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Determination of thermal conductivity and interfacial energy of solid Zn solution in the Zn–Al–Bi eutectic system

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ABSTRACT

The equilibrated grain boundary groove shapes for solid Zn solution (Zn–3.0 at.% Al–0.3 at.% Bi) in equilibrium with the Zn–Al–Bi eutectic liquid (Zn–12.7 at.% Al–1.6 at.% Bi) have been observed from quenched sample with a radial heat flow apparatus. Gibbs–Thomson coefficient, solid–liquid interfacial energy and grain boundary energy for solid Zn solution in equilibrium with Al–Bi–Zn eutectic liquid have been determined to be $(5.1 \pm 0.4) \times 10^{-8}$ K m, $(80.1 \pm 9.6) \times 10^{-3}$ and $(158.6 \pm 20.6) \times 10^{-3}$ J m^{-2} from the observed grain boundary groove shapes, respectively. The thermal conductivity variation with temperature for solid Zn solution has been measure with radial heat flow apparatus and the value of thermal conductivity for solid Zn solution has been determined to be 135.68 W/km at the eutectic melting temperature. The thermal conductivity ratio of equilibrated eutectic liquid to solid Zn solution, $R = K_{L(\mathrm{Zn})}/K_{S(\mathrm{Zn})}$ has also been measured to be 0.85 with Bridgman type solidification apparatus.

1. Introduction

The solid–liquid interfacial energy, σ_{SL}, is recognized to play a key role in a wide range of metallurgical and materials phenomena from wetting [1] and sintering through to phase transformations and coarsening [2]. Thus, a quantitative knowledge of σ_{SL} values is necessary. However, the determination of σ_{SL} is difficult. Since 1985, a technique for the quantification of solid–liquid interfacial free energy from the grain boundary groove shape has been established and measurements have been reported for several systems [3–21]. The grain boundary groove shape formed at the solid–liquid interface in a thermal gradient can be used to determine the interfacial energy and the interface near the groove must everywhere satisfy

$$\Delta T_r = \left[\frac{1}{\Delta S_f}\right]\left[\left(\sigma_{SL} + \frac{d^2\sigma_{SL}}{dn_1^2}\right)\kappa_1 + \left(\sigma_{SL} + \frac{d^2\sigma_{SL}}{dn_2^2}\right)\kappa_2\right] \tag{1}$$

where ΔT_r, is the curvature undercooling, ΔS_f is the entropy of fusion per unit volume, $n(n_x, n_y, n_z)$ is the interface normal, κ_1 and κ_2 are the principal curvatures, and the derivatives are taken along the directions of principal curvature. Eq. (1) is valid only if the interfacial free energy per unit area is equal to surface tension per unit length, $\sigma_{SL} = \gamma$. When interfacial free energy differs from surface tension, the problem is more complicated and the precise modification of the Gibbs Thomson equation is not yet established [21]. When the solid–liquid interfacial free energy is isotropic, Eq. (1) becomes

$$\Delta T_r = \frac{\sigma_{SL}}{\Delta S_f}\left(\frac{1}{r_1} + \frac{1}{r_2}\right) \tag{2}$$

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, $r_2 = \infty$ and the Eq. (2) becomes

$$\Gamma = r\Delta T_r = \frac{\sigma_{SL}}{\Delta S_f} \tag{3}$$

where Γ is the Gibbs–Thomson coefficient. This equation is called the Gibbs–Thomson relation [13].

Gündüz and Hunt [13] also developed a finite difference model to calculate the Gibbs–Thomson coefficient. This numerical method calculates the temperature along the interface of a measured grain boundary groove shape rather than attempting to predict the equilibrium grain boundary groove shape. 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's numerical method.

One of the common techniques for measuring solid–liquid interfacial free energy is the method of grain boundary grooving in a temperature gradient. In this technique, the solid–liquid interface is equilibrated with a grain boundary in a temperature gradi-

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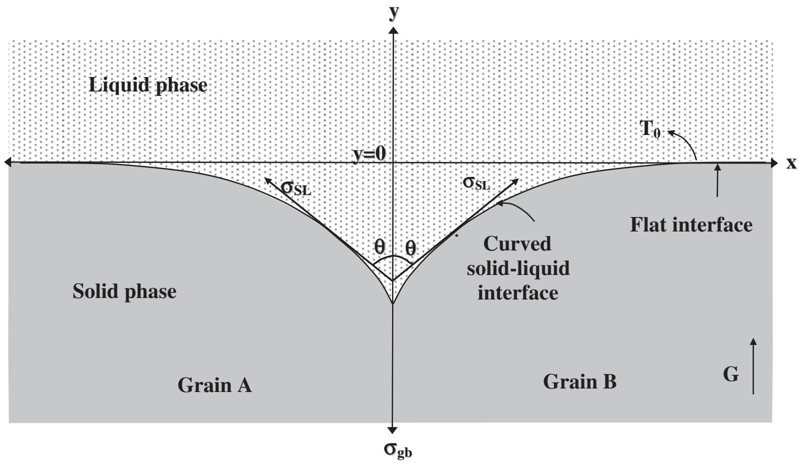

