J Mater Sci (2006) 41:7939–7943
DOI 10.1007/s10853-006-0861-6

Experimental determination of solid–liquid interfacial energy for succinonitrile solid solution in equilibrium with the succinonitrile–(D) camphor eutectic liquid

K. Keşlioğlu · U. Böyük · M. Erol · N. Maraşlı

Received: 5 July 2005 / Accepted: 16 November 2005 / Published online: 22 September 2006

Abstract The equilibrated grain boundary groove shapes for Succinonitrile (SCN) solid solution in equilibrium with the Succinonitrile (SCN)–D Camphor (DC) eutectic liquid were directly observed. From the observed grain boundary groove shapes, the Gibbs–Thomson coefficient and solid–liquid interface energy for SCN solid solution in equilibrium with the SCN–DC eutectic liquid has been determined to be $(5.39 \pm 0.27) \times 10^{-8}$ K m and $(7.88 \pm 0.79) \times 10^{-3}$ J m^{-2} with present numerical method and Gibbs–Thomson equation, respectively. The grain boundary energy of SCN rich phase of the SCN–DC eutectic system has been determined to be $(14.95 \pm 1.79) \times 10^{-3}$ J m^{-2} from the observed grain boundary groove shapes. Thermal conductivity ratio of the liquid phase to the solid phase for SCN–0.16 mole % DC alloy has also been measured.

Introduction

The solid–liquid interface energy, σ_{SL} is defined as the reversible work required creating a unit area of the interface at constant temperature, volume and chemical potentials and plays a critical role in many phase transformations. The measurement of σ_{SL} in pure materials and alloys is difficult. Over the last half-century, various attempts have been made to determine the value of crystal-melt interfacial free energy in variety of materials. One of the most common techniques to determine the solid–liquid interfacial energy is use the equilibrated grain boundary groove shapes. In this technique, the solid–liquid interface is equilibrated with a grain boundary in a temperature gradient as shown in Fig. 1. The Gibbs–Thomson coefficient and solid–liquid interface energy are obtained using the equilibrium shape of the groove profile. This technique has been used to directly measure the solid–liquid interface energy for transparent materials [1–9]. The technique was extended to measure solid–liquid interface energies for opaque materials by Gündüz and Hunt [10–11].

The Gibbs–Thomson coefficient, Γ is expressed in the form of a change in undercooling, ΔT_r with radius, r as

$$\Delta T_r = \frac{\Gamma}{r}. \tag{1}$$

Equation (1) may be integrated in the y direction (perpendicular to the macroscopic interface) from the flat interface to a point on the cusp [10]

$$\int_0^y \Delta T_r \mathrm{d}y = \Gamma \int_0^y \frac{1}{r} \mathrm{d}y. \tag{2}$$

The right hand side of Equation (2) may be evaluated [11] for any shape by defining d$s = r$ dθ as shown in Fig. 1 (s is the distance along the interface and θ is the angle of the interface to y) giving

K. Keşlioğlu · N. Maraşlı (✉)
Department of Physics, Faculty of Arts and Sciences,
Erciyes University, 38039 Kayseri, Turkey
e-mail: marasli@erciyes.edu.tr

