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Solid-liquid interfacial energy of Al-Zn solid-solutions in equilibrium with Al-Zn liquid

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Abstract. The grain boundary groove method has been successfully used to measure solid-liquid interfacial energies, σ_{SL}, experimentally for binary eutectic and peritectic systems, multi-component systems as well as pure materials and for opaque materials as well as transparent materials. It was shown that the grain boundary groove method can be use to obtain σ_{SL} for any alloy system provided that the prepared alloy sample can be held at the evaluated temperature for a long enough time with a very stable temperature gradient. In order to show the applicability of the groove method to any system, a part of the Al-Zn phase diagram was chosen. Equilibrated grain boundary groove shapes for solid Alα solution (Al-30wt%Zn) in equilibrium with AlZn liquid (Al-60wt%Zn) have been directly observed with a radial heat flow apparatus. The Gibbs-Thomson coefficient, Γ, was determined with a numerical method using observed groove shapes. The measured thermal conductivities of the solid Alα solution and AlZn liquid phases and the temperature gradient in the solid phase at the solid-liquid interface were used for the calculation of Γ and then σ_{SL} was determined using the Gibbs-Thomson equation. The grain boundary energy for the same system was also obtained from the observed groove shapes. The results of the work were compared with the results of the related experimental works.

1. Introduction

The solubility of Zn in Al is the largest among all elements, showing a maximum of 67at% at 654K [1]. In lower Zn content (Co=40at%Zn), Al and Zn do not form intermetallic phases since the interaction between Al and Zn is fairly week [2]. Al has a FCC structure and is slightly anisotropic whereas Zn has a HCP structure and is strongly anisotropic. This difference in anisotropy involves a variation of solid-liquid interfacial energy, σ_{SL}, modifying morphologies and directions of dendritic growth. σ_{SL} plays a key role in a wide range of materials and metallurgical phenomena, such as nucleation, solidification processing, welding and sintering, through to phase transformation, wetting and coarsening etc. [3-11]. Thus, a quantitative knowledge of σ_{SL} values is necessary. The present most useful and powerful technique for the experimental measurement of σ_{SL} in multi-component systems as well as pure materials and opaque materials as well as transparent materials, has been found to be the "grain boundary groove, GBG," method. The method has been successfully used to measure σ_{SL} in eutectic, peritectic and monotectic systems [12-21]. In this study, it has been shown that the GBG method is not limited to these systems only. This method can be used to obtain σ_{SL} for any alloy system. Over the last 50 years, determining the values of the σ_{SL} in a variety of materials has been used through various attempts. There

are various techniques for estimating σ_{SL}. The GBG consist of intersection of grain boundaries with the equilibrated planar solid-liquid interfaces (Figure 1).

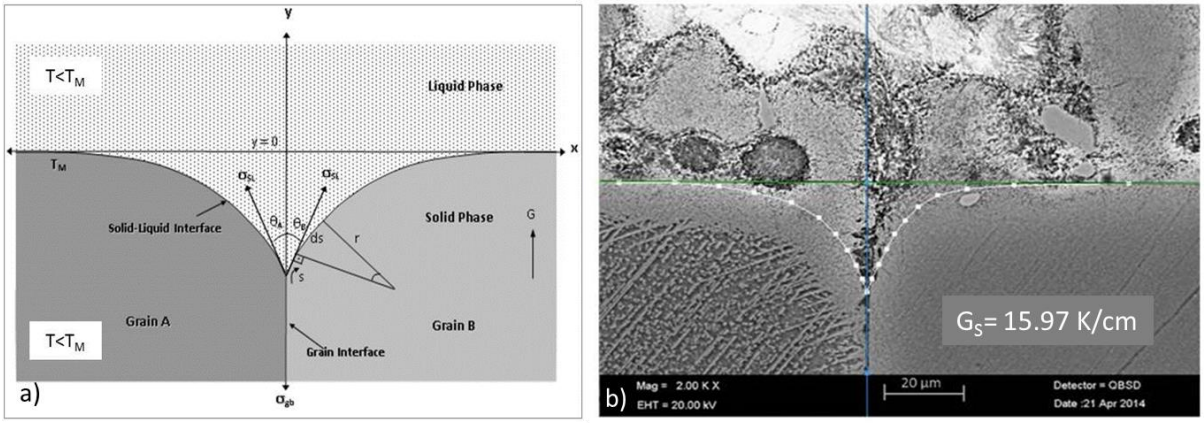

Figure 1. Equilibrated GBG shapes: **(a)** Schematic illustration of an equilibrated GBG shape showing the x, y coordinates and angle θ. **(b)** Alα solid solution equilibrated with the liquid AlZn

