



Mitigating grain growth in binary nanocrystalline alloys through solute selection based on thermodynamic stability maps



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ABSTRACT

Mitigating grain growth at high temperatures in binary nanocrystalline alloys is important for processing nanocrystalline alloy systems. The objective of this research is to develop a methodical design-based approach for selecting solutes in binary nanocrystalline alloys by revisiting grain boundary thermodynamics and the internal processes of grain growth and solute segregation in a closed system. In this work, the grain boundary energy is derived and systematically studied in terms of temperature, grain size, concentration, and solute segregation for binary systems of 44 solvents and 52 solutes, using readily-available elemental data, such as moduli and liquid enthalpy of mixing. It is shown that through solute segregation, the grain boundary energies of some binary systems can be reduced, resulting in thermodynamically stable grain structures and successful prediction of solutes that inhibit grain growth in some nanocrystalline alloys. Parametric studies reveal trends between equilibrium grain size, solute distribution and temperature for various binary systems culminating in the generation of nanocrystalline thermodynamic stability maps as a tool for solute selection in binary nanocrystalline alloys.

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1. Introduction

Nanocrystalline (nc) alloys [1] are an important subset of metallic materials due to their small grain size (<100 nm) which imparts properties and potential applications that may not be achievable using conventional coarse-grained polycrystalline materials. For instance, they tend to possess extremely high strengths [2–8] that are associated with grain boundary strengthening (*i.e.*, the Hall–Petch effect [9,10]). A fundamental limitation to their use comes from their inherent thermal instability, which has been extensively explored using both experiments [11–19] and computational approaches [20–33]. The small grain size produces an extremely large driving force for grain growth. If not kept in check, grain growth can occur at modest temperatures, even at room temperature in pure materials such as copper and palladium [34]. Since bulk nanocrystalline alloys are often produced via mechanical alloying [35,36], this grain growth phenomenon provides a significant obstacle to consolidating the nanocrystalline powders by traditional powder metallurgy techniques where high temperature sintering is common.

There are several methods that have been devised to circumvent this temperature sensitivity and stabilize the grain size.

Grain size stabilization commonly involves adding small quantities of an insoluble element (*i.e.*, solute). Nonequilibrium processing (*e.g.*, mechanical alloying, rapid solidification, etc.) is often used to force the solute into solution and, upon heating, the solute segregates to interfaces such as grain boundaries [37,38]. Alternatively, the solute will remain in solution or precipitate out as a second phase. These two basic mechanisms for stabilization are known as thermodynamic and kinetic stabilization, respectively [39]. For kinetic stabilization, the solute acts to hinder grain boundary mobility by diffusion-related means such as solute drag [40] or by pinning boundaries with a fine dispersion of precipitates [41]. For thermodynamic stabilization, solute is expected to segregate to grain boundaries and reduce the grain boundary energy so as to minimize or eliminate the driving force for grain growth [16,20,32,42–49]. Since grain boundary energy is the driving force for grain growth, a reduction in grain boundary energy can impede or even entirely inhibit grain growth. The reduction in grain boundary energy provided by a segregating solute is determined by the segregation energy, ΔG_{seg} [16,20,32,42–49]. Since the values of ΔG_{seg} are usually not available, they are estimated. Wynblatt and Chaitain [50] recently reviewed the analytical models on segregation to grain boundaries (GBs) and surfaces and addressed the difficulty of meaningful definitions of segregation enthalpy, entropy, and free energy among various issues. The central equation for all models is as follows for a binary system:

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$$\frac{x_B^{GB}}{1 - x_B^{GB}} = \frac{x_B^I}{1 - x_B^I} \exp \left[-\frac{\Delta G_{seg}^{ex}}{RT} \right], \quad (1)$$

where x_B^{GB} and x_B^I are the mole fractions of component B (solute) in the grain boundary and grain interior, respectively, ΔG_{seg}^{ex} is the excess Gibbs energy of segregation, and R and T are the gas constant and absolute temperature, respectively. The Gibbs energy of segregation is thus defined as follows:

$$\begin{aligned} \Delta G_{seg} &= \Delta H_{seg} - T\Delta S_{seg} = \left(\Delta H_{seg} - T\Delta S_{seg}^{ex} \right) - T\Delta S_{seg}^{ideal} \\ &= \Delta G_{seg}^{ex} - T\Delta S_{seg}^{ideal}, \end{aligned} \quad (2)$$

where ΔH_{seg} and ΔS_{seg} are the enthalpy and entropy of segregation, respectively, and the entropy of segregation can be broken into two parts: the excess entropy of segregation ΔS_{seg}^{ex} and the ideal entropy of segregation ΔS_{seg}^{ideal} . The ideal entropy of segregation is defined as the ideal entropy change of the system, including both grain and grain boundary regions, due to segregation:

$$\Delta S_{seg}^{ideal} = -R \ln \frac{x_A^I x_B^{GB}}{x_B^I x_A^{GB}}. \quad (3)$$

where the component A refers to the solvent. Hence, Eq. (1) is obtained by substituting the functional form for the entropy term (Eq. (3)) and setting Eq. (2) equal to zero (i.e., $\Delta G_{seg} = 0$), which indicates zero driving force for solute segregation to the interface (e.g., see Ref. [50]). With a given model for ΔG_{seg}^{ex} the compositions in the grain boundary and grain interior can be obtained and are further used to evaluate the grain boundary energy of isotropic or anisotropic systems.