U. Böyük · M. Erol
Institute of Science and Technology, Erciyes University,
38039 Kayseri, Turkey

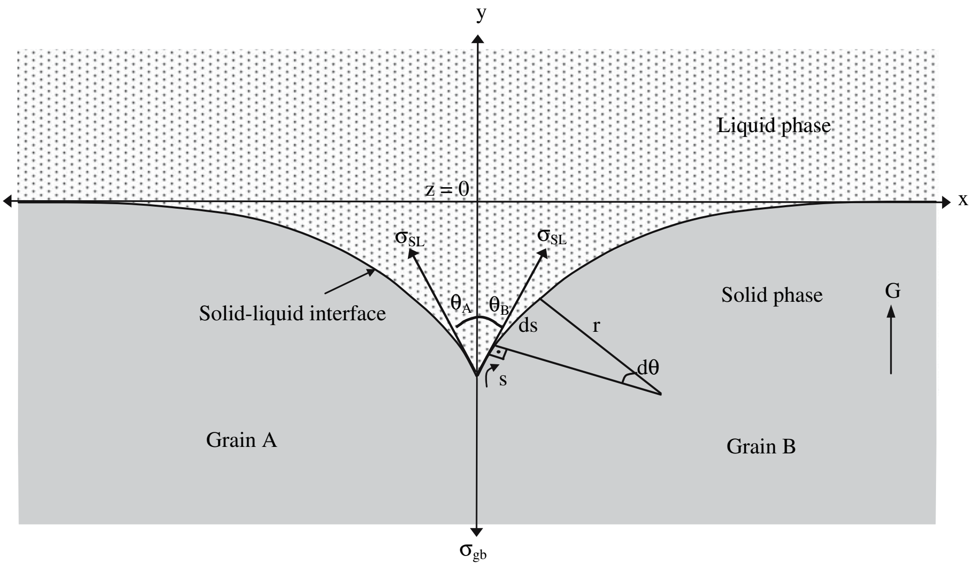

Fig. 1 Schematic illustration of an equilibrated grain boundary groove formed at a solid- liquid interface in a temperature gradient showing the x, y coordinates and θ angle

$$\int_0^y \frac{1}{r}\,\mathrm{d}y = (1 - \sin\theta). \tag{3}$$

The left-hand side of Eq. (2) may be evaluated if ΔT_r is known as a function of y.

The left hand side of Eq. (2) was integrated numerically using the values of ΔT_r calculated numerically and the right hand side of the Eq. (2) was evaluated by measuring the value of θ (obtained by fitting a Taylor expansion to the adjacent points on the cusp) by Gündüz and Hunt [10]. This allows the Gibbs–Thomson coefficient to be determined for a measured grain boundary groove shape. 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. To get accurate values of the Gibbs–Thomson coefficient with the Gündüz and Hunt's numerical method, the coordinates of grain boundary groove shape, the temperature gradient in the solid phase, G_S and the thermal conductivity ratio of the liquid phase to solid liquid phase, $R = K_L/K_S$ must be known or measured.

The solid–liquid interface energy is obtained from the thermodynamic definition of the Gibbs–Thomson coefficient, which is expressed as

$$\Gamma = \frac{\sigma_{SL}}{\Delta S^*} \tag{4}$$

where ΔS^* is the entropy change of fusion per unit volume.

Measurements of the solid–liquid interface energies have been made in the Al–Cu, Al–Si, Pb–Sn, Al–Mg, Al–Ni, Al–Ti, Al–Zn and Bi–Cd binary eutectic or peritectic metallic alloys [10–17].

Bayender et al. [18, 19] and Maraşlı et al. [20], have directly observed the equilibrated grain boundary groove shapes for transparent materials. They applied Gündüz and Hunt's numerical method to determine Gibbs–Thomson coefficients, solid–liquid interface energies and grain boundary energies in camphene, pivalic acid, succinonitrile and succinonitrile–carbon tetra bromide transparent organic materials.

Recently, the phase diagram of SCN–DC eutectic-based system has been determined [21] and the thermo physical and chemical properties of SCN are well established. Thus, the goal of the present work is to determine the Gibbs–Thomson coefficient, solid–liquid interfacial energy and grain boundary energy for SCN solid solution in equilibrium with the SCN–DC eutectic liquid.

Experimental details

Sample production

The equilibrated solid SCN solutions in equilibrium with the SCN–DC eutectic liquid have been directly observed by a temperature gradient stage. The details of the apparatus are given in [18]. The specimen cell was made by sticking two glass cover slips (50 mm long, 24 mm wide and 0.15 mm thick) with silicone elastomer glue. The slides were placed with their largest surface in the x–y plane and spaced a distance of about 80–100 μm apart in the z direction to minimise heat flow and curvature in the z direction and observe the equilibrated grain boundary groove shapes in *x*–*y* plane (2D). Organic materials usually react with this type glue. Before filling the cell with alloy, the cell was annealed at 523 K to prevent the reaction with glue.

Consider a binary eutectic system as shown in Fig. 2. Above the eutectic temperature, a binary eutectic system consists of solid and liquid provided the alloy composition, $C_\alpha < C_0 < C_E$ or $C_E > C_0 < C_\beta$, where C_E, C_α, 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 can grow on the eutectic structure 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. If the alloy composition is near the eutectic composition, above the eutectic temperature, a binary eutectic system consists of liquid. If the system, which has a composition near the eutectic composition is held in a very stable temperature gradient there will be no liquid droplets behind the solid phase and two solid phases can grow together on the eutectic structure. Equilibrating time for this system should be shorter because of the small freezing range.

