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Experimental determination of thermal conductivity and interfacial energies of solid Pb solution in the Pb–Sb eutectic system

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ABSTRACT

The equilibrated grain boundary groove shapes of solid Pb solution in equilibrium with the Pb–Sb eutectic liquid have been observed from quenched sample. The Gibbs–Thomson coefficient, solid–liquid interfacial energy and grain boundary energy of solid Pb solution have been determined. The thermal conductivity values for Pb–5.8 at.% Sb and Pb–17.5 at.% Sb and the thermal conductivity ratio of eutectic liquid phase to eutectic solid for Pb–17.5 at.% Sb alloy at the melting temperature have also been measured with a radial heat flow apparatus and Bridgman type growth apparatus, respectively.

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1. Introduction

The solid–liquid interfacial energy, σ_{SL} , is recognised 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 [3–18]. Observation of groove shape in a thermal gradient can be used to determine the interfacial energy, in dependent of the grain boundary energy because the interface near the groove must everywhere satisfy

$$\Delta T_{\rm r} = \left[\frac{1}{\Delta S_{\rm f}}\right] \left[\left(\sigma_{\rm SL} + \frac{d^2 \sigma_{\rm SL}}{d_{n_1^2}}\right) \kappa_1 + \left(\sigma_{\rm SL} + \frac{d^2 \sigma_{\rm SL}}{d_{n_2^2}}\right) \kappa_2 \right] \tag{1}$$

where $\Delta T_{\rm r}$, is the curvature undercooling, $\Delta S_{\rm f}$ 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. Thus, the curvature undercooling 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, $\sigma_{\rm SL} = \gamma$. 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 [19]. When the solid–liquid interfacial free energy is isotropic, Eq. (1) becomes

$$\Delta T_{\rm r} = \frac{\sigma_{\rm SL}}{\Delta S_{\rm f}} \left(\frac{1}{r_1} + \frac{1}{r_2} \right) \tag{2}$$

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

$$\Gamma = r\Delta T_{\rm r} = \frac{\sigma_{\rm SL}}{\Delta S_{\rm f}} \tag{3}$$

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

At present the most powerful method to measure solid–liquid interfacial energy experimentally 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, $R = K_L/K_S$.

Lead-antimony solders are one of the most familiar materials used for various microelectronic connections in computer industry. Different compositions of lead-antimony solders have considerable potential for advanced structural and electronic applications. The intensive interest in these solder alloys is attributed to their low cost and unique material properties including the high super plastic properties, low melting temperature, wettability. At this time, it is very interesting to study the some thermo-physical properties such as solid-liquid interfacial energy, Gibbs-Thomson coefficient, grain boundary energy and thermal conductivity of solid and liquid phases of Pb–Sb alloy. These thermo-physical properties could be used to people doing comparisons between experimentally observed solidification morphology and predictions from theoretical models. Thus the aim of the present work

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was to determine the thermal conductivity, Gibbs–Thomson coefficient, solid–liquid interfacial energy and grain boundary energy for solid Pb solution in the Pb–Sb alloy.

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. If the alloy composition (C_0) is near the eutectic composition ($C_0 \cong C_E$) above the eutectic temperature, a binary eutectic system consists of liquid. 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. Since the composition of Pb–Sb alloy in our experiment is far from the eutectic composition only one solid phase can grow on the cast structure. As can be seen from Figure 1, the temperature gradient on the sample is radial and single solid Pb solution phase grows from eutectic liquid on the cast structure.

From the phase diagram of Pb–Sb alloy, solid solubility of Sb in solid Pb is 5.8 at.% Sb at the eutectic temperature, 525 K and the eutectic liquid composition is Pb–17.5 at.% Sb [20]. Thus, the composition of alloy was chosen to be Pb–5.8 at.% Sb to grow single solid Pb solution on the cast structure. Pb–5.8 at.% Sb alloy was prepared in a vacuum furnace by using 99.99% lead and 99.99% antimony. 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 temperature of alloy. The molten alloy 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 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 Pb–Sb eutectic system.

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 283 K (10 °C) by 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 heating wire and the specimen was annealed in a very stable temperature gradient for a long time. In this condition, the solid and liquid phases 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 on the eutectic cast phase. If the temperature difference between solidus and liquidus lines is high, the freezing range would be larger. As can be seen from the phase diagram of Pb-Sb system in Ref. [20], the temperature difference between solidus and liquidus lines for Pb-5.8 at.% Sb alloy is approximately 60 °C. Because of this larger temperature difference the annealing time will be long. We have experimentally found the optimum annealing period for Pb-5.8 at.% Sb allov is 17 days after several experiments. 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 of ±0.025 K for hours and ±0.05 K for up to 17 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 30 ml acetic acid and 20 ml hydrogen peroxide for 5 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 $(200 \times 0.01 = 2 \text{ mm})$ 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, 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 $\pm 10 \,\mu$ m by following Maraşlı and Hunt's geometrical method so that appropriate corrections to the shape of the grooves could be deduced [14]. The uncertainty in the measurements of equilibrated grain boundary groove coordinates is 0.1%.

