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Kinetics of grain boundary segregation in multicomponent systems – The example of a Mo-C-B-O system

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ABSTRACT

A model for kinetics of segregation of several interstitial and substitutional components to different kinds of traps at grain boundaries is derived by applying the Thermodynamic Extremal Principle. Evolution equations for the site fractions of the segregating elements at the grain boundary, considered as independent variables, are presented and solved numerically. The kinetic model is applied to the case of Mo containing C, O, and B as impurities and a spectrum of trapping energies obtained from first principles simulations. This newly developed model offers an efficient tool for understanding segregation from several kinds of components at different types of traps.

Grain boundary (GB) segregation is of high practical relevance as origin of GB embrittlement or strengthening. Here we refer to a very recent overview by Lejček et al. [1] and an overview on hundreds of calculations concerning the change of GB cohesion by Gibson and Schuh [2]. GB segregation of interstitial and substitutional migrating atoms has been also studied experimentally in numerous papers, see, e.g., [3] and the references there. The GB segregation can be treated thermodynamically, as stated in the review paper by Kalidindi et al. [4]. Since the segregation is a time-dependent process controlled by bulk diffusion, kinetic models have been developed, see e.g. [5–7]. Some of the authors recently applied the Thermodynamic Extremal Principle (TEP) [8] for deriving an equation for segregation kinetics of one interstitial component to one kind of traps, see [9]. When comparing to segregation in a real material, the assumption of one single trap is, however, a strong restriction. Real grain boundaries exhibit several trapping sites with different trapping energies and, thus, a distribution of trapping energies must be assumed [10]. Furthermore, real materials usually contain several species of impurities simultaneously and the so-called site-competition effect can strongly alter the GB content. Hence, we extend the previous approach and develop a multicomponent and multitrapping kinetic thermodynamic model which can be coupled in a straightforward way to density functional theory calculations [11,12] providing the distribution of trapping energies. The simulation approach is demonstrated for a simple example of high practical relevance where a metal is heated to a high temperature T_0 and cooled down with certain kinetics. In general one cannot assume that the segregation state is the equilibrium state corresponding to T_0 since during cooling the solutes (especially the interstitials) can diffuse and increase the GB occupation. It is also not trivial to find out at which temperatures the GB state is "freezed in" and, hence, a full multi-component and multi-trapping kinetic simulation accounting for the temperature history represents the only possibility to quantify the segregation state.

In our kinetic model we assume N components with fixed mean site fractions x_k in the system, $k = 1, \ldots, N$ segregating to n types of traps in grain boundaries with the volumetric fractions (related to the whole system) $f^i, \quad i = 1, \ldots, n, \sum_{i=1}^{n} f^i = f$. To each segregating component k and type of trap i a molar trapping energy E_k^i is assigned. As a system of total volume Ω we consider a polycrystal of grains with effective radius R_G involving one mole of lattice positions. To describe the state of the system, we introduce as internal variables:

- $\bar{x}_k, k = 1, \ldots, N$ being the site fraction of segregating component k in the bulk of grains,
- $\hat{x}_k^i, k = 1, \ldots, N, i = 1, \ldots, n$ being the site fraction of segregating component k at traps of type i.

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The mass balance enforces for $k = 1, \ldots, N$

$$x_k = (1-f)\bar{x}_k + \sum_{i=1}^{n} f^i \hat{x}_k^i, \tag{1}$$

which allows calculating the constraints for rates $\dot{\bar{x}}_k$ and $\dot{\hat{x}}_k^i$ as

$$(1-f)\dot{\bar{x}}_k + \sum_{i=1}^{n} f^i \dot{\hat{x}}_k^i = 0, k = 1, \ldots, N \tag{2}$$

As already outlined in [9] the Gibbs energy G of a system can be calculated based on the so-called trapping concept. The Gibbs energy G consist of three terms, i.e. G_0 as contribution independent of the variables $\bar{x}_k$ and $\hat{x}_k^i$, $\overline{G}$ as contribution of untrapped atoms in the bulk of the grains, and $\hat{G}$ as contribution of trapped atoms in grain boundaries, yielding

$$G = G_0 + \overline{G} + \hat{G}. \tag{3}$$

The contributions $\overline{G}$ and $\hat{G}$ follow with R_g as gas constant and T as temperature

$$\overline{G} = (1-f)R_g T\left[\sum_{k=1}^{N}(\bar{x}_k \ \ln\bar{x}_k) + \left(1-\sum_{k=1}^{N}\bar{x}_k\right) \ \ln\left(1-\sum_{k=1}^{N}\bar{x}_k\right)\right] \tag{4}$$

and

$$\hat{G} = R_g T\sum_{i=1}^{n} f^i\left[\sum_{k=1}^{N}\left(\hat{x}_k^i \ \ln\hat{x}_k^i\right) + \left(1-\sum_{k=1}^{N}\hat{x}_k^i\right) \ \ln\left(1-\sum_{k=1}^{N}\hat{x}_k^i\right)\right] + \sum_{i=1}^{n} f_i\left[\sum_{k=1}^{N}\left(\hat{x}_k^i E_k^i\right)\right]. \tag{5}$$

The quantity E_k^i represents the change of the energy of the system, if one mole of atoms of component k occupies the traps of type i. Atoms are trapped for $E_k^i < 0$ and escape for $E_k^i > 0$. The partial derivatives of G with respect to $\bar{x}_k$ and $\hat{x}_k^i$ read after some analysis as

$$\frac{\partial G}{\partial \bar{x}_k} = (1-f)R_g T \ \ln\left[\bar{x}_k/\left(1-\sum_{l=1}^{N}\bar{x}_l\right)\right], k = 1, \ldots N \tag{6}$$

$$\frac{\partial G}{\partial \hat{x}_k^i} = f^i\left\{R_g T \ \ln\left[\hat{x}_k^i/\left(1-\sum_{l=1}^{N}\hat{x}_l^i\right)\right] + E_k^i\right\}, k = 1, \ldots N, \quad i = 1, \ldots, n. \tag{7}$$

As the individual traps in the GB are very near to each other and also interconnected by fast diffusion paths [13–15], it is justified to assume thermodynamic equilibrium amongst the traps for each component.