σ_{SL} might be calculated from the equilibrated GBG shapes formed at the solid-liquid interface under a gradient G. When σ_{SL} is isotropic the interface at the groove must everywhere satisfy;

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

where ΔT_r is the curvature undercooling, ΔS_f is the entropy of fusion per unit volume, r_1 and r_2 are the principal radii of the curvature. For the case of a GBG shape intersecting a planar solid–liquid interface, $r_2 = \infty$ and Gibbs-Thomson equation, (Equation 1), becomes;

$$\Gamma = r\Delta T_r \quad (2)$$

where Γ is the Gibbs–Thomson coefficient. The GBG shape for an applied gradient in two dimensions has been calculated theoretically using Equation 2 by Bolling and Tiller for the case of equal thermal conductivities in the solid-liquid phases [22]. The theoretical description of Bolling and Tiller model was modified by Nash and Glicksman [13] to account for different thermal conductivities in the solid and liquid phases. Gündüz and Hunt [6] solved the heat flow problem numerically through the experimentally observed GB shape using different thermal conductivities for the solid and liquid phases and the G in the solid phase at the solid-liquid interface, G_S value with appropriate boundary and temperature distribution conditions. A finite difference method was used to calculate the difference in temperature between the flat surface and points on the GBG shape (Figure 1). The numerical method allows Γ to be obtained for any equilibrated GBG shape provided that G_S, K_L and K_S values and the size of the groove are known. Then, σ_{SL} is obtained from Equation 1. Over the last 30 years, the equilibrated GBG shapes in variety of eutectic, peritectic and monotectic systems have been observed and measurements of σ_{SL} have been made from the observed GBG shapes [12-21].

The aims of the present work were to observe the GBG shapes for the solid Alα solution, in equilibrium with the AlZn liquid, and to determine the Γ, σ_{SL} and grain boundary energy, σ_{gb}.

2. Experimental Procedure

2.1. Sample Preparation

The Al-30wt%Zn samples were prepared in a vacuum furnace from 4-9s Al and Zn. The molten alloy was mixed several times and then poured into a graphite crucible held in a specially manufactured casting furnace which is heated to above 100K of the liquidus temperature of the alloy. Subsequently, the samples were directionally solidified from the bottom to top. The cast sample was placed in the radial heat flow apparatus and the thermocouples were placed in the alumina tubes and then the sample was placed in the radial heat flow apparatus. The apparatus can give a very stable temperature, (± 0.1K), for a long period of time and allows a wide range of G. The detail of the experimental procedure, sample preparation and obtaining of the GBG shapes are given in references [6, 7, 14-21].

2.2. Temperature Gradient Measurements

In the steady-state condition, the temperature gradient in the solid, G_S, at the radius, r, of a long cylindrical sample is given by;

$$G_S=\left(\frac{dT}{dr}\right)_s=-\frac{Q/l}{2\pi r K_S} \tag{3}$$

where Q is the input power, r is the distance of the planar solid-liquid interface from the center, l is the length of central heating element, and K_S is the thermal conductivity in the solid phase. The average G_S was calculated for each GBG shape. The Q was determined by measuring the voltage drop across the heating element and the current flowing through the wire and the r value measured on the polished sample surface where the GBG shape was observed.