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

The thermal conductivity ratio of equilibrated eutectic liquid phase (Pb–17.5 at.% Sb) to solid Pb solution (Pb–5.8 at.% Sb) phase, $R = K_{L(eutectic liquid)}/K_{S(Pb)}$ must be known or measured to evaluate the Gibbs–Thomson coefficient with the present numerical method. The radial heat flow method is an ideal technique for measuring the thermal conductivity of the solid phase. The thermal conductivity of the solid Pb solution phase is also needed to evaluate the temperature gradient in the solid phases. 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 condition. At the steady–state condition, the temperature gradient in the cylindrical specimen is given by Fourier's law,

$$G_{\rm S} = \frac{\mathrm{d}T}{\mathrm{d}r} = -\frac{Q}{2\pi r\ell K_{\rm S}} \tag{4}$$

where *Q* is the total input power, *r* is the distance of the solid–liquid interface to the centre of the sample, ℓ is the length of the heating wire which is constant and *K*_S is the thermal conductivity of the solid phase. Integration of the Eq. (4) gives

$$K_{\rm S} = a_0 \; \frac{\rm Q}{T_1 - T_2} \tag{5}$$

where $a_0 = \ln(r_2/r_1)/2\pi\ell$ is an experimental constant, r_1 and r_2 ($r_2 > r_1$) are fixed distances from the central axis of the specimen, T_1 and T_2 are the temperatures at the fixed positions, r_1 and r_2 . Eq. (5) could be used to obtain the thermal conductivity of the solid phase by measuring the difference in temperature between two fixed points for a given power level provided that the vertical temperature variation are minimum or zero.

The thermal conductivities of solid Pb solution (Pb–5.8 at.% Sb) and eutectic solid (Pb–17.5 at.% Sb) were measured with the radial heat flow apparatus. Sufficient amount of metallic materials were melted to produce an ingot of approximately 100 mm in length and 30 mm in diameter in a vacuum furnace by using 99.99% pure Pb and 99.99% pure Sb. After stirring, the molten metallic alloy was poured into a graphite crucible held in a specially constructed hot filling furnace at approximately 100 K above the melting temperature of alloy. The molten metallic alloy was then directionally frozen from bottom to top to ensure that the crucible was completely

full. The specimen was then placed in the radial heat flow apparatus.

The specimen was heated from the centre using a single heating wire (140-190 mm in length and 2.5 mm in diameter, Kanthal A-1) in steps of 50 K up to 10 K below the melting temperature of the alloy and the outside of the specimen was cooled to maintain a radial temperature gradient. To obtain a reliable value of thermal conductivity in the thermal conductivity measurement, a larger radial temperature gradient is desired. For this purpose, the gap between the cooling jacket and the specimen was filled with free running sand or graphite dust and the outside of the specimen was kept at 283 K using a heating/refrigerating circulating bath. The length of central heating wire was chosen to be 10 mm longer than the length of specimen to make isotherms parallel to the vertical axis.

The specimen was kept at steady-state condition for at least two hours for a setting temperature. At steady state, the total input power and the stationary thermocouple temperatures were recorded with a *Hewlett Packard* 34401 type multimeter and a *Pico TC–08* data–logger. The temperatures on the different parts of the specimen were measured with mineral insulated metal sheathed, 0.5 mm in diameter K type thermocouples. The zero or minimum vertical temperature gradient is desired in thermal conductivity measurements. The vertical temperature for each setting was tried to be made as parallel as possible to the vertical axis by moving the central heater up and down. After all desired power settings and temperature measurements had been completed during the heating procedure, the cooling procedure was started in same steps down to room temperature.

Then the sample was removed from the furnace and cut transversely near to the measurement points, after that the specimen was ground and polished for the measurements of r_1 and r_2 . The positions of the thermocouples were then photographed with an Olympus DP12 CCD digital camera placed in conjunction with an Olympus BX51 type light optical microscope. A graticule $(200 \times 0.01 = 2 \text{ mm})$ was also photographed using the same objective. The photographs of the positions of the thermocouples and the graticule were superimposed on one another using Adobe PhotoShop 8.0 software so that accurate measurement of the distances of stationary thermocouples could be made to an accuracy of ±10 µm. The transverse and longitudinal sections of the specimen were examined for the porosity, crack and casting defects to make sure that these would not introduce any error to the measurements. The experimental value of a_0 for solid Pb solution and Pb–Sb eutectic solid were 1.470, 1.487 m⁻¹, respectively in the present work.

The thermal conductivities of solid Pb solution and eutectic solid versus temperature are shown in Figure 2. A comparison of thermal conductivities of solid Pb solution and Pb–Sb eutectic solid with the thermal conductivity of Pb [21] and Sb [22] are also given in Figure 2. The values of K_S for the solid Pb solution and Pb–Sb eutectic solid at the eutectic melting temperature were obtained to be 28.7 and 26.8 W/Km, respectively by extrapolating to the eutectic temperature as shown in Figure 2. The thermal conductivities of solid and liquid phases for solid Pb solution and Pb–Sb eutectic solid and their ratios are given in Table 1.