Fig. 1. Schematic illustration of an equilibrated grain boundary groove formed at a solid–liquid interface in a temperature gradient.

ent as shown in Fig. 1, and the mean value of solid–liquid interfacial free energy is obtained from the measurements of equilibrium shape of the groove profile. The grain boundary groove method is the most useful and powerful technique at present available for measuring the solid–liquid interface energy and can be applied to measure σ_{SL} for multi-component systems as well as pure materials, for opaque materials as well as transparent materials, for any observed grain boundary groove shape and for any $R = K_S/K_L$ value. Over last 25 years, the equilibrated grain boundary groove shapes in variety of materials have been observed and the measurements of the solid–liquid interfacial free energies were made from observed grain boundary groove shapes [3–21].

The phase diagram of Zinc (Zn)–Aluminum (Al)–Bismuth (Bi) eutectic system has been evaluated [22]. Some thermal properties such as solid–liquid interfacial energy, Gibbs–Thomson coefficient, grain boundary energy and thermal conductivity of solid and liquid phases in the Zn–Al–Bi eutectic system have not been well known. The values of solid–liquid interfacial energy, Gibbs–Thomson coefficient and grain boundary energy could be of use to people doing comparisons between experimentally observed solidification morphology and predictions from theoretical models. Thus the aims of the present work were to observe the equilibrated grain boundary groove shapes for solid Zn solution in equilibrium with Zn–Al–Bi eutectic liquid and to determine the thermal conductivity of solid and liquid phases, the Gibbs–Thomson coefficient, solid–liquid interfacial energy and grain boundary energy for solid Zn solution in the Zn–Al–Bi eutectic system.

2. Experimental procedure

2.1. Experimental apparatus

In order to observe the equilibrated grain boundary groove shapes in opaque materials, Gündüz and Hunt [13] designed a radial heat flow apparatus. Maraşlı and Hunt [14] improved the experimental apparatus for higher temperature. The details of the apparatus and experimental procedures are given in Refs. [13–17]. In the present work, a similar apparatus was used to observe the grain boundary groove shapes in the Zn–Al–Bi eutectic system and the block diagram of the experimental set up is shown in Fig. 2.

2.2. Sample production

As can be seen from the phase diagram of Zn–Al–Bi eutectic system shown in Fig. 3, the eutectic liquid composition is Zn–12.7 at.% Al–1.6 at.% Bi [20]. Thus, the composition of alloy was chosen to be Zn–12.7 at.% Al–1.6 at.% Bi to grow the solid Zn solution phase on the eutectic structure in a short annealing time. Zn–12.7 at.% Al–1.6 at.% Bi alloy was prepared in a vacuum furnace by using Zinc, Aluminum and Bismuth. The purity of bismuth, zinc and aluminum used in the preparation of alloy were four nine (99.99). After stirring, the molten alloy was poured into a graphite crucible, held in a specially constructed casting (hot filling) furnace at approximately 50 K above the melting point of alloy. The molten metal was then directionally solidified from bottom to top to ensure that the crucible was completely full. The sample was then placed in the radial heat flow apparatus.

The experiments were carried out in two steps. In the first step, the thermocouples were calibrated by detecting the melting point during very slow heating and cooling. In the second step, the specimen was heated from the centre using a single heating wire (1.7 mm in diameter, Kanthal A-1) and the outside of the specimen was kept at 293 K using a *Poly Science digital 9102* model heating/refrigerating circulating bath. A thin liquid layer (1–2 mm thick) was melted around the central heater and the specimen was annealed in a very stable temperature gradient for a long time. In this condition, the solid and liquid layers were mixed together. During the annealing period, the liquid droplets move up towards the hot zone of the sample by temperature gradient zone melting and single solid phase can grow. The annealing time for Zn–12.7 at.% Al–1.6 at.% Bi alloy was 4 days. During the annealing period, the temperature in the specimen and the vertical temperature variations on the sample were continuously recorded by the stationary thermocouples and a moveable thermocouple, respectively by using a data logger via computer. The input power was also recorded periodically. The temperature in the sample was stable to about ±0.025 K for hours and ±0.05 K for up to 4 days. At the end of the annealing time the specimen was rapidly quenched by turning off the input power which was sufficient to get a well defined solid–liquid interface, because the liquid layer around the central heating wire was very thin (typically smaller than 1 mm).

2.3. Measurements of the coordinates of equilibrated grain boundary groove shapes

The quenched sample was cut transversely into lengths typically of 25 mm, and transverse sections were ground flat with 180 grit SiC paper. Grinding and polishing were then carried out by following a standard route. After polishing, the samples were etched with 40 gr. chromic acid (CrO_3), 1.5 gr. sodium sulphate