

Solid-liquid interfacial free energy

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Abstract

The solid-liquid interfacial free energy has been estimated by a broken-bond model modified to take the entropy loss of the liquid in contact with the crystal into account. The predictions for f.c.c., h.c.p., b.c.c., diamond and s.c. structures are compared with experimental data from supercooling and dihedral angle measurements.

1. Introduction

The interfacial free energy of the crystal-melt interface (γ) plays a central role in determining the nucleation rate and growth morphology of crystals. γ has been derived mostly from the maximum supercooling [1], the kinetics of nucleation [2] and the dihedral angle at the intersection of a grain boundary and the solid-liquid interface [3-5]. Despite these efforts, experimental data are scarce and show a considerable scatter.

Most of the data are derived from supercooling experiments with the assumption of homogeneous nucleation [1]. It has been found that the gram-atomic interfacial free energy is proportional to the melting enthalpy with a coefficient $\alpha = 0.45$ for materials of closely packed structures (e.g. f.c.c., h.c.p., A5, A10 and A13), while 0.33 was found for elements with an open structure [diamond (d.c.) and As-type]. The γ -values derived from the dihedral angle are typically 20% higher; however, they show the same trends. This grouping of the elements seems to be related to the crystal structure, but its origin is not well understood.

The need for a reliable estimate of the interfacial free energy led to considerable theoretical activity [6]. Still there is a need for a method which could predict the magnitude of γ as a function of the crystal structure, orientation, supercooling and composition.

In this paper a simple model is presented to estimate the solid-liquid interfacial free energy

for elements of various structure as a function of orientation and temperature. The predictions are compared with the results from the maximum supercooling and dihedral angle measurements.

2. Model of the solid-liquid interface

We have applied a version of the broken-bond theory [7]. The interfacial free energy is expressed by the number of the solid-liquid bonds per interface area, while a free energy contribution is associated with every solid-liquid bond.

It is assumed that the atoms are on the same crystal lattice in the solid and at the interface, while the coordination (Z) is uniform in the solid and the liquid. Only the nearest-neighbour interaction is taken into account.

The enthalpy contribution of a solid-liquid bond to the free energy of the interface is approximated by the energy of formation of a single solid-like-liquid-like pair from bulk atoms, $\Delta h = \epsilon_{SL} - (\epsilon_{LL} + \epsilon_{SS})/2$, where ϵ_{LL} , ϵ_{SS} and ϵ_{SL} are the pair energy of liquid-liquid, solid-solid and solid-liquid bonds, respectively. In keeping with the results of Spaepen that the density of the melt is unchanged right up to the crystal surface [8], we assume that $\epsilon_{SL} = \epsilon_{LL}$. The pair energy difference between the liquid-liquid and solid-solid bonds may be expressed as $\epsilon_{LL} - \epsilon_{SS} = 2\Delta H(T)/(ZN_0)$, where $\Delta H(T) = H_L(T) - H_S(T)$ is the molar enthalpy difference between the bulk liquid and

crystal at temperature T , while N_0 is the Avogadro number. In this way:

$$\Delta h(T) = \frac{\Delta H(T)}{ZN_0} \quad (1)$$

In the present treatment a formal entropy contribution is attributed to the solid-liquid bonds. The solid-like neighbours limit the number of configurations available for the liquid-like atoms, thus increasing the number of solid-like neighbours the corresponding entropy/atom decreases.

A simple realization of this idea is to assume that the entropy associated with a liquid atom changes linearly with the number of the solid neighbours between the values characteristic of the bulk phases. The difference of the entropy/atom corresponding to these limits can be expressed as $\Delta S(T)/N_0$, where $\Delta S(T) = S_L(T) - S_S(T)$ is the molar entropy difference between the bulk liquid and crystal at temperature T . The change of the entropy associated with a liquid atom having Z_S solid neighbours relative to the bulk liquid is $Z_S \Delta s(T)$, where

$$\Delta s(T) = -\frac{\Delta S(T)}{ZN_0} \quad (2)$$

Thus the formal free energy associated with a single solid-liquid bond (bond free energy) can be expressed as

$$g_{SL}(T) = \Delta h(T) - T\Delta s(T) = \frac{\Delta H(T) + T\Delta S(T)}{ZN_0} \quad (3)$$

Having determined the bond free energy, one can calculate the free energy of a crystal-liquid interface as

$$\gamma = n_{hkl} g_{SL}(T) \quad (4)$$

where n_{hkl} is the density of the solid-liquid bonds on a crystal plane of Miller indices hkl .

3. Results and discussion

3.1. γ of plane surfaces

Using the formulae of Wolff and Gualtieri [7] for n_{hkl} calculations have been performed for different orientations of the f.c.c., h.c.p., b.c.c., d.c. and s.c. structures. Expressing the lattice constant by the molar volume (v) and applying Turnbull's

approximation ($\Delta H = \mathcal{H}_m$ and $\Delta S = \mathcal{H}_m/T_m$, where T_m and \mathcal{H}_m are the melting point and enthalpy, [1]) it has been found that the interfacial free energy can be expressed as

$$\gamma = \alpha \frac{\mathcal{H}_m}{N_0^{1/3} v^{2/3}} \quad (5)$$

where the coefficient α depends on the structure, the orientation and the temperature. The minimum of α calculated for the f.c.c., h.c.p., b.c.c., d.c. and s.c. structures at the melting point are $\alpha_{\min} = 0.458, 0.458, 0.445, 0.289$ and 0.333 , respectively, while the maximum values are $\alpha_{\max} = 0.592, 0.582, 0.630, 0.500$ and 0.577 . The value of α corresponding to an "average" surface (the average for all the orientations) has also been determined for f.c.c., b.c.c., d.c. and s.c. structures: $\alpha_a = 0.561, 0.546, 0.433$ and 0.500 .