Conventionally, the interfacial energy is defined as the reversible work needed to create a unit area of surface (e.g., grain boundary) at constant temperature, volume (or pressure), and chemical potentials, i.e., for an open system [50]. However, in practical applications, the interfacial energy is measured in a closed system (i.e., constant compositions). In the present work, we will first derive the expression of grain boundary energy for a closed system by differentiating the internal and external variables and defining the internal processes, and then predict the effect of segregating solutes on the grain boundary energy in binary systems of 44 solvents and 52 solutes. Here, we are only considering two internal processes: grain growth and grain boundary segregation. Thus, we are assuming that no secondary phases are forming, which is a reasonable approximation in the dilute case where phase formation will be kinetically hindered [42]. Section 2 describes the thermodynamic details of the present model. This reduction in grain boundary energy modeled herein can then be used to select binary nanocrystalline alloys in terms of thermal stability maps. Section 3 applies the present model first to the case of Fe–Zr and then considers a large number of binary systems in several relevant metals. The significance of this research is in the development of thermodynamic stability design maps as a way to organize and select alloy compositions for nanocrystalline grain growth mitigation.

2. Thermodynamics of grain growth and segregation

The combined first and second laws of thermodynamics of a system can be written as [51]

$$dG = -SdT + VdP + \sum_i \mu_i dN_i - Dd\xi, \quad (4)$$

where G , S , V , and μ_i are the Gibbs energy, entropy, volume, and chemical potential of component i of the system; T , P , and N_i are temperature, pressure, and moles of component i controlled from surroundings; ξ and D represent the extent of an internal process and its driving force and more than one simultaneous internal pro-

cesses can be considered as shown below. For a system with a grain boundary area of A which reaches a metastable equilibrium under constant temperature, pressure, and compositions, each term in Eq. (4) becomes zero, i.e., $dG = 0$.

Let us now consider an internal process with the grain boundary area changed by dA . Due to the composition difference between the grain boundary and the grain interior, there will be a simultaneous re-distribution of elements, commonly referred to as segregation. These two internal processes contribute to the change of Gibbs energy of the system as follows [51]:

$$dG = \sum_i (\mu_i^{GB} - \mu_i^I) dn_i + \gamma_0 dA, \quad (5)$$

where μ_i^{GB} and μ_i^I are the chemical potentials of component i in the grain boundary and grain interior, respectively, dn_i is the change of component i from the grain interior to the grain boundary, and γ_0 is the change in G due to a change in A at constant n_i , i.e.,

$$\gamma_0 = \left(\frac{\partial G}{\partial A} \right)_{n_i, T, P, N_i}. \quad (6)$$

$\mu_i^{GB} - \mu_i^I$ can be further written as

$$\mu_i^{GB} - \mu_i^I = RT \ln \left(\frac{x_i^{GB}}{x_i^I} \right) + G_i^{ex/GB} - G_i^{ex/I}, \quad (7)$$

where $G_i^{ex/GB}$ and $G_i^{ex/I}$ are the partial excess Gibbs energy of component i in the grain boundary and grain interior, respectively. For a binary A–B system, we have $dn_A = -dn_B$, and Eq. (5) can be re-written as

$$\begin{aligned} dG &= \left[RT \ln \left(\frac{x_B^{GB}}{1 - x_B^{GB}} \frac{1 - x_B^I}{x_B^I} \right) + \Delta G_{seg}^{ex} \right] dn_B + \gamma_0 dA \\ &= \Delta G_{seg} dn_B + \gamma_0 dA, \end{aligned} \quad (8)$$

where ΔG_{seg}^{ex} and ΔG_{seg} are defined as

$$\begin{aligned} \Delta G_{seg}^{ex} &= G_B^{ex/GB} - G_B^{ex/I} - \left(G_A^{ex/GB} - G_A^{ex/I} \right) \\ &= G_B^{ex/GB} - G_A^{ex/GB} - \left(G_B^{ex/I} - G_A^{ex/I} \right), \end{aligned} \quad (9)$$

and

$$\Delta G_{seg} = \left(\frac{\partial G}{\partial n_B} \right)_{A, T, P, N_A, N_B}, \quad (10)$$

It is evident from the above equations that the grain boundary energy for a closed system is defined as [52]

$$\gamma = \left(\frac{\partial G}{\partial A} \right)_{T, P, N_A, N_B} = \Delta G_{seg} \frac{\partial n_B}{\partial A} + \gamma_0, \quad (11)$$

There are two significant observations from the above derivations: (1) ΔG_{seg}^{ex} is related to the partial quantities of excess Gibbs energy of grain and grain boundary, not the excess Gibbs energies themselves, and (2) $\gamma = \gamma_0$ when $\Delta G_{seg} = 0$, meaning there is no redistribution of elements during a change of grain boundary area. The latter is a constrained equilibrium, because it poses a limitation on an internal process for a closed system, which would otherwise take place to reduce the Gibbs energy of the system. Therefore, the widely used Eq. (1), commonly referred to as Langmuir–McLean (or Fowler–Guggenheim) segregation isotherm is applicable when the redistribution of elements is negligible during measurements of grain boundary energies. If this is not the case, Eq. (11) should be used for grain boundary energy.

There are many models on how to treat ΔH_{seg} and ΔS_{seg}^{ex} in Eq. (2) as discussed by Wynblatt and Chatain [50] including their dependence on five degrees of freedom of grain boundaries. In the present model, the grain boundary character, or the distribution of grain boundaries, is not explicitly modeled. Rather, it is anticipated

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