Solid–liquid interfacial energy of solid succinonitrile solution in equilibrium with succinonitrile–neopentylglycol eutectic liquid

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ABSTRACT

The grain boundary groove shapes for solid succinonitrile solution (SCN–5 mole% NPG) in equilibrium with the succinonitrile (SCN)–neopentylglycol (NPG) eutectic liquid (SCN–9.55 mole% NPG) have been directly observed by using a horizontal linear temperature gradient apparatus at 317.1 K equilibrium temperature. From the observed grain boundary groove shapes, the Gibbs–Thomson coefficient (Γ) and solid-liquid interfacial energy (σ_{SL}) of solid SCN solution have been determined to be $(5.43 \pm 0.50) \times 10^{-8}$ K m and $(8.09 \pm 1.21) \times 10^{-3}$ J m^{-2}, respectively. The grain boundary energy of solid SCN solution has been determined to be $(14.22 \pm 2.28) \times 10^{-3}$ J m^{-2} from the observed grain boundary groove shapes. The thermal conductivity for SCN–9.55 mole% NPG eutectic solid phase and the thermal conductivity ratio of eutectic liquid phase to eutectic solid phase at the melting temperature have also been measured with a radial heat flow apparatus and Bridgman type growth apparatus, respectively.

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1. Introduction

The solid–liquid interfacial energy (σ_{SL}) plays a key role in a wide range of metallurgical and materials phenomena from wetting [1] and sintering through to phase transformations and coarsening [2]. For example, any meaningful comparison between experimentally observed solidification morphology and predictions from theoretical models requires an accurate knowledge of solid–liquid interfacial energy. Thus, a quantitative knowledge of σ_{SL} values is necessary. However, the determination of σ_{SL} is difficult. The earliest direct determinations were derived from droplet undercooling measurements on the supposition that maximum observed undercooling signified homogeneous nucleation. An empirical relationship between the interfacial energy and enthalpy of fusion to estimate the interfacial energy were proposed by Turnbull [3] and it is expressed as

$$\sigma_{SL} = \frac{\tau \Delta H_M}{V_S^{2/3} N_a^{1/3}} \tag{1}$$

where τ is a coefficient, found to be 0.45 for metals (especially closely packed metals) and 0.34 for nonmetallic systems at about

20% of undercooling below the melting point [3], ΔH_M is the enthalpy of fusion, V_S is molar volume of solid phase and N_a is the Avogadro constant. However, the subsequent experiments generated substantially larger values of undercooling resulting in larger values of σ_{SL}, indicating that such experiments typically underestimate σ_{SL}, except where there is an independent evidence that homogenous rather than heterogeneous nucleation was operative. Other disadvantages of deriving σ_{SL} from undercooling experiments were discussed by Jones [4] and Eustathopoulos [5].

The solid–liquid interfacial energy (σ_{SL}) is the reversible work required to create a unit area of the solid–liquid interface at constant volume, temperature and chemical potential. However, the surface tension (γ_{SL}) is the force per unit length. The relationship between σ_{SL} and γ_{SL} is given by

$$\gamma_{SL} = \sigma_{SL} + A\left(\frac{\partial \sigma_{SL}}{\partial A}\right) \tag{2}$$

where A is the surface area. In the case of a liquid film the interfacial energy is independent of the area of the interface and $(\partial \sigma_{SL}/\partial A) = 0$. This leads to the well-known result,

$$\gamma_{SL} = \sigma_{SL} \tag{3}$$

In the case of interfaces involving solids, however, it is not immediately obvious that σ_{SL} is independent of area. Since a liquid

is unable to support shear stresses the atoms within the liquid can rearrange during the stretching process and thereby maintain a constant surface structure. Solids, however, are much more viscous and the transfer of atoms from the bulk to the surface, which is necessary to maintain an unchanged surface structure and energy will take much longer. If this time is long in comparison to the time of the experiment then $(\partial\sigma_{SL}/\partial A)\neq0$ and interfacial energy and surface tension will not be identical. Nevertheless, at temperatures near the melting point the atomic mobility is usually high enough for Eq. (3) to be applicable [6].

The equilibrated solid–liquid interface in metallic systems will tend to maintain the equilibrium configuration of atoms on the interface so that the difference between the interfacial energy and surface tension may be negligible. Thus, experimental studies on solids which are based on equilibrium shapes of interfaces are preferable to the dynamic experiments in which the time of relaxation is much larger than the rate of motion of the interface. For this reason the grain boundary groove method for determining the solid–liquid interface energies will be emphasised [7].

A technique for the quantification of solid–liquid interfacial energy from the grain boundary groove shape has been established [8–17]. Observation of groove shape in a thermal gradient can be used to determine the interfacial energy, independent of the grain boundary energy because the interface near the groove must satisfy the following relationship everywhere:

$$\Delta T_r = \left[\frac{1}{\Delta S_f}\right]\left[\left(\sigma_{SL} + \frac{d^2\sigma_{SL}}{d\theta_1^2}\right)\kappa_1 + \left(\sigma_{SL} + \frac{d^2\sigma_{SL}}{d\theta_2^2}\right)\kappa_2\right] \quad (4)$$

where ΔT_r is the undercooling curvature, ΔS_f is the entropy of fusion per unit volume, κ_1 and κ_2 are the principal curvatures, and θ_1 and θ_2 refer the orientations of interface. Thus, the curvature undercooling is a function of curvature and orientation of the interface [7]. Since the equilibrating time in the present experiment is long enough (2 days) the difference between interfacial energy and surface tension may be negligible and can be assumed to be identical. As can be seen in the Ref. [18] for a cubic metal, taken on a {001} plane, the interfacial energy becomes