In the present work, the alloy composition was chosen to be SCN–1 mole % DC to observe the SCN solid solution (SCN–0.16 mole % DC) in equilibrium with the eutectic liquid (SCN–13.9 mole % DC liquid). SCN–1 mole % DC alloy was prepared from the >99 % purity SCN and 99% purity DC supplied by Sigma-Aldrich Chemical Company. No attempt was made to purify the compounds. Known masses of SCN and DC were placed in a flask. The flask was then tightly sealed and heated in a hot water bath. Thus, an alloy was formed by the mixing of the components.

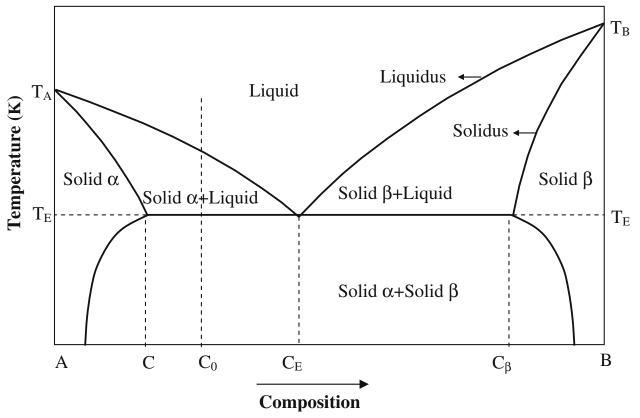

Fig. 2 A binary eutectic equilibrium phase diagram

The temperature gradient measurement

After the specimen cell filled with organic alloy, the specimen was placed in temperature gradient stage. One side of the specimen was heated and the other side of the specimen was kept cool with a water-cooling system to get a constant temperature gradient on the specimen. The temperatures in the specimen were measured using three insulated K-type thermocouples wires with 50 μm thick. One ends of the thermocouple wires were spark welded. Thermocouples were placed at a distance about 1.5–2 mm from each other and perpendicular to the heat flow direction in the specimen. The thermocouples were calibrated by detecting the eutectic melting point of SCN–1 mole % DC alloy. The melting point of SCN–1 mole % DC alloy was measured to be 311.2 K and the thermocouple's reading was different by only 0.3 K than the eutectic temperature of SCN–1 mole% DC alloy [22]. The specimen was melted until the one of three thermocouples were in the liquid phase and left to reach equilibrium. Then, planar growth was begun with very low growth rate. When the planar interface was grown, the temperature of the planar interface was measured with two thermocouples. The difference between two thermocouple's readings was ±0.2 K.

A thin liquid layer (2 or 3 mm thick) was melted to get uniform eutectic liquid and the specimen was annealed in a constant temperature gradient. The annealing time was 5 days for SCN–1 mole % DC alloy. When the solid–liquid interface reached equilibrium, the temperature differences between two thermocouples, ΔT were measured using a Hewlett Packard 34401A model digital multimeter. The multimeter has a 1 μV resolution for direct voltage measurements. The positions of the thermocouples and the equilibrated grain boundary groove shapes were then photographed with a CCD digital camera placed on the top of Olympus BH2 light optical microscope. The distance between three thermocouples, ΔX was measured from the photographs of the thermocouple's positions using Adobe PhotoShop 7.0 version software.

The temperature gradient, $G = \Delta T/\Delta X$ for the equilibrated grain boundary groove shapes was determined using the values of ΔT and ΔX. The estimated error in the measurements of temperature gradient, G is about 5% [20].

The coordinates of equilibrated grain boundary groove shapes were measured with an optical microscope to an accuracy of ±10 μm. The uncertainty in the measurements of equilibrated grain boundary coordinates was 0.1%.

The thermal conductivity ratio of the liquid phase to solid phase, $R = K_L/K_S$ must be known or measured to obtain Gibbs–Thomson coefficient with present numerical method. The thermal conductivity ratio of the equilibrated liquid phase to solid phase for SCN–0.16 mol % DC alloy was measured in a directional growth apparatus. The time–temperature trace enables the conductivity ratio of the liquid to solid to be calculated [10]. The thermal conductivity ratio, $R = K_L/K_S$ for SCN–0.16 mol % DC alloy was found to be 0.45.

Results and discussion

The Gibbs–Thomson coefficient

If the thermal conductivity ratio of the liquid phase to solid phase, $R = K_L/K_S$, the coordinates of the grain boundary groove shapes and the temperature gradient in the solid phase, G are known, then the Gibbs–Thomson coefficient can be obtained using the numerical method described in detail in [10]. As mentioned above, the experimental error in the determination of Gibbs–Thomson coefficient was about 5%.

