



Modeling solute segregation in grain boundaries of binary substitutional alloys: Effect of excess volume



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ARTICLE INFO

Article history:

Received 2 December 2015

Received in revised form

15 April 2016

Accepted 26 April 2016

Available online 27 April 2016

Keywords:

EAM

GB segregation

Excess volume

Helmholtz free energy

ABSTRACT

The effect of excess volume in grain boundary (GB) on GB solute segregation was quantitatively evaluated by means of thermodynamic modeling. Helmholtz free energies of bulk (grain interior) and GBs in binary substitutional systems with fcc (face centered cubic) and bcc (body centered cubic) crystal structures were derived as functions of composition, temperature and atomic volume by applying Embedded-atom-method (EAM) to standard thermodynamic relations under random site occupation assumption. The equilibrium solute distribution between GBs and bulk was then obtained in terms of the parallel tangent construction between bulk and GB phases' Helmholtz free energy curves. By modeling the Cu–Ag (fcc) and W–Nb (bcc) systems, an enhanced GB segregation with increased GB excess volume was predicted. The segregation enthalpy and the solute enrichment ratio were further calculated, showing good agreements with the experimental and simulated results.

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1. Introduction

Beneficial from solute-segregation induced decrease in grain boundary (GB) energies, solute addition becomes an effective approach to improve the thermal stability of nanocrystalline materials and has been widely applied in grain size refining [1–5]. Accordingly, the mechanism of enhanced thermal stability of nanocrystalline alloys by GB segregation has been intensively investigated [6–16]. Of which, the thermodynamic modeling of alloys plays an increasingly important role in design of alloy composition and evaluation of thermal stability, by formulating some GB segregation related essential thermodynamic quantities (such as segregation enthalpy and GB energy reduced by GB segregation) and further establishing a relationship between metastable grain size and total solute concentration at a given temperature [6–13]. For instance, Saber et al. developed a thermodynamic model [12] incorporating both the chemical (from bond energies) and elastic (from strain energy) contributions to GB segregation to predict a composition- and temperature-dependent metastable grain size in nanocrystalline alloys and further extended it to ternary alloy systems [13]. Recently, a nanostructured stability map [17] was constructed to specify the types of

solute elements that can stabilize the nanostructured tungsten alloys against coarsening at elevated temperatures. This strongly highlights the importance of thermodynamic modeling on evaluating the thermal stability of nanocrystalline alloys.

Although it has been demonstrated that GB segregation is strongly dependent on the intrinsic structure of GBs [18], the effect of intrinsic GB structure has rarely been involved in the aforementioned researches, considering the diversity and complexity of GB structures in polycrystalline alloys. Hence, simplification of GB structures would be exploited in order to enable a reliable prediction of average/overall GB segregation behavior. It has been found that GB excess volume, ΔV , arising from reduced atomic density in GBs, may be one of the most significant quantities in reflecting the intrinsic structure and thermodynamic properties of GBs [19–22]. Thus a philosophy [23–25] that GBs can be simplified as an expanded lattice possessing larger interatomic distance and excess volume when compared with equilibrium lattice (i.e. bulk), was proposed. On this basis, a GB segregation model was derived by Kirchner and Kieback [26] by combing Hillert's classical thermodynamic treatment [27] with this GB-structure assumption [23–25].

It should be pointed out that, in Kirchner and Kieback's model, under the premise of dilute solution, two important model parameters, i.e. bulk modulus and anharmonicity parameter of solution are set equivalent to those of solvent element. However, in the case of alloys with strong tendency of GB segregation, high GB

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solute concentration would be desired so that the GB cannot be considered as a dilute solution and thereby this treatment would not be applicable. As a consequence, the present work aims to establish a thermodynamic relation between GB segregation and GB excess volume, and thus to formulate some crucial thermodynamic quantities (e.g. segregation enthalpy and GB energy) under the framework of thermodynamics. Furthermore, based on these derived thermodynamic quantities, the thermal stability of alloy systems will be evaluated. Note that, this model is designed to work irrespective of whether the tendency of GB segregation of a system is strong or weak.

2. Model derivation

In this work, for the sake of simplicity, only binary substitutional system is concerned. A philosophy, which draws the overall solute segregation in GBs of binary polycrystalline alloys as well as the related GB energy affected by GB segregation, has been proposed by Hillert [27], see Fig. 1. For this, the whole system is assumed to remain at equilibrium and GBs are treated as a thermodynamic phase with a constant thickness, free energy function, composition, and molar volume. The molar free energy curve of GB phase can then be included in a free energy diagram of a binary polycrystalline alloy $A_{1-x}B_x$ (A and B represent solvent and solute, respectively, and x the molar ratio of solute). Assuming that the partial molar volumes of the two phases are independent of the composition, and only a pairwise exchange of atoms is possible between bulk and GB phases under a given GB volume fraction. At equilibrium, the total change of free energy must be zero for the process of atoms exchange. This condition requires $\mu_A^{GB} - \mu_A^{bulk} = \mu_B^{GB} - \mu_B^{bulk}$ (μ the chemical potential) and can be met, provided that x_B^{GB} and x_B^{bulk} are defined by the parallel tangent construction of Helmholtz free energy (F_{mix}) curves, i.e. [27],

$$\frac{\partial F_{mix}^{GB}}{\partial x_B^{GB}} = \frac{\partial F_{mix}^{bulk}}{\partial x_B^{bulk}} \quad (1)$$

