Available online at www.sciencedirect.com
SCIENCE DIRECT®
Acta Materialia 53 (2005) 3695–3701
Acta MATERIALIA
www.actamat-journals.com

Determination of low-temperature interfacial energies from a pair interaction model

Christine Borchers [a,*], Rüdiger Bormann [b]

[a] Institute of Materials Physics, University of Göttingen, Friedrich-Hund-Platz 1, 37077 Göttingen, Germany
[b] Department of Materials Science and Technology, Technical University of Hamburg-Harburg, 21071 Hamburg, Germany

Received 8 February 2005; received in revised form 5 April 2005; accepted 14 April 2005
Available online 31 May 2005

Abstract

The chemical contribution to the energy of coherent interfaces is calculated from a pair interaction model, which represents an extension of the model presented by Becker in 1938. Nearest neighbour interaction is assumed, and entropy contributions are not considered. Concentration dependence of the pair interaction energies, as well as a change of crystal structure and/or a breakdown of long-range order at the interface are taken into account in the presented model. As examples, the interfacial energy is evaluated for coherent Cu–Co, Fe–Ag, and Cu–Cu_4Ti interfaces. The necessary interaction parameters can be derived from the thermodynamic functions of the system determined experimentally or by thermodynamic calculations, e.g., by using the CALPHAD method.

Keywords: Interfacial energy; Long-range order; Multilayers; Thermodynamics; CALPHAD

1. Introduction

Solid–solid interfaces are omnipresent in engineering materials. Interfaces govern many important properties of the solids which play vital roles in their performance, such as precipitation and coarsening of second phases in bulk materials, or interface sharpness, smoothness and flatness in multilayer structures. In order to predict the performance of a material being considered for possible use, knowledge of the energetics of its internal interfaces is imperative. While the energies of homo-phase boundaries (grain boundaries) are easily accessible from experiments, e.g. [1], and from computational studies, e.g. [2], those of hetero-phase boundaries are difficult to get through experiments in a straightforward manner. Often interfacial energies are fitted to results gained in unmixing experiments, e.g. [3–6]. Spaepen and different co-workers used zero creep [7,8] and calorimetric and magnetic [9] methods. All of these methods give rise to serious uncertainties. Consequently, a number of calculations of this energy have been performed.

Becker [10] employed a nearest neighbour broken bond model under the assumption that both phases are homogeneous up to their common interface. Cahn and Hilliard [11] developed a continuum model of the coherent interphase boundary energy, describing it in terms of the so-called gradient energy, replacing the interfacial energy, when the concentration profile across the boundary is not a step. Lee and Aaronson and before them other scientists cited in their work [12], developed a discrete lattice plane analysis, based on the Becker model, where they analyzed the concentration of not only the boundary lattice planes, but also that of a number of planes beneath. They also calculated the temperature and orientation dependence of interfacial boundary energy. They found that the concentration gradient over the boundary is steeper the lower the temperature, hence Becker's model can successfully be applied at low temperatures, whereas Cahn

* Corresponding author. Tel.: +49 551 395 584; fax: +49 551 395 012.
E-mail address: chris@ump.gwdg.de (C. Borchers).

1359-6454/$30.00
doi:10.1016/j.actamat.2005.04.022

and Hilliard's model is promising at high temperatures. Above that, they found that interfacial energies are dependent on interface orientation, which is not surprising, since the density of bonds across a unit interface depends on its orientation. This discrete lattice plane analysis has been carried out for face-centered cubic (fcc)/fcc metal interfaces [12], fcc/hexagonal close-packed (hcp) metal interfaces [13,14], and more recently to metal/ceramic interfacial energies by Enomoto coworkers [15–17].

One fundamental limitation of these models is that they are restricted to systems with a positive heat of mixing, since otherwise the concentration step at the interface will be unstable and flatten out in the above models. It is on the other hand well known that there do exist stable interfaces in systems with negative heat of mixing, e.g., the interface Ni–Ni_3Al. Moreover, the models do work with regular solution thermodynamics, which assume that binding energies in an alloy system are independent of concentration.

Khachaturyan and Morris [18] developed a model to calculate the interfacial tension of a sharp antiphase domain boundary. Their model is suitable for ordered systems with negative interaction energies. Contrary to the model presented in this work, they take higher neighbour interactions into consideration. Their results can be expressed in terms of the Fourier transforms of the interaction energies, quantities which are in principle accessible through scattering experiments.