It is interesting that the α_{\min} data are in a good agreement with those from the supercooling experiments of Turnbull [1] (the As structure can be described as a somewhat distorted s.c. [9]). It is reasonable that the nuclei tend to minimize their surface energy, thus they are bounded by crystal planes of low γ . This agreement can, however, be an apparent one since the data of Turnbull refer to a supercooled state. The correction would reduce α (cf. eqn. (3)). In contrast, the shape corresponding to the minimum of the surface energy is necessarily bounded by planes different from that with the minimum γ [7]. Thus a more detailed analysis is required.

The dihedral angle (ψ) measurements are performed near T_m . ψ is determined by the minimum of the free energy which, in this case, depends on not only γ but also on the grain boundary energy (influenced by the relative orientation of the grains). Thus a scattering of γ is expected. The experimental results for f.c.c. elements are compared with the average and limiting values predicted by our model in Fig. 1 where the gram-atomic interfacial free energy, $\gamma_g = \gamma N_0^{1/3} v^{2/3}$ is plotted as a function of \mathcal{H}_m . The experimental data are somewhat higher than both the average and the upper limit. Considering the experimental error of γ (approx. 15%) the agreement is satisfactory.

3.2. Homogeneous nucleation

Utilizing the concept of minimal surface free energy for a given volume the optimum shape of clusters has been determined for the f.c.c., b.c.c.,

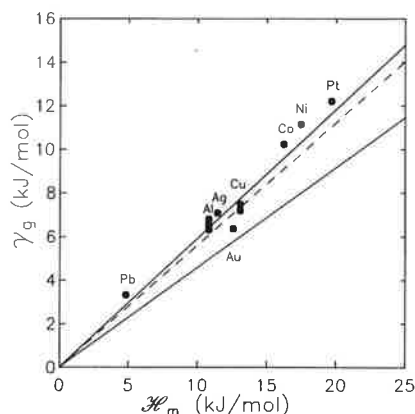


Fig. 1. The gram-atomic interfacial free energy vs. enthalpy of melting calculated for different orientations of the f.c.c. structure at $T = T_m$. (Solid lines: theoretical upper and lower limits; dashed line: average for all the orientations; ●: data for elements from dihedral angle measurements [3–5]).

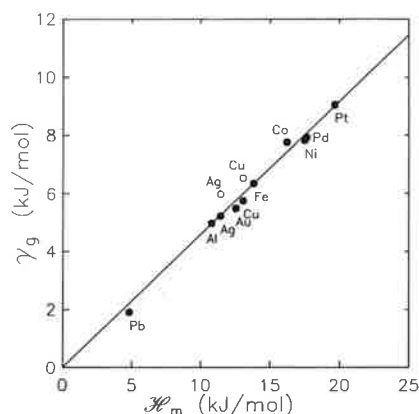


Fig. 2. The gram-atomic interfacial free energy vs. enthalpy of melting calculated for the optimum shape in case of f.c.c. structure at $T = 0.82T_m$. (Solid line: theory; ●: supercooling experiments [1, 4]; ○: nucleation kinetics [2]).

d.c. and s.c. structures. The corresponding polyhedra are the truncated octahedron, the rhombododecahedron, the octahedron and the cube. Expressions have been derived for the number of atoms and the number of the broken bonds as the function of the cluster size [10]. The size of the nucleus has been determined from the maximum of the free energy of cluster formation (ΔG_{\max}). For sake of a direct comparison with the experiments γ has been calculated from ΔG_{\max} with the assumption of a spherical shape (as in case of the experiments [1]).

We have calculated γ_g for f.c.c., b.c.c., d.c. and s.c. structures as a function of \mathcal{H}_m . Since the maximum supercooling is near to $\Delta T = 0.18 T_m$ in the experiments [1, 2], γ_g and α has been calculated with this value resulting in $\alpha = 0.473, 0.447, 0.313$ and 0.376 for the f.c.c., b.c.c., d.c. and s.c. structures, respectively.

The predictions for the f.c.c. structure are compared with experimental results from the measurement of the maximum supercooling [1] and nucleation kinetics [2] in Fig. 2. The agreement between the theory and the experiments is good. A similar agreement has been found for the other structures [10].

Using Turnbull's approximation for the thermodynamical properties we have calculated the critical cluster as a function of supercooling. The temperature dependence of α is shown in Fig. 3. It is found that the temperature coefficient of α is positive and agrees well with the estimate given on the basis of nucleation kinetics measurements [2].

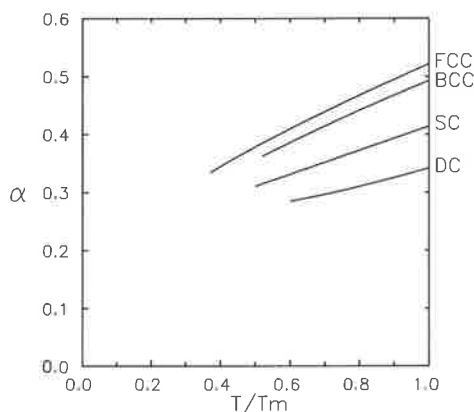


Fig. 3. The temperature dependence of the coefficient α [see eqn. (5)] calculated for the optimum shape of the critical nucleus for different crystal structures.

4. Summary

A new method without free parameters has been proposed for the calculation of the crystal-liquid interfacial free energy. The results are in a good agreement with the experimental data supplied by the maximum supercooling, nucleation kinetics and dihedral angle measurements.

Acknowledgments

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