$$\sigma_{SL}(\theta) = \sigma_0[1 + \varepsilon_4\cos(4\theta)] \quad (5)$$

where the anisotropy is described with a single parameter ε_4. In Ref. [18] ε_4 values have been given from the previous works for SCN. Glicksman et al. have obtained the value $\varepsilon_4 = 0.005$ for SCN [19]. Experiments were also carried out Muschol et al. who obtained the value $\varepsilon_4 = 0.00554$ for SCN [20]. In Eq. (5) the value of $\cos(4\theta)$ can be 1 maximum. When we multiply ε_4 with $\cos(4\theta)$ the value will be always smaller than 0.005 for SCN. So the effect of anisotropy on interfacial energy for SCN will be smaller than 0.5% and can be neglected. When the solid–liquid interfacial free energy is isotropic, Eq. (4) becomes

$$\Delta T_r = \frac{\sigma_{SL}}{\Delta S_f}\left(\frac{1}{r_1} + \frac{1}{r_2}\right) \quad (6)$$

where r_1 and r_2 are the principal radii of the curvature. For the case of a planar grain boundary intersecting a planar solid–liquid interface ($r_2 = \infty$), the Eq. (6) becomes

$$\Gamma = r\Delta T_r = \frac{\sigma_{SL}}{\Delta S_f} \quad (7)$$

where Γ is the Gibbs–Thomson coefficient and r is radius of the groove profile as shown in Fig. 1. Thus, the curvature undercooling, ΔT_r, is a function of curvature radius, solid–liquid interfacial energy and the entropy of fusion per unit volume. This equation is called the Gibbs–Thomson equation for a curved interface having an isotropic solid–liquid interfacial energy and useful for considering the effect of solid–liquid interfacial energy on solidification and
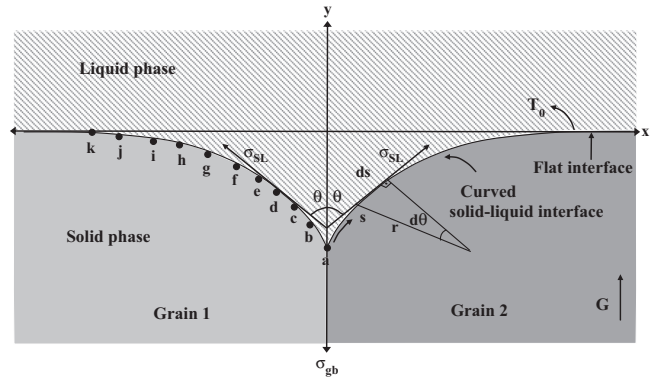

Fig. 1. Schematic illustration of an equilibrated grain boundary groove formed at a solid–liquid interface in a temperature gradient showing the definitions of r, θ and y in Eq. (4).

melting as it expresses the effective change in melting point for a curved interface.

Eq. (7) may be integrated in the y direction (perpendicular to the macroscopic interface) from the flat interface to a point on the cusp as shown in Fig. 1.

$$\int_0^{-y}\Delta T_r dy = \Gamma\int_0^{-y}\frac{1}{r}dy \quad (8)$$

The right hand side of Eq. (8) may be evaluated for any shape by noting that by definition $ds = rd\theta$ and $dy = ds\cos\theta = r\cos\theta d\theta$ (s and θ are shown in Fig. 1.) so that

$$\Gamma\int_0^{-y}\frac{1}{y}dy = -\Gamma\int_0^y\frac{1}{y}dy = -\Gamma\int_{\pi/2}^\theta\frac{1}{r}r\cos\theta d\theta = \Gamma(1-\sin\theta) \quad (9)$$

The left-hand side of Eq. (8) may be evaluated if ΔT_r is known as a function of y. When the thermal conductivities of solid and liquid phases are equal, the temperature just depends on temperature gradient and the distance: that is

$$\Delta T_r = Gy \quad (10)$$

so that,

$$\frac{1}{2}Gy^2 = \Gamma(1-\sin\theta) \quad (11)$$

The value of Γ may be obtained from the slop of a plot of y^2 against $(1-\sin\theta)$. The difficulty in this method is the observation of grain boundary groove shapes, especially in an opaque system. Gündüz and Hunt [21] developed an apparatus to observe the equilibrated grain boundary groove shapes in opaque binary eutectic systems. The details of apparatus and experimental procedures are given in Ref. [21]. Gündüz and Hunt [21] also developed a finite difference model to calculate the Gibbs–Thomson coefficient. Usually the points from b to i were used to obtain more reliable Γ values with Gündüz and Hunt's model as shown in Fig. 1. If the grain boundary groove shape, the temperature gradient in the solid (G_S) and the ratio of thermal conductivity of the equilibrated liquid phase to solid phase ($R=K_L/K_S$) are known or measured the value of the Gibbs–Thomson coefficient (Γ) is then obtained with the Gündüz and Hunt numerical method. Measurements of the solid–liquid interface energies were made in metallic binary eutectic based systems [21–23].

Bayender et al. [24,25] modified the apparatus originally designed by Hunt et al. [26] to directly observe the equilibrated grain boundary groove shape for transparent materials. They applied the Gündüz and Hunt's numerical method to determine the Gibbs–Thomson coefficients, the solid–liquid interfacial energy and the grain boundary energy. Measurements of the solid–liquid