Anisotropic solid–liquid interfacial energy measurement by grain boundary groove method

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ABSTRACT

Solid–liquid interfacial energy and its anisotropy play an important role in microstructure formation during solidification, which is responsible for the final performance of materials. Grain boundary groove (GBG) method has been developed as a common measurement method for the absolute solid–liquid interfacial energy over the past several decades, but it still can't resolve the anisotropy. In this paper, an improved GBG method for measuring not only the absolute interfacial energy but also the anisotropy was presented and examined in a typical metal analog—pivalic acid (PVA). The equilibrated GBG's in a quasi-2D sample cell under a constant temperature gradient with different orientation angles were observed in PVA. The GBG shapes, the temperature gradient and the crystal orientation were measured and combined to determine the absolute interfacial energy and the anisotropy of PVA. For comparison, the anisotropy of PVA was also measured independently by equilibrium shape method. The results given by the improved GBG method and equilibrium shape method were consistent. It suggests that the improved GBG method can be used to measure the anisotropic solid–liquid interfacial energy accurately.

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1. Introduction

Solidification occurs commonly in material processing, such as casting, welding, crystal growth, etc. Solid–liquid interfacial energy and its anisotropy play an important role in entire solidification process from nucleation to subsequent grain growth, which determines the solidified microstructure and final performance of materials [1]. Specifically, it has been known that the interfacial energy anisotropy is a key factor in dendritic growth during solidification [2,3]. Therefore, the accurate determination of the solid–liquid interfacial energy and its anisotropy is very helpful for understanding and controlling solidification microstructure.

Around 1950, Turnbull [4] first obtained the solid–liquid interfacial energy of metals by nucleation undercooling measurement on the basis of classic homogeneous nucleation theory. However, the existence of heterogeneous nucleation sites inevitably results in underestimating of the interfacial energy.

Another common method for measuring the solid–liquid interfacial energy is based on the grain boundary groove (GBG) shape. Early in 1960, the theoretical GBG shape under a temperature gradient for a pure material was first given by Bolling and Tiller

[5]. Nash and Glicksman [6] further modified the theoretical GBG shape considering different solid and liquid thermal conductivities in 1971. Subsequently, the effect of the anisotropic interfacial energy on the GBG shape was analyzed by Arbel and Cahn [7] and Voorhees et al. [8], respectively. Recently, Napolitano et al. [9] calculated the coupled shapes of the general tilt-boundary grooves with consideration of the anisotropic interfacial energy. Based on these theoretical studies, it has been considered that GBG measurement is an effective method for determining the anisotropic interfacial energy [7,10]. Experimentally, GBG method has been employed for determining the absolute solid–liquid interfacial energy in transparent organic materials [11–15], opaque metallic alloys [16–20] and colloidal system [21] over the past several decades. Recently, Jones [22] reviewed the interfacial energy measurement in metallic alloys by GBG method. It is concluded that the GBG shape measurements have provided a set of benchmark values of the measured interfacial energy for assessing the reliability of the measurements by nucleation method. However, the interfacial energy anisotropy still can't be resolved from GBG measurement. Moreover, recent study [23] indicates that neglect of the anisotropy influences accuracy of the measured absolute interfacial energy by GBG method.

Actually, the solid–liquid interfacial energy anisotropy is quite difficult to measure for metals because their interface is atomically rough and their interfacial energy anisotropy is very weak. Up to

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now, the most straightforward method for measuring the interfacial energy anisotropy is based on the relationship between the crystal equilibrium shape and the interfacial energy plot described by Wulff theorem. Hence it is often referred to as equilibrium shape (ES) method. Generally, micro-sized droplets embedded within a crystalline solid or micro-sized grains entrained within a liquid phase are annealed at a uniform temperature for a long period to equilibrate. Then their equilibrium shapes are captured and employed to extract the interfacial energy anisotropy according Wulff theorem. So far, this method has just been used in a few transparent systems [24,25] and metallic alloys [9,26,27], because high experimental requirements for forming and stabilizing so small droplets or grains still limit its applications.

In addition, with the rapid development of computing capacity, atomistic simulations, such as classical nucleation theory based approach [28,29], cleaving method [30,31] and capillary fluctuation method [32], have become another attractive techniques for determining the anisotropic solid–liquid interfacial energy. These numerical methods have been applied to a wide range of systems from pure metals to alloys [33,34]. Nevertheless, the theoretical calculation results through atomistic simulation still need examination by experimental measurement.

In this paper, a simple 2D GBG model considering the anisotropic interfacial energy is constructed. Then theoretical calculation is carried out to analyze the measuring relevance of the absolute interfacial energy and the anisotropy from GBG shapes. Accordingly, an improved GBG method for measuring both the absolute interfacial energy and the anisotropy accurately from double GBG shapes is presented and examined in PVA—a typical metal analog. For comparison, the interfacial energy anisotropy of PVA is also measured by ES method independently. In the end, the measured results of PVA and the reliability of the improved GBG method is discussed.