For fixed values of x_k the global equilibrium corresponds to minimum of $\hat{G}$ with respect to $\hat{x}_k^i$ and $\bar{x}_k$ obeying the constraints Eq. (1). The necessary conditions for the constrained minimum read with the Lagrange multipliers λ_k, $k = 1, \ldots, N$ as

$$\frac{\partial}{\partial \hat{x}_k^i}\left[G-\lambda_k\left(\sum_{j=1}^{n} f^j \hat{x}_k^j + (1-f)\bar{x}_k - x_k\right)\right] = 0, k = 1, \ldots N, \quad i = 1, \ldots, n, \tag{8}$$

$$\frac{\partial}{\partial \bar{x}_k}\left[G-\lambda_k\left(\sum_{j=1}^{n} f^j \hat{x}_k^j + (1-f)\bar{x}_k - x_k\right)\right] = 0, k = 1, \ldots, N \tag{9}$$

Performing the derivatives in Eqs. (8)–(9) using Eqs. (6)–(7) yields immediately

$$R_g T \ \ln\left[\hat{x}_k^i/\left(1-\sum_{l=1}^{N}\hat{x}_l^i\right)\right] + E_k^i - \lambda_k = 0, \quad k = 1, \ldots N, \quad i = 1, \ldots, n, \tag{10}$$

$$R_g T \ \ln\left[\bar{x}_k/\left(1-\sum_{l=1}^{N}\bar{x}_l\right)\right] - \lambda_k = 0, k = 1, \ldots, N. \tag{11}$$

From Eqs. (10)−(11) the Lagrange multipliers λ_k can be eliminated for each k reading with $\tilde{E}_k^i = E_k^i/R_g T$ as

$$\ln\left[\hat{x}_k^i/\left(1-\sum_{l=1}^{N}\hat{x}_l^i\right)\right] + \tilde{E}_k^i - \ln\left[\bar{x}_k/\left(1-\sum_{l=1}^{N}\bar{x}_l\right)\right] = 0, k = 1, \ldots, N, i = 1, \ldots, n. \tag{12}$$

A generalized *McLean equation* is obtained directly from Eq. (12) as

$$\hat{x}_k^i/\left(1-\sum_{l=1}^{N}\hat{x}_l^i\right) = \bar{x}_k/\left(1-\sum_{l=1}^{N}\bar{x}_l\right) \ \exp\left(-\tilde{E}_k^i\right), k = 1, \ldots, N, i = 1, \ldots, n. \tag{13}$$

This equation combines the White-Coghlan extension to multiple sites [10–12] with the extension to multiple solutes as outlined in e.g. [1]. Similar as in these earlier models we do not take into account direct interactions between the solutes. That would require trapping energies being dependent on the solute concentrations of all sites. While such effects are interesting to explore in general, we do not include them here. Recent work on C, O and B in Mo has shown that such interactions are very weak at the GB [16]. Finding of equilibrium values of $\hat{x}_k^i$ and for a given x_k requires, with using Eq. (2), the solution of the set of $N \cdot n$ non-linear equations, Eq. (13). However, we are not only interested in equilibrium values but also in the segregation kinetics. For this reason we engage the TEP [8] and have to formulate the dissipation D and the dissipation function Q.

The total dissipation D of the system, see [9], Sect. 1.4, is given by

$$D = -\sum_{k=1}^{N}\left(\frac{\partial G}{\partial \bar{x}_k}\dot{\bar{x}}_k + \sum_{i=1}^{n}\frac{\partial G}{\partial \hat{x}_k^i}\dot{\hat{x}}_k^i\right) \tag{14}$$

and using Eq. (2) as

$$D = \sum_{k=1}^{N}\sum_{i=1}^{n}\left(\frac{f^i}{1-f}\frac{\partial G}{\partial \bar{x}_k} - \frac{\partial G}{\partial \hat{x}_k^i}\right)\dot{\hat{x}}_k^i. \tag{15}$$

Inserting Eqs. (6)–(7) yields

$$D = -\sum_{k=1}^{N}\sum_{i=1}^{n} f^i R_g T\left\{ \ \ln\left[\frac{\hat{x}_k^i\left(1-\sum_{l=1}^{N}\bar{x}_l\right)}{\bar{x}_k\left(1-\sum_{l=1}^{N}\hat{x}_l^i\right)}\right] + \tilde{E}_k^i\right\}\dot{\hat{x}}_k^i. \tag{16}$$

As next step towards kinetic equations the dissipation function Q is introduced (for details, see [8], Sect. 1.4). The dissipation function Q is formulated by the squares of the diffusive fluxes, see, e.g., [17], Sect. 3.2 and [9], accounting both for bulk diffusion in the grain, characterized by coefficients D_k (first term in Eq. (17)) and also for exchange of the components amongst traps in the GB (second term in Eq. (17)), as

$$Q = \sum_{k=1}^{N}\frac{R_g T R_G^2(1-f)^2}{15\bar{x}_k D_k}\left(\dot{\bar{x}}_k\right)^2 + \sum_{i=1}^{n}\sum_{k=1}^{N} U_k^i\left(f^i \dot{\hat{x}}_k^i\right)^2. \tag{17}$$

R_G denotes the effective radius of a grain (do not confuse R_G and R_g).