The Gibbs–Thomson coefficients for SCN solid solution in equilibrium with the SCN–DC eutectic liquid were determined by the numerical method using ten observed grain boundary groove shapes and the results are given in Table 1. A typical grain boundary groove shape of SCN solid solution in equilibrium with the SCN–DC eutectic liquid examined in present work is shown in Fig. 3.

The average value of Γ with experimental error from Table 1 is $(5.39 \pm 0.27) \times 10^{-8}$ K m for SCN solid solution in equilibrium with the SCN–DC eutectic liquid.

Table 1 Gibbs–Thomson coefficients for SCN solid solution equilibrium with the SCN–DC eutetic liquid

Groove No	$G_S \times 10^2$ (K/m)	Gibbs–Thomson coefficient Γ (K m)	
		$\Gamma_{LHS} \times 10^{-8}$	$\Gamma_{RHS} \times 10^{-8}$
a	16.82	5.23	5.43
b	17.21	5.46	5.28
c	15.45	5.46	5.49
d	14.99	5.55	5.32
e	14.07	5.37	5.12
f	15.91	5.37	5.30
g	15.91	5.52	5.47
h	15.16	5.37	5.42
i	14.39	5.33	5.41
j	17.68	5.35	5.54

The subscripts LHS and RHS refer to the left hand side and right hand side of groove, respectively

$\overline{\Gamma} = (5.39 \pm 0.27) \times 10^{-8}$ K m for SCN solid solution in equilibrium with the SCN–DC eutectic liquid

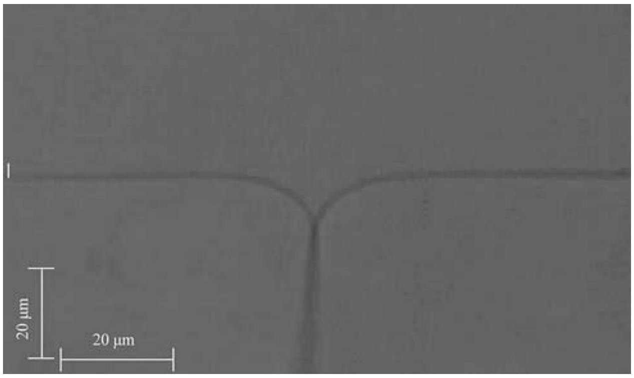

Fig. 3 A typical grain boundary groove shape for SCN solid solution in equilibrium with the SCN–DC eutectic liquid

The entropy change of fusion

To determine the solid–liquid interface energy, it is also necessary to know the entropy change of fusion per unit volume. The entropy change of fusion per unite volume is given by

$$\Delta S^* = \frac{\Delta H}{T_M} \frac{1}{V_S} \tag{5}$$

where ΔH is the enthalpy of single solid phase in the binary eutectic system, T_M is the melting temperature and V_S is the molar volume of single solid phase. The values of ΔH, T_M, V_S and ΔS^* are given in Table 2. The error in the determined entropy change of fusion per unit volume is estimated to be about 5% [10].

The solid–liquid interface energy

If the values of the Gibbs–Thomson coefficient and the entropy change of fusion per unit volume are measured or known, the solid–liquid interface energy can be obtained from Eq. (4). The experimental error in the determined solid–liquid interface energy is the sum of experimental errors of Gibbs–Thomson coefficient and entropy change of fusion per unit volume. Thus, the experimental error for the solid–liquid interface energy measurement in present work is about 10% [20]. The value of the solid–liquid interface energy for SCN solid solution in equilibrium with the SCN–DC eutectic liquid was found to be $(7.88 \pm 0.79) \times 10^{-3}$ J m^{-2}.

The grain boundary energy

The grain boundary energy can be expressed by

Table 2 The entropy change of fusion per unit volume, ΔS^* for SCN–DC eutectic system

System	Solid phase C_S	Liquid phase C_L	T_M (K)	$V_S \times 10^{-6}$ (m^3/mol)	ΔH (J/mol)	$\Delta S^* \times 10^5$ (J K^{-1} m^{-3})
SCN–DC	SCN–0.16 mole % DC	SCN–13.9 mole % DC	311.5 [21]	76.5 [22]	3484 [21]	1.462

Table 3 Comparison of the experimental results obtained in present work with previous measurements of the Gibbs–Thomson coefficient, solid–liquid interface energy and grain boundary energy for pure SCN and SCN bases binary eutectic alloys