2. Methods

2.1. Theoretical model

One can assume that there are three grains inside a quasi-2D sample cell: the middle grain orients its {0 0 1} crystal plane parallel to the sample plane and its neighboring left and right grains orients very differently. When the sample cell is imposed in a constant temperature gradient, two grain boundary grooves will form at the intersection between the solid–liquid interface and the grain boundaries, as shown in Fig. 1. The equilibrated GBG shape $y(x)$ satisfies Gibbs–Thomson equation, that is:

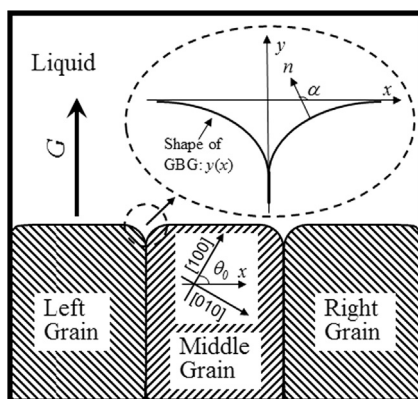$$\Delta T = \frac{1}{\Delta S}(\gamma + \gamma_{\theta\theta})K \tag{1}$$

Fig. 1. Schematic diagram of grain boundary grooves.

where ΔT is the curvature undercooling, ΔS is the entropy of fusion, γ is θ-dependent interfacial energy, θ is the crystal orientation, $\gamma_{\theta\theta}$ is the second derivative of γ with respect to θ and K is the solid–liquid interface curvature.

Let x-axis denotes the macroscopic planar part of the solid–liquid interface and y-axis denotes the temperature gradient direction from the triple-point of GBG, as defined in Fig. 1. Then according to the definition of x–y coordinates, there are:

$$\Delta T = -G \times y \tag{2}$$

$$\theta = \alpha - \theta_0 \tag{3}$$

$$K = \cos \alpha \times d\alpha/dy \tag{4}$$

$$y_x = -\cot \alpha \tag{5}$$

where G is the temperature gradient, α is the angle between the interface normal direction and x-axis, θ_0 is the tilting angle of the ⟨1 0 0⟩ crystal axis from x-axis.

For a cubic structure crystal, the solid–liquid interfacial energy in {0 0 1} crystal plane can be simplified as [10]:

$$\gamma(\theta) = \gamma_0 [1 + \varepsilon_4 \cos(4\theta)] \tag{6}$$

where γ_0 is the absolute interfacial energy, and ε_4 is the interfacial energy anisotropy.

Combining above expressions and integrating it, we obtain:

$$y^2 = \frac{2\gamma_0}{G\Delta S}\left[1 - \sin \alpha + \frac{5}{2}\varepsilon_4 \sin(3\alpha - 4\theta_0) + \frac{3}{2}\varepsilon_4 \sin(5\alpha - 4\theta_0) + \varepsilon_4 \cos(4\theta_0)\right] = \gamma_0 F(\alpha) \tag{7}$$

where the function $F(\alpha)$ is just used for clarity.

Eq. (7) can be used to describe the two-dimensional GBG shape under a constant temperature gradient of the middle grain, whose {0 0 1} crystal plane parallels to the sample plane. In this equation, y and α are evaluated from the experimental GBG shape $y(x)$, G is measured directly, θ_0 is determined by orientation analysis and ΔS is a known physical constant. So γ_0 and ε_4 are two only unknowns.

Theoretically, Eq. (7) can be used to solve both the absolute interfacial energy and the anisotropy from a single GBG shape as described by the traditional GBG method. However, from our analysis, it is found that their solution accuracy in this way is very bad. The solved absolute interfacial energy will be influenced significantly by a little perturbation of the anisotropy. That is to say, both the absolute interfacial energy and the anisotropy are hardly determined accurately from a single groove shape. In order to illustrate it clearly, a theoretical analysis on the fitting relationship of the absolute interfacial energy and the anisotropy is given. First, the anisotropy ε_4 is set at an assumed value ε, then the absolute interfacial energy as an only unknown parameter can be determined by linearly fitting $\left(F(\alpha)\big|_{\varepsilon_4 = \varepsilon}, y^2\right)$ of a groove shape. We label this fitted interfacial energy at $\varepsilon_4 = \varepsilon$ as γ_e to distinguish the true value γ_0. A factor $D = (\gamma_e - \gamma_0)/\gamma_0$ is used to describe the deviation of γ_e from γ_0. In this way, the relationship between D and ε can be obtained. As a theoretical example, Fig. 2 shows the obtained D–ε curves by separately fitting the left and right groove shapes of the middle grain at three cases of $\theta_0 = 80°$, 65° and 50°. The point at $D = 0$ and $\varepsilon = 0.02$ corresponds to the presupposed true values of the absolute interfacial energy and the anisotropy in this example. The error bars in the figure denote the standard deviation of fit (σ). It can be seen that σ decreases to zero when the fitted values approach to the true value. But σ just varies a little as ε changes significantly, especially in the case of the left groove at $\theta_0 = 80°$. This suggests that a series of (γ_e, ε) can be obtained by fitting any of the left or the right groove shapes and the goodness of these fits has a little difference. That is to say, in practice, the fitted interfacial energy and the anisotropy from a single groove shape will be disturbed significantly by experimental noise and