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Interfacial energies of solid $CuAl_2$ in the $CuAl_2$–Ag_2Al pseudo binary alloy

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ABSTRACT

Gibbs–Thomson coefficient, solid–liquid interfacial energy and grain boundary energy are important parameters for people doing comparisons between experimentally observed solidification morphology and predictions from theoretical models. Thus the Gibbs–Thomson coefficient, solid–liquid interfacial energy and grain boundary energy of solid $CuAl_2$ in the $CuAl_2$–Ag_2Al pseudo binary system have been determined from observed grain boundary groove shapes. The variation of thermal conductivity of solid $CuAl_2$ with temperature has also been measured by using a radial heat flow 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 [3–19]. 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 everywhere satisfy

$$\Delta T_r = \left[\frac{1}{\Delta S^*}\right]\left[\left(\sigma_{SL} + \frac{d^2\sigma_{SL}}{d_{n_1^2}}\right)\kappa_1 + \left(\sigma_{SL} + \frac{d^2\sigma_{SL}}{d_{n_2^2}}\right)\kappa_2\right] \qquad (1)$$

where ΔT_r, is the curvature under cooling, ΔS^* is the entropy of fusion per unit volume, $\mathbf{n} = (n_x, n_y, \text{and } n_z)$ is the interface normal, κ_1 and κ_2 are the principal curvatures, and the derivatives are taken along the directions of principal curvature. Thus, the curvature under cooling is a function of curvature, interfacial free energy and the second derivative of the interfacial free energy. 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 the interfacial energy differs from surface tension, the problem is more complicated and the precise modification of the Gibbs–Thomson equation is not yet established [20]. When the solid–liquid interfacial free energy is isotropic, Eq. (1) becomes

$$\Delta T_r = \frac{\sigma_{SL}}{\Delta S^*}\left(\frac{1}{r_1} + \frac{1}{r_2}\right) \qquad (2)$$

where r_1 and r_2 are the principal radii of curvature. For the case of a planar grain boundary intersecting a planar solid–liquid interfacial, $r_2 = \infty$ and the Eq. (2) becomes

$$\Gamma = r\,\Delta T_r = \frac{\sigma_{SL}}{\Delta S^*} \qquad (3)$$

where Γ is the Gibbs–Thomson coefficient. This equation is called the Gibbs–Thomson relation [9].

At present the most powerful method to experimentally measure the solid–liquid interface energy is the grain boundary groove method. This method is based on the direct application of the Gibbs–Thomson equation 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 value of the thermal conductivity ratio of the equilibrated liquid phase to solid phase, $R = K_L/K_S$.

More recently, the phase diagram of $CuAl_2$–Ag_2Al pseudo binary system has been determined [21]. Some thermo physical properties such as solid–liquid interfacial energy, Gibbs–Thomson coefficient, grain boundary energy and thermal conductivities of solid and liquid

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phases have not been well known. These thermo physical properties 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 of solid $CuAl_2$ in $CuAl_2$–Ag_2Al pseudo binary system and determine the Gibbs–Thomson coefficient, solid–liquid interfacial energy and grain boundary energy for solid $CuAl_2$ from the observed grain boundary groove shapes.

2. Materials and methods

2.1. Sample production

It is necessary to consider what is happening during the annealing period. Consider a binary eutectic system as shown in Fig. 1. Above the eutectic temperature, a eutectic system consists of solid and liquid provided the alloy composition C_0 which satisfies $C\alpha < C_0 < C_E$ or $C_E < C_0 < C_\beta$, where C_E, $C\alpha$, and C_β are the composition of the eutectic, solid α and solid β phases, respectively. If this eutectic system is held in a very stable temperature gradient, the liquid droplets move up the temperature gradient by temperature gradient zone melting (TGZM) and single solid α phase can grow on the casting phase during the annealing period. When the composition of alloy is far from the eutectic composition, the experiment usually needs a long time to reach equilibrium due to larger freezing range. Above the eutectic temperature, a ternary eutectic system consists of liquid if the alloy composition (C_0) is near the eutectic composition ($C_0 \cong C_E$). If this system is held in a very stable temperature gradient there will be no liquid droplets behind the solid phase and two or more solid phases (α, β and γ) can grow together on the eutectic structure. Equilibrating time for this system should be shorter because of the small freezing range.