System	Solid phase	Liquid phase	$\Gamma \times 10^{-8}$ (K m)	$\sigma_{SL} \times 10^{-3}$ (J m^{-2})	$\sigma_{gb} \times 10^{-3}$ (J m^{-2})
Pure SCN	SCN	SCN	6.17 5.54 [20]	8.94 ± 0.5 [4] 8.02 [20]	15.95 [20]
SCN	SCN	SCN	5.43 ± 0.27 [20]	7.86 ± 0.79 [20]	15.03 ± 1.95 [20]
SCN–CTB	SCN	SCN–4 mole % CTB	5.56 ± 0.28 [20]	8.80 ± 0.88 [20]	16.51 ± 2.15 [20]
SCN–DC	SCN–0.16 mole % DC	SCN–13.9 mole % DC	5.39 ± 0.27 [present]	7.88 ± 0.79 [present]	14.95 ± 1.79 [present]

$$\sigma_{gb} = 2\,\sigma_{SL}\cos\theta \qquad (6)$$

where $\theta = \frac{\theta_A + \theta_B}{2}$ is the angle that the solid–liquid interfaces make with the y axis [20, 23]. The angles, θ_A and θ_B were obtained from the cusp coordinates, x, y using a Taylor expansion for parts at the base of the groove. The grain boundary energy was then calculated from Eq. (6) using the solid–liquid interface energy and the values of θ. The estimated error in determination of angles was found to be 2% from standard deviation. Thus, the total experimental error in the resulting grain boundary energy is about 12%. The value of σ_{gb} for SCN solid solution was found to be $(14.95 \pm 1.79) \times 10^{-3}$ J m^{-2}.

A comparison of the experimental results obtained in present work with previous measurements of the Gibbs–Thomson coefficient, solid–liquid interface energy and grain boundary energy for pure SCN and SCN bases binary eutectic alloys is given in Table 3.

Conclusions

The equilibrated grain boundary groove shapes for SCN solid solution in equilibrium with the SCN–DC eutectic liquid were directly observed. From the observed grain boundary groove shapes, the Gibbs–Thomson coefficient, solid–liquid interface energy and the grain boundary energy for SCN solid solution in equilibrium with the SCN–DC eutectic liquid have been determined. The thermal conductivity ratio of the liquid phase to the solid phase for SCN–0.16 mole % DC alloy has also been measured.

Acknowledgements This project was supported by the Erciyes University Scientific Research Project Unit under the contract no FBT-05-06. Authors would like to thank to Erciyes University Scientific Research Project Unit for their financial supports.

References

1. Jones DRH, Chadwick GA (1970) Phil Mag 22:291
2. Jones DRH, Chadwick GA (1971) J Cryst Growth 11:260
3. Jones DRH (1978) Phil Mag 27:569
4. Schaefer RJ, Glicksman ME, Ayers JD (1975) Phil Mag 32:725
5. Hardy SC (1977) Phil Mag 35:471
6. Nash GE, Glicksman ME (1971) Phil Mag 24:577
7. Bolling GF, Tiller WA (1960) J Appl Phys 31/8:1345
8. Singh NB, Glicksman ME (1989) J Cryst Growth 98:573
9. Stalder I, Bilgram JH (2003) J Chem Phys 118:7981
10. Gündüz M, Hunt JD (1985) Acta Metall 33/9:651
11. Gündüz M, Hunt JD (1989) Acta Metall 37/7:839
12. Maraşlı N, Hunt JD (1996) Acta Mater 44/3:1085
13. Keşlioğlu K, Maraşlı N (2004) Mater Sci Eng A 369:294
14. Keşlioğlu K, Maraşlı N (2004) Metall Mater Trans A 35A:3665
15. Keşlioğlu K, Gündüz M, Kaya H, Çadırlı E (2004) Mater Lett 58:3067
16. Erol M, Maraşlı N, Keşlioğlu K, Gündüz M (2004) Scripta Mater 51:131
17. Keşlioğlu K, Erol M, Maraşlı N, Gündüz M (2004) J Alloy Compd 385:207
18. Bayender B, Maraşlı N, Çadırlı E, Şişman H, Gündüz M (1998) J Cryst Growth 194/1:119
19. Bayender B, Maraşlı N, Çadırlı E, Gündüz M (1999) Mater Sci Eng A 270:343
20. Maraşlı N, Keşlioğlu K, Arslan B (2003) J Cryst Growth 247:613
21. Witusiewicz VT, Sturz L, Hecht U, Rex S (2004) Acta Mater 52:4561
22. Derollez P, Lefebvre J, Descamps M, Press W, Fontaine H (1990) Condens Matter 2:6893
23. Woodruff DP (1973) The solid–liquid interface. Cambridge University Press, Cambridge, p 4