Incorporating the Helmholtz free energy functions of bulk and GB phases into Eq. (1), GB solute concentration x_B^{GB} can be thus solved under the given bulk solute concentration x_B^{bulk} . Therefore, the crucial point lies in constructing the Helmholtz free energy functions of bulk and GB phases; simplification of GB structure would be convenient to develop an analytical expression of GB free energy. As depicted in Introduction, GBs can be simplified as an expanded lattice characterized by GB excess volume, which is

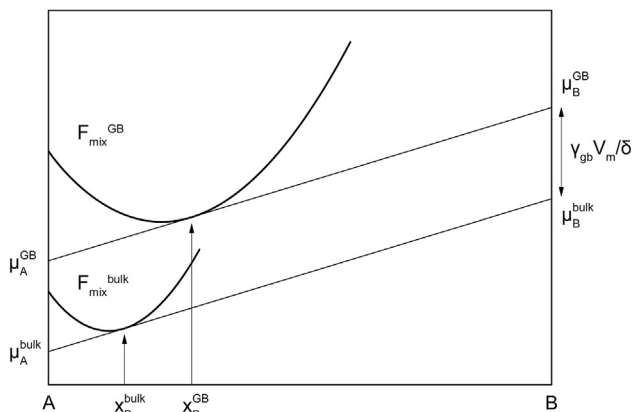


Fig. 1. Illustration of Helmholtz free energy for binary system $A_{1-x}B_x$ containing GB and bulk parts (modified from Ref. [24]).

employed in the current work. This means that the derivations of the free energy functions of both bulk and GB phases can be performed with the same procedure but different atomic volume involved.

2.1. Helmholtz free energy

With the Helmholtz free energy of pure element (as shown in Appendix A), according to regular solution approximation, the Helmholtz free energy F_{mix} of binary substitutional system $A_{1-x}B_x$ can be depicted as a function of composition, temperature, and atomic volume (i.e. $V = (1 + \Delta V)V_0(T_R)$ with ΔV the excess volume and $V_0(T_R)$ the equilibrium atomic volume of solvent A at reference temperature T_R):

$$F_{mix} = E_{mix} + C_V(T - T_R) - T[(1-x)S_A + xS_B] - TC_V \ln(T/T_R) + RT[(1-x)\ln(1-x) + x\ln x] \quad (2)$$

where E_{mix} denotes the internal energy of $A_{1-x}B_x$ at T_R , C_V the heat capacity at constant volume, T the absolute temperature, and S the entropy at T_R with the subscripts "A" and "B" representing solvent and solute respectively, and R the molar gas constant. The explicit expressions of C_V , S_A and S_B are also shown in Appendix A. Generally, the term E_{mix} would deviate from the weighted average value of components, i.e. $(1-x)E_A + xE_B$, and thereby requires a precise evaluation.

Embedded-atom-method (EAM), an effective way to evaluate the internal energy of alloys which is dependent on the interatomic distance, has been combined successfully with computer simulation and/or mathematical modeling to predict material properties and to elucidate some physical phenomena [28–33]. Note that, interatomic distance is definitely related to atomic volume and thus excess volume, which would then enable us to apply EAM to evaluate the internal energy of $A_{1-x}B_x$, E_{mix} . Considering EAM is more applicable in body-centered cubic (bcc) and face-centered cubic (fcc) structures, in this work, only bcc and fcc systems will be concerned.

The basic equations of EAM are shown as [29,32],

$$E_{tot} = \sum_i E_i \quad (3)$$

$$E_i = F_i(\rho_i) + \frac{1}{2} \sum_{j \neq i} \phi_{ij}(r_{ij}) \quad (4)$$

$$\rho_i = \sum_{j \neq i} f_j(r_{ij}) \quad (5)$$

where E_{tot} represents the total internal energy of an assembly of atoms, E_i the internal energy of atom i , ρ_i the electron density at atom i due to the other atoms in the system, $F_i(\rho_i)$ the energy to embed atom i into the electron density ρ_i , $\phi_{ij}(r_{ij})$ the two-body potential between atoms i and j with the separation distance r_{ij} , and $f_j(r_{ij})$ the contribution to the electron density at atom i due to atom j with the distance r_{ij} .

For alloys, atomic electron density function $f(r)$ and embedding function $F(\rho)$ must be specified for each species meanwhile a two-body potential $\phi(r)$ should also be identified for each possible combination of atomic species. Based on the assumptions that the electron density at any location is set as a linear superposition of atomic electron densities and that the embedding energy is independent of the source of electron density [30], $f(r)$ and $F(\rho)$ for

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