The composition of the alloy was chosen to be near the eutectic composition ($CuAl_2$-23.6 at.% Ag_2Al) to grow solid $CuAl_2$ on the eutectic structure in a short annealing time. $CuAl_2$-23.6 at.%Ag_2Al alloy was prepared in a vacuum furnace by using 99.9% pure aluminum, 99.99% pure silver and 99.9% pure copper. After stirring, the molten alloy was poured into a graphite crucible held in a specially constructed casting furnace at approximately 50 K above the melting point of the 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.

In the present work, a radial heat flow apparatus originally designed Gündüz and Hunt [13] and modified Maraşlı and Hunt [14] was used to observe the grain boundary groove shapes in the Al–Cu–Ag ternary alloy. The details of the apparatus and experimental procedures are given in Refs. [13–18].

The sample was heated from its centre by a single heating wire and the outside of the sample was kept constant to an accuracy of ±0.01 K at 293 K (20 °C) using a *Poly Science digital 9102* model heating/refrigerating circulating bath to maintain a constant radial temperature gradient on the sample. 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. The annealing time for $CuAl_2$-23.6 at.% Ag_2Al was 6 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 6 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 less than 0.5–1 mm).

2.2. 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 a 14 ml sulfuric acid, 2.5 g molybdic acid in 50 ml water for 10 s.

The equilibrated grain boundary groove shapes were then photographed with an *Olympus DP12 type CCD* digital camera placed on top of an *Olympus BX51* type light optical microscope. A graticule (200 × 0.01 = 2 mm) was also photographed using the same objective. The photographs of the equilibrated grain boundary groove shapes and the graticule were superimposed on one another using *Adobe PhotoShop 8.0* version software so that accurate measurement of the groove coordinate points on the groove shapes could be made.

2.3. Geometrical correction for the groove coordinates

The coordinates of the cusp, *x*, *y* should be measured using the coordinates *x*, *y*, and *z* where the *x* axis is parallel to the solid–liquid interface, the *y* axis is normal to the solid–liquid interface and the *z* axis lies at the base of the grain boundary groove. Maraşlı and Hunt [14] devised a geometrical method to make appropriate corrections to the groove shapes and the details of the geometrical method are given in Ref. [14].

The coordinates of equilibrated grain boundary groove shapes were measured with an optical microscope to an accuracy of ±10 μm by following Maraşlı and Hunt geometrical method [14] so that appropriate corrections to the shape of the grooves could be deduced. The uncertainty in the measurements of equilibrated grain boundary groove coordinates is 0.2% [14].

2.4. Measurements of the thermal conductivity of solid and liquid phases

The thermal conductivity ratio of the equilibrated eutectic liquid phase ($CuAl_2$-23.6 at.% Ag_2Al) to solid $CuAl_2$ (Al-32.21 at.% Cu-0.04 at.% Ag) phase, $R = K_{L(\text{eutectic liquid})}/K_{S(CuAl_2)}$ must be known or measured to evaluate the Gibbs–Thomson coefficients with the present numerical method. The radial heat flow method is an ideal technique for measuring the thermal conductivity of the solid phases. The thermal conductivity of the solid $CuAl_2$ phase is also needed to evaluate the temperature gradient in the solid phase. In the radial heat flow method, a cylindrical sample was heated by using a single heating wire along the axis at the centre of the sample and the sample was kept in a very stable temperature gradient for a period to achieve a steady state

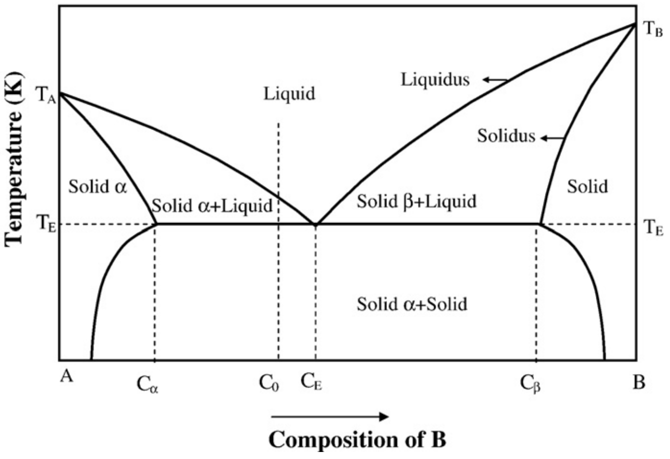

Fig. 1. A phase diagram of binary eutectic system.