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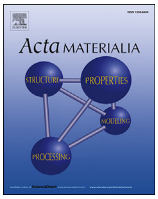

Full length article

Embedded-atom study of grain boundary segregation and grain boundary free energy in nanosized iron–chromium tricrystals

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ABSTRACT

We present a theoretical study of equilibrium grain boundary (GB) segregation in a tricrystal setup using a thermodynamically accurate iron–chromium embedded-atom potential. Through continuous variation of the chemical potentials, the full concentration range is explored in the temperature range of 600 K –1100 K, evaluating segregation below and above the critical temperature of the miscibility gap. Key findings are: i) the GB excess entropy is rather small and shows only weak variation with temperature; ii) due to the small lattice mismatch in the iron–chromium system, segregation can reasonably be predicted by comparing the $T = 0$ energies of iron and chromium; iii) every atomic site in the defects undergoes the occupation probability transition at a different chemical potential, resulting in stepwise segregation isotherms; iv) the extraordinary thermodynamic properties of the iron–chromium system lead to negative GB free energies on the chromium-rich side; v) the width of the GB segregation zone decreases with temperature and depends significantly on the bulk concentration; vi) the additional triple junction (TJ) excess segregation is small relative to the GBs and for the most part a geometric effect of the finite width of the GB segregation zones. Available experimental data of GB segregation on the iron-rich side are in good quantitative agreement with the presented results.

1. Introduction

While it is well established that point defects like vacancies belong to the thermodynamic equilibrium in pure solids, it is less clear whether extended defects like grain boundaries (GBs) can belong to the thermodynamic equilibrium as well [1–6]. The consequences of GBs as equilibrium defects are versatile in materials science, leading to e.g. experimentally reported inhibited grain growth [4,5] or easy formation of kinks in GBs. In single component systems, configurational effects are not believed to decrease the GB free energy sufficiently enough to establish a stable part of the system [2]. However, multi-component systems provide a further mechanism of reducing the free energy by solute segregation to the GBs.

The relationship between interfacial free energy γ and excess segregation Γ of a component with chemical potential μ has already been studied by Gibbs [7] and is known as the interfacial adsorption equation for liquids (and should be used with caution in solids as will be noted in subsection 2.1):

$$d\gamma = -\Gamma d\mu. \tag{1}$$

This equation implies the general assumption that the component with lower interfacial energy segregates at interfaces embedded in the component of higher interfacial energy. It is questionable whether segregation can change the energetics in such a way that the interfacial energy becomes zero or even negative. In order to induce a negative GB free energy, the energy density of the segregating atoms in the interface needs to be considerably lower than the one of the surrounding matrix so that the structural energy of the interface becomes over-compensated.

In the vast majority of systems, the energy density of the GB is higher than the one of the matrix. However, there might be exceptions. In the present study, we focus on the iron–chromium system, since it reveals an extraordinary thermodynamic behavior which is reflected by the data in Table 1. Although chromium has the higher GB energy than iron, it nevertheless shows weaker bonding. The higher GB energy of chromium induces strong segregation of iron to the GBs in chromium, while the considerably better bonding of iron should help drive the excess energy of the GB into the negative regime.

In this work, we investigate an iron–chromium tricrystal

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Table 1
Thermodynamic key parameters: differences in cohesive energy ΔU_0 and in specific GB ($\Sigma 5(\bar{1}02)$) energy $\Delta\gamma_{\mathrm{GB}}$ of iron and chromium. Density functional theory (DFT) calculations were not fully relaxed.

	$\Delta U_0 = U_0^{(\mathrm{Cr})} - U_0^{(\mathrm{Fe})}$ (eV)	$\Delta\gamma_{\mathrm{GB}} = \gamma_{\mathrm{GB}}^{(\mathrm{Cr})} - \gamma_{\mathrm{GB}}^{(\mathrm{Fe})}$ (J m^{-2})
Exp. [8]	0.18	
DFT [9,10]		0.52
EAM (this work)	0.18	0.41

configuration by means of an atomistic study using the embedded-atom method (EAM), in order to analyze the stability of nanocrystalline materials in terms of free energy reduction by equilibrium GB segregation at different temperatures over the whole concentration range. The used interatomic EAM potential does not only reproduce the quantitative relations between GB and binding energies of iron and chromium (Table 1), but also describes the phase boundaries of the metastable α/α' miscibility gap with high accuracy [11].

The paper is organized as follows: In section 2, we introduce the concepts of GB thermodynamics and the evaluation scheme for the excess properties. In section 3, we give a brief overview of the computational details. The results of GB and triple junction (TJ) segregation are compiled in section 4, indeed revealing negative GB energies on the chromium-rich side. Finally, we discuss the results in section 5 and relate our findings to available experimental data.

In the following, concentrations will always refer to chromium as the second component in the system, i.e. $c \equiv c_2 \equiv c_{\mathrm{Cr}}$. Hence, the excess segregation Γ will also refer to chromium, i.e. a negative value of the excess Γ will indicate segregation of iron. Differences between a particular property of the two components, e.g. the difference in GB energy, will be stated as $\Delta\gamma = \gamma_2 - \gamma_1 = \gamma_{\mathrm{Cr}} - \gamma_{\mathrm{Fe}}$.

2. Methodology

2.1. Thermodynamics of grain boundaries

For the description of GB thermodynamics, we use the rigorous mathematical framework developed by Frolov and Mishin [12,13]. In the following, the total GB excess of a particular quantity Z will be denoted in the form $[Z]$.