2.3 Thermal Conductivities of the Phases

In order to calculate the Γ from the GBG shapes, the solid and liquid phases, thermal conductivities of K_S and K_L as well as G_S and coordinates of the GBG shapes at the solid-liquid interface must be known as accurately as possible. The K_S and K_L values of the phases are generally unknown. The radial heat flow apparatus can be used to measure the K_S value. Equation 3 may be integrated to give;

$$K_S=\frac{1}{2\pi}ln\left(\frac{r_2}{r_1}\right)\frac{Q/l}{T_2-T_1} \tag{4}$$

where T_1 and T_2 are the temperatures at two fixed distances, that is, at r_1 and r_2 from the centre. The specimen is heated with a central heating wire to 10K below the solidus temperature in 50K steps. The specimen was kept at least two hours at each measurement temperature. In the steady-state conditions, Q, T_1, T_2 and vertical temperature change were measured. The K_S value was obtained by using the measured T_1, T_2, r_1, r_2, l and Q values in Equation 4 and shown in Figure 2.

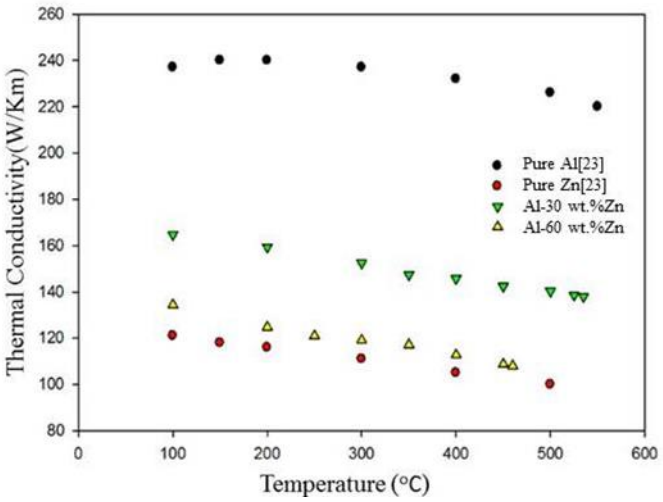

Figure 2. Plots of thermal conductivity of the solid phases with temperature

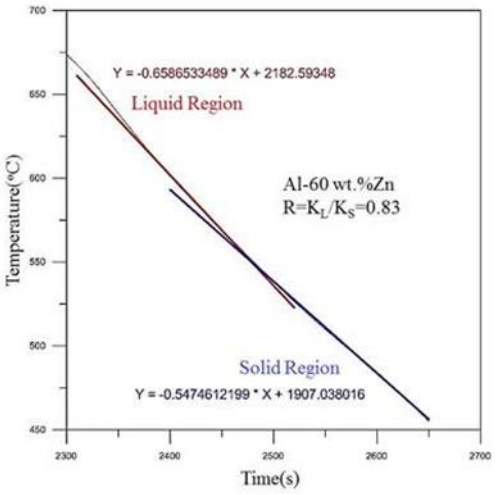

Figure 3. The time-temperature trace and R value for Al-60wt% Zn alloy

K values used in the calculations were obtained by extrapolation to the equilibrium temperature. The K_S of the Alα solution was found to be as 138.61 W/Km and K_S value of the Al-60wt%Zn alloy was found to be as 108.80 W/Km at the equilibrium temperature. The temperature-time trace enables $R=K_L/K_S$ ratio of the phases to be calculated. The $R=K_L/K_S$ ratio of the Al-60wt%Zn alloy was obtained to be as 0.83 by using the trace obtained with a Bridgman type directional growth apparatus (Figure 3). The K_L value was calculated to be as 89.64 W/Km by using the measured K_S and R values for the Al-60wt% Zn alloy. Thus, the ratio of the equilibrated Alα solid phase to AlZn liquid phase was obtained as 0.65.

3. Result and Discussion

3.1. Determination of the Gibbs-Thomson Coefficient

The Gibbs-Thomson constant, Γ, is one of the basic parameters required in the solidification theories. To obtain the Γ using the numerical method, G_S, K_S, K_L values and the coordinates of the equilibrated GBG shape must be known. The numerical method is described in detail in Ref [6]. The Γ values for the equilibrium solid Alα (Al-30wt%Zn) and liquid AlZn (Al-60wt%Zn) were calculated using at least 10 equilibrated symmetrical GBG shapes (e.g. Figure 1b and Figure 4). The determined average values of Γ for the solid Alα solution in equilibrium with the AlZn liquid was found (Table 1). The experimental error in the Γ obtained by considering the fractional error in each of the measured quantities was estimated to be in the order of 7-9%.

