasing the second term at the right-hand side of Eq. (2). Since x_α corresponds to the saturated GBs with zero GB energy, σ_0 must be according to Eq. (2) positive if $x_g < x_\alpha$. So, Eq. (2) holds for this case.

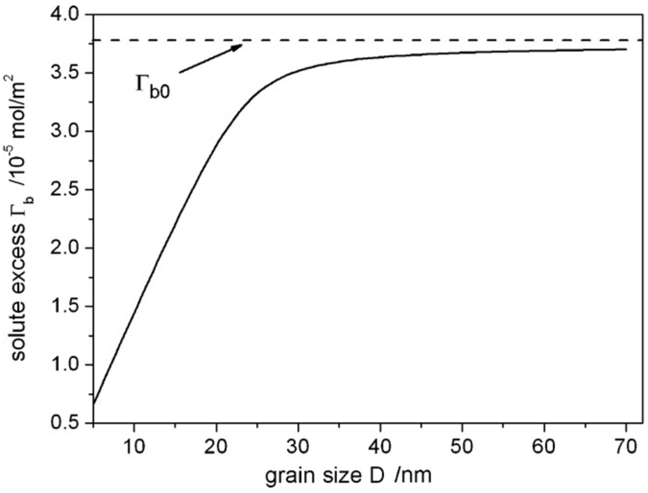

Fig. 2. Solute excess Γ_b as function of grain size D. Using Eq. (8) and adopting typical values of $\Delta H_{seg} = 50$ kJ/m^2, $\Gamma_{b0} = 3.8 \times 10^{-5}$ mol/m^2, $\delta\rho = 4.8 \times 10^{-5}$, $T = 1000$ K and $x_0 = 10$ at.% give an evolution of Γ_b with D. It is shown that Γ_b increases continuously and approaches infinitely to its saturated value Γ_{b0}.

describe grain growth. This is compatible with the description shown in Refs. [17,18], i.e., grain growth is a kinetic process controlled by thermodynamic factor (reduced GB energy with grain growth), but the thermodynamic factor is physically different from the drag force (i.e., the kinetic factor).

From Eq. (4), for the stop of grain growth with saturated GBs, Eq. (6) can be rewritten as,

$$0 = \left|\sigma_0 - \frac{D^*(x_0 - x_\alpha)}{3V_m}\left[RT\ln(x_\alpha) + \Delta H_{seg}\right]\right| \tag{8}$$

The state of $\sigma_b = 0$ leads to,

$$D^* = \frac{3V_m\sigma_0}{(x_0 - x_\alpha)(RT\ln(x_\alpha) + \Delta H_{seg})} \tag{9}$$

The combination with Eq. (6) gives,

$$\sigma_b = \left|\sigma_0 - \frac{D^*(x_0 - x_\alpha)}{3V_m}\left[RT\ln(x_g) + \Delta H_{seg}\right]\right| = \sigma_0\left|1 - \frac{RT\ln x_g + \Delta H_{seg}}{RT\ln x_\alpha + \Delta H_{seg}}\right| \tag{10}$$

So far, the thermodynamic relationships among parameters, σ_b, x_g, Γ_b and D have been derived and given by Eqs. (6), (7) and (10), which imply the kinetic process of the grain growth. The stable grain size can be achieved when $\sigma_b = 0$ (Eqs. (8) and (9)). In combination with Fig. 1, Eq. (10) can be described as follows. Only if x_g is equal to x_α, i.e., Γ_{b0} is satisfied, GB energy can reduce to zero. So far, two kinds of evolution of x_g with grain growth have been observed, i.e., $x_g \geq x_\alpha$ and $x_g \leq x_\alpha$ (Fig. 1). As shown in Fig. 3, for segregation couples such as Ni–P [24], Pd–Zr [12] and Ni–Hf [26] with high ΔH_{seg}, $x_g \geq x_\alpha$ holds, i.e., x_g decreases upon growth, whereas, for Ni–W [25] with small ΔH_{seg}, $x_g \leq x_\alpha$ holds i.e., x_g increases upon growth. For the former case, the effect of high ΔH_{seg} makes Eq. (10) close to zero, even if x_g is not equal to x_α; if ΔH_{seg} is sufficiently high, the state of $\sigma_b = 0$ probably results. For the latter case, if ΔH_{seg} is so small (e.g. near to $RT\ln x_g$), then the state of $x_g \neq x_\alpha$ leads to the GB energy deviating substantially from zero.

Generally, x_g approaches but is not equal to x_α i.e., $\sigma_b \neq 0$, even if grain growth stops. With reference to Ref. [25], a stable nanostructure in Ni–W system has been found despite a subtle degree of GB segregation. Using atomistic computer simulations, a GB energy of about 0.35 J/m^2 is obtained through comparison with the experimental relation of D *vs.* x_g; an approximation of 60% reduction from the pure Ni value of 0.87 J/m^2 is proved to be able to stabilize the NC growth.

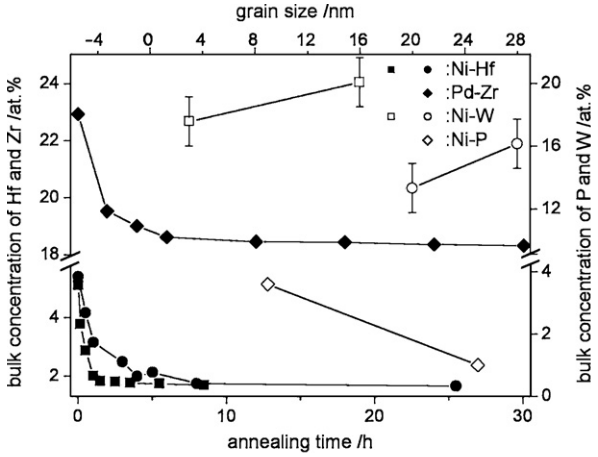

Fig. 3. Bulk concentration as function of grain size D for NC Ni–W [25] and Ni–P [24] alloys and as function of annealing time for NC Ni–Hf [26] and Pd–Zr [12] alloys. Symbols -■- and -●- show the evolution of Hf concentration with time in Ni (Hf) solid solution isothermally annealed at 586 K and 570 K, respectively. Symbol -◆- shows the evolution of Zr concentration with time in Pd-Zr solid solution isothermally annealed at 873 K. Symbols -□- and -○- show the evolution of W concentration with grain size in NC Ni-13 at.%W and Ni-21 at.%W alloys isothermally annealed at 600 °C for 0.5 h and 3 h, respectively. Symbol -◇- shows the change of P concentration in NC Ni-3.6 at.%P alloy isochronally heated with a rate of 5 °C/min to 400 °C.

4. Conclusions

In summary, nano-scale grain growth belongs to a kinetic process controlled by thermodynamic factor (reduced GB energy with grain growth). The changes of the parameters describing the kinetic process of grain growth are implied by the thermodynamic relations among them. For a given segregation couple, the bulk concentration and GB excess at saturation are fixed, which correspond to zero GB energy as grain growth stops. Generally, the bulk concentration and GB excess are not equal to their ideal values at the stop of grain growth, and the GB energy is not equal to zero. The deviation from zero depends mainly on the segregation couple itself, i.e., the magnitude of ΔH_{seg}.

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