According to Becker [10], the interface free energy is determined by the energy of the bonds across the interface. This assumption seems reasonable, if the interface is coherent, atomically sharp, has a small misfit and a small curvature. Becker considers a binary alloy with components A and B with regular solution behaviour. This implies that only pair interactions between nearest neighbour atoms are taken into account, that a mean field approximation is applicable to interfaces, that all interface stress contributions to the Gibbs free energy of the crystal can be separated from the chemical contributions, and that entropic contributions are so small that they can be neglected. The model requires thermodynamic equilibrium or a metastable state of which the thermodynamics are known. In this work, we extend the model of Becker to alloys showing (small) deviations from the regular solution model, and to alloy systems with negative heats of mixing. Furthermore it will be shown that all necessary pair interaction coefficients can be derived from the thermodynamic functions of the system, gained e.g., by the CALPHAD method [19]. Since Becker's model works best at low temperatures, as stated above, and the calculation of interfacial entropies is beyond the scope of this work, we present interfacial enthalpies, or energies for $T \to 0$ K. In this work, we assume low temperatures and will not distinguish between binding enthalpy and binding energy, and therefore refer to energies. The reader must keep in mind, though, that at elevated temperatures additional entropic terms must be considered.

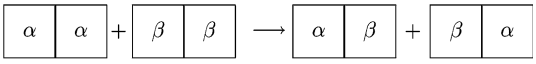
2. Becker's model

Let there be an alloy AB, two compositions α and β of which are separated by a coherent boundary. As Haasen has pointed out [20], the mean-field model is based on the probability P_{ij} to find a bond between the species i and j, $i, j \in \{A, B\}$ across the interface.[1] For a statistical distribution of A and B atoms, the probability of finding an i–j bond is $P_{ij} = c_i c_j$ with c_i, c_j the atomic fractions of the species i and j, $i, j \in \{A, B\}$. The mean energy $\tilde{\epsilon}$ per bond is described as follows:

$$\begin{aligned}\tilde{\epsilon} &= \tfrac{1}{2}[P_{AA}\epsilon_{AA} + P_{BB}\epsilon_{BB} + P_{AB}\epsilon_{AB}] \\ &= \tfrac{1}{2}[(1-c)\epsilon_{AA} + c\epsilon_{BB} + 2c(1-c)\epsilon],\end{aligned} \tag{1}$$

where c is the atomic fraction of species B and ϵ_{ij} is the binding energy per bond between i and j, and $\epsilon = \epsilon_{AB} - \frac{1}{2}(\epsilon_{AA} + \epsilon_{BB})$ is the pair interaction energy per bond, which in the framework of the regular solution model is independent of both temperature and the composition of the alloy.

For the calculation of the interface enthalpy, Becker [10] considered two alloys α and β with different concentrations to be cut in half. Then each half of one alloy is imagined to be rejoined with one half of the other alloy:



The interfacial energy can now be determined by calculating energy differences of the atomic bonds across the interface. The binding energies across the interface $\tilde{\epsilon}_{\alpha\beta}$ correspond to the bulk values of the energy per bond:

$$\begin{aligned}\tilde{\epsilon}_{\alpha\beta} = \frac{1}{2}\{&(1-c^{\alpha})(1-c^{\beta})\epsilon_{AA} + c^{\alpha}c^{\beta}\epsilon_{BB} \\ &+ [(1-c^{\alpha})c^{\beta} + c^{\alpha}(1-c^{\beta})]\epsilon_{AB}\}.\end{aligned} \tag{2}$$

The interface energy γ can now be given:

$$\gamma = z_{\text{int}}\left(c^{\beta} - c^{\alpha}\right)^2\epsilon \equiv z_{\text{int}}(\Delta c)^2\epsilon, \tag{3}$$

where z_{int} is the density of atomic bonds across a unit interface.

The deviation from an ideal mixing of the species A and B is described by the excess enthalpy $\Delta h^{\text{xs}}(c)$. If the excess energy per bond $\Delta\tilde{h}^{\text{xs}}(c) = (1-c)c\epsilon$ is known, e.g., from measurements of the heat of mixing, the pair interaction energy ϵ can be calculated by

$$\epsilon = -\frac{1}{2}\frac{\mathrm{d}^2\Delta\tilde{h}^{\text{xs}}}{\mathrm{d}c^2}. \tag{4}$$

[1] A list of the used symbols can be found in Appendix B.