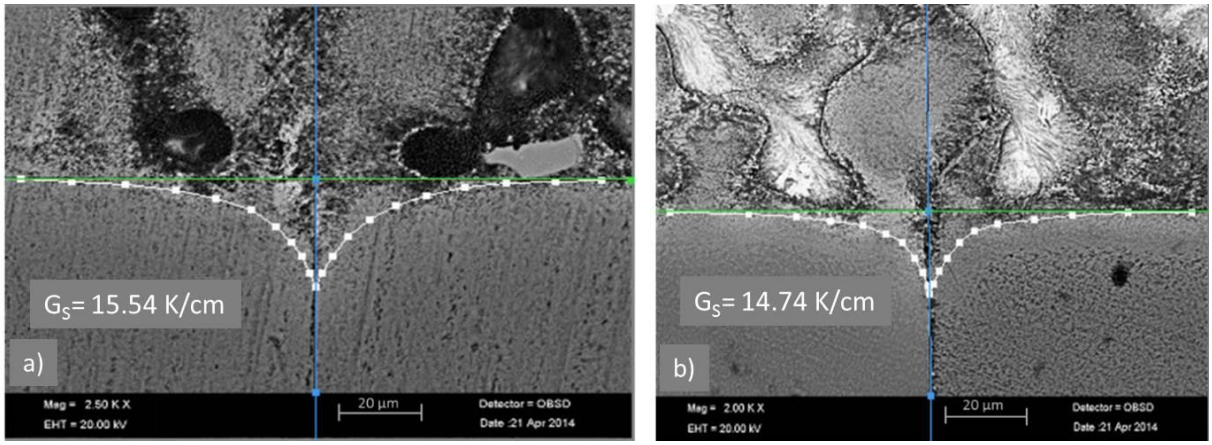

Figure 4. Typical GBG shapes for the solid Alα solution in equilibrium with the liquid AlZn alloy

3.2. Determination of Entropy of Fusion

In order to determine $\sigma_{SL,}$ it is also necessary to know the entropy of fusion per unit volume, ΔS_f. The entropy of fusion for a binary alloy, is written as [6,7];

$$\Delta S_f = \frac{RT_M}{m_L V_S} \frac{C_S - C_L}{(1-C_L)C_L} \quad (5)$$

where R is the gas constant, T_M is the melting temperature, C_S is the composition of the solid phase, C_L is the composition of the liquid phase, m_L is the slope of liquidus and V_S is the molar volume of the solid phase. The values of the constants used in the determination of the ΔS_f were obtained from the Al-Zn phase diagram [1]. The ΔS_f value was obtained by using the R, T_M, m_L, V_S, C_S, and C_L values (Table 1). The error in the determination of ΔS_f is estimated to be about 3-4% [6,7].

Table 1. A comparison of Γ, ΔS_f and σ_{SL} measured in the present work (pw) with previous work

Alloy	**Solid Phase**	**Liquid Phase**	**Γx10^{-6}** (K.cm)	**ΔS_f x10^7** (erg/K.cm^3)	**σ_{SL}** (erg/cm^2)	**σ_{gb}** (erg/cm^2)	**$\frac{\sigma_{gb}}{\sigma_{SL}}$**	**Ref.**
Al-Zn	Al-30wt.%Zn	Al-60wt.%Zn	5.25	3.01	158.03	304.7	1.93	pw
Al-Zn	Al-40wt.%Zn	Al-70wt.%Zn	4.18	3.52	161.58	316.14	1.96	[24]
Al-Zn	Al-66.5at.%Zn	Al-88.7at.%Zn	3.41	3.14	106.94	204.72	1.91	[15]
Zn-Al	Zn-1wt.%1Al	Zn-5wt.%5Al	5.80	1.61	93.496	182.3	1.95	[25]