The total free excess energy of the GB with cross-sectional area A for a two-component system at temperature T, chemical potential difference $\Delta\mu = \mu_2 - \mu_1$, and pressure p is then given by

$$\gamma A = [U] - T[S] - \Delta\mu[N_2] + p[V], \tag{2}$$

where γ is the specific (i.e. per area) GB free energy, $[U]$ the total internal excess energy, $[S]$ the total excess entropy, $[N_2]$ the total amount of excess segregation of the second component in the GB, and $[V]$ is accounting for the total excess volume. Equation (2) describes the thermodynamic potential of the GB, in analogy to the thermodynamic potential of a homogeneous bulk phase.

The GB interfacial adsorption equation describes the dependence of the differential of γA on the differentials of the independent intensive variables of the system. This equation can be derived from the first and second law of thermodynamics [12,13] and is given by

$$\mathrm{d}(\gamma A) = -[S]\mathrm{d}T - [N_2]\mathrm{d}\Delta\mu + [V]\mathrm{d}p + A\sum_{i=1,2}\tau_{ii}\mathrm{d}e_{ii}. \tag{3}$$

Note that in contrast to a homogeneous bulk phase, additional mechanical work has to be performed against the intrinsic GB tension τ_{ii} upon expansion e.

Using the relations $\mathrm{d}(\gamma A) = A\mathrm{d}\gamma + \gamma\mathrm{d}A$ and $\mathrm{d}A = A\sum_{i=1,2}\mathrm{d}e_{ii}$, Equation (3) can be rearranged in the form

$$\mathrm{d}\gamma = -\frac{[S]}{A}\mathrm{d}T - \frac{[N_2]}{A}\mathrm{d}\Delta\mu + \frac{[V]}{A}\mathrm{d}p + \sum_{i=1,2}(\tau_{ii} - \gamma)\mathrm{d}e_{ii}. \tag{4}$$

Equation (4) now contains the GB specific excess quantities (i.e. per area) $S_{\mathrm{ex}} \equiv \frac{[S]}{A}$, $\Gamma \equiv \frac{[N_2]}{A}$, and $V_{\mathrm{ex}} \equiv \frac{[V]}{A}$. Note that a change in chemical potential in Equation (4) will also induce compositional strain in the bulk due to the lattice mismatch of the components [13]. As a consequence, the segregation isotherm contains an additional work term stemming from the GB tensions τ_{ii}. Equation (1) will only be recovered for liquids, where $\tau = \gamma$, or in systems with practically no lattice mismatch ($\mathrm{d}e \approx 0$). Equation (4) also leads to mechanochemical Maxwell relations of the GB, which have been demonstrated and proven in Refs. [12,13].

2.2. Grain boundary and triple junction excess quantities

We simulate a cylindrical tricrystal setup as shown in Fig. 1(a), where the TJ is aligned along the cylinder z-axis with periodic boundary conditions along this axis. The three GBs extend in radial r-direction from the TJ center to the free surfaces.

The evaluation of GB excesses in this particular setup requires a more formal treatment of their definitions, since the GB area is not limited in radial direction by periodic boundary conditions, as would be the case in the study of isolated GBs. Therefore, we introduce the GB solute excess $\frac{[N_2]}{A} \equiv \Gamma_{\mathrm{GB}}$ appearing in Equation (4) on the basis of particle densities $\rho_2(\overrightarrow{r})$, i.e. particles per volume, of component 2.

The GB with cross-sectional area A in the x–z-plane is schematically depicted in the right part of Fig. 1(b). In this way, Γ_{GB} can be defined by

$$\Gamma_{\mathrm{GB}} = \frac{1}{A}\sum_{i=1}^{2}\int_V \left(\rho_2^{(i)}(\vec{r}) - \rho_2^{(0)}\right)\mathrm{d}V \tag{5}$$

$$= \frac{1}{x}\int_x \left(\frac{1}{z}\sum_{i=1}^{2}\int_y\int_z \left(\rho_2^{(i)}(\vec{r}) - \rho_2^{(0)}\right)\mathrm{d}z\mathrm{d}y\right)\mathrm{d}x$$

$$=: \frac{1}{x}\int_x \Gamma_{\mathrm{GB}}(x)\mathrm{d}x, \tag{6}$$

where the sum is accounting for the two grains forming the GB, $\rho_2^{(i)}(\overrightarrow{r})$ is the particle density of component 2 in the respective grain, and $\rho_2^{(0)}$ is the particle density in the defect-free bulk.

After rearranging the volume integration, Equation (6) defines the *local* GB excess segregation $\Gamma_{\mathrm{GB}}(x)$, which oscillates according to the periodic GB structure. Equation (6) averages over this periodic structure and converges to the desired specific GB excess value Γ_{GB} if the integration range chosen is large enough. In addition, the integration in y-direction needs to be sufficiently extended into the bulk (dashed lines in Fig. 1(b)), so that convergence of the particle densities $\rho_2^{(i)}(\overrightarrow{r})$ to the bulk value $\rho_2^{(0)}$ is ensured.

Since atomistic simulations deal with discrete positions $\overrightarrow{r}_j$, the particle density $\rho_2(\overrightarrow{r})$ is expressed by the Dirac δ distribution:

$$\rho_2(\overrightarrow{r}) = \sum_j \delta(\overrightarrow{r} - \overrightarrow{r}_j)n_j. \tag{7}$$

Here, n_j describes the probability that atomic site r_j is occupied by a particle of type 2, which is equivalent to the concentration c_2 if the average over several equivalent positions is taken. Equation (5) then simply reduces to conventional "counting" of excess atoms as compared to the bulk.

By dimensional consideration following King [14], the TJ excess quantities can be defined relative to the joining GBs by reducing the