3.3. Solid-Liquid Interfacial Energy

The σ_{SL} can be obtained from the thermodynamic definition of the Gibbs-Thomson equation for isotropic σ_{SL} and it is expressed as;

$$\Gamma = \frac{\sigma_{SL}}{\Delta S_f} \quad (6)$$

If the values of Γ and ΔS_f are measured or known, then the σ_{SL} can be obtained from Equation 6. The σ_{SL} of the solid Alα solution in equilibrium with the AlZn liquid was determined by using the values of

Γ and ΔS_f (Table 1). Thus, the total experimental error of the σ_{SL} evaluation in the present study is approximately 12%. A comparison of the σ_{SL} with previous work is shown in Table 1.

3.4. Grain Boundary Energy

The GBG shapes allow the grain boundary energies, σ_{gb} to be determined once σ_{SL} have been obtained. The grain boundary energy can be expressed as;

$$\sigma_{gb} \leq 2\sigma_{SL} cos\theta \quad (7)$$

where $\theta = (\theta_A + \theta_B)/2$ is the angle that the GBG interfaces make with the y axis (Figure 1). The angle, θ was obtained from the cusp coordinates, x, y, using a Taylor expansion for parts at the base of the grooves. According to Equation 7, the value of σ_{gb} should be smaller or equal to twice the σ_{SL} i.e. $\sigma_{gb} \leq 2\sigma_{SL}$. The value of σ_{gb} for the solid Alα solution was found to be as 304.7±43.8 erg/cm^2 using the values of the σ_{SL} and θ in Equation 7. σ_{gb} / σ_{SL} ratio suggest that small θ, so that Cosθ ≈1 (Table 1). The estimated error in determination of angles θ was found to be 1%. Thus, the total experimental error in the resulting σ_{gb} is approximately 13%. A comparison of the values of ΔS_f, Γ, σ_{SL} and σ_{gb} for the solid Alα solution in equilibrium with the AlZn liquid determined in the present work with the values of previous ΔS_f, Γ, σ_{SL}, and σ_{gb} for different Al-Zn alloy systems has been given in Table 1 and refs [6,7,14-21,25]. The value of ΔS_f is in reasonably good agreement with the value of Keslioglu and Marasli [15], but Γ, σ_{SL} and σ_{gb} were found to be higher than their values. A reasonably good agreement was obtained with the other Al based alloys for σ_{SL} and σ_{gb} values. It should be noted that all previous works considered eutectic and peritectic systems having different compositions of solid and liquid phases and different equilibrium temperatures. The alloying elements of the phases and the equilibrium temperatures in the systems probably affect the Γ and thus σ_{SL} values.

4. Conclusion

1. The equilibrated GBG shapes for the solid Al solution (Al-30wt%Zn) in equilibrium with the Al-Zn liquid (Al-60wt%Zn) were observed.
2. From the observed GBG shapes, the Γ, σ_{SL}, and σ_{gb} have been determined for the solid Al solution in equilibrium with the Al-Zn liquid.
3. The K_S values of the solid phases for Al-30wt.%Zn and the Al-60wt%Zn alloys have been measured. The K_L /K_S ratio of the liquid phase to the solid phase has been obtained by using a Bridgman type directional apparatus for the Al-60wt%Zn alloy, and K_L value of Al-60wt%Zn was measured.
4. It has been shown that the radial heat flow apparatus can be used to obtain equilibrated solid-liquid interfaces and GBG shapes in not only eutectic, peritectic and monotectic systems but also any other alloy system. Thus, the GBG method may be use to determine σ_{SL} as a function of temperature and composition for any alloy system. σ_{SL} energies might be used to measure at different compositions and temperatures in the Al-Zn system by using GBG method as shown in this work. In this way it might be possible to extrapolate the σ_{SL} obtained for alloys to that for pure Al. So, the experimentally obtained pure Al, σ_{SL}, could be compared with the σ_{SL} obtained by using the homogeneous nucleation method, theoretical methods and other methods.

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