It is not possible to measure the thermal conductivity of the liquid phase with the radial heat flow apparatus since a thick liquid layer (10 mm) is required. A layer of this size would certainly have led to convection. If the thermal conductivity ratio of the liquid phase to the solid phase is known and the thermal conductivity of the solid phase is measured at the melting temperature, the thermal conductivity ratio can be obtained during directional growth with a Bridgman type growth apparatus. The detail of the experimental procedure was given in Refs. [13–17].



Figure 2. Thermal conductivities of solid Pb solution and eutectic solid versus temperature in the Pb–Sb system.

Table 1

The thermal conductivity of solid and liquid phases and their ratios at the eutectic melting temperature in the Pb–Sb eutectic system.

Pb-Sb Eutectic liquid 525.15 21.7 0.81 (Pb-17.5 at.% Sb) Eutectic solid 26.8 0.92	
Eutectic solid 26.8 (Pb-17.5 at.% Sb)	
Eutectic liquid 525.15 21.7 0.76 (Pb–17.5 at.% Sb)	
Solid Pb solution28.7(Pb-5.8 at.% Sb)	

The thermal conductivity ratio of the eutectic liquid (Pb–17.5 at.% Sb) to the eutectic solid (Pb–17.5 at.% Sb), $R = K_{L(eutectic)}/K_{S(eutectic)}$ was measured to be 0.81 as shown in Figure 3. The thermal conductivity of eutectic solid at the eutectic melting temperature was also measured to be 26.8 W/Km. Thus, the thermal conductivity of eutectic liquid was determined to be 21.7 W/Km. The value of $R = K_{L(eutectic)}/K_{S(Pb)}$ is also found to be 0.76 by using the values of $K_{L(eutectic)}$ and $K_{S(Pb)}$. The values of K_L and K_S used in the determination of Gibbs–Thomson coefficient are also given in Table 1.



Figure 3. The cooling rate of Pb-17.5 at.% Sb eutectic alloy.

2.5. Measurement of temperature gradient in the solid phase

The average temperature gradient of the solid phase must be determined for each grain boundary groove shape. This was done by measuring the input power, the length of heating wire, the position of the solid–liquid interface and the value of $K_{\rm S}$ for solid Pb solution phase at the eutectic melting point. By using these measured values in Eq. (4), temperature gradient can be determined for each grain boundary groove shape. The total fractional uncertainty in the measurement of temperature gradient is about 6.5% [14].

3. Results and discussions

3.1. Determination of Gibbs-Thomson coefficient

If the thermal conductivity ratio of equilibrated liquid phase to solid phase, the coordinates of the grain boundary groove shape and the temperature gradient of the solid phase are known, the Gibbs–Thomson coefficient (Γ) can be obtained using the numerical method described in detail Ref. [13]. The experimental error in the determination of Gibbs–Thomson coefficient is the sum of experimental errors in the measurement of the temperature gradient, thermal conductivity and groove coordinates. Thus the total error in the determination of Gibbs–Thomson coefficient is estimated to be about 7% [14].

The Gibbs–Thomson coefficients for solid Pb solution in equilibrium with the eutectic liquid (Pb–17.5 at.% Sb) were determined with the present numerical model by using ten equilibrated grain boundary groove shapes. Typical grain boundary groove shape for solid Pb solution in equilibrium with the eutectic liquid (Pb– 17.5 at.% Sb) is shown in Figure 4. As can be seen from Figure 4, solid Sb solution phase first nucleates on the surface of the Pb solid solution phase, then both solid Sb solution and the Pb solid solution phases grow together to form a eutectic grain and this allows a well defined solid–liquid interface to be observed during the quench and also the phases, grains and interfaces of the system are very clear.

The values of Γ for solid Pb solution are given in Table 2. The average value of Γ from Table 2 is $(13 \pm 1.0) \times 10^{-8}$ Km for solid Pb solution in equilibrium with the Pb–Sb eutectic liquid.

3.2. Determination of entropy of fusion per unit volume

In order to determine the solid–liquid interfacial energy it is also necessary to know the entropy of fusion per unit volume, ΔS_f for the solid phase. The entropy of fusion per unit volume for an alloy is given by [13],



Figure 4. Typical grain boundary groove shape for solid Pb solution in equilibrium with the Pb–17.5 at% Sb eutectic liquid.

Table 2

The Gibbs–Thomson coefficients for solid Pb solution in equilibrium with the Pb–Sb eutectic liquid. The subscripts LHS and RHS refer to left hand side and right hand side of the groove respectively.

Grove no.	$G_{\rm K}\times 102$	α°	β°	Gibbs-Thomson coefficient		
	(K/m)			$\frac{\Gamma_{LHS}\times 10^{-8}}{(Km)}$	$\frac{\Gamma_{\text{RHS}}\times 10^{-8}}{(\text{Km})}$	
a	30.4	15.4	13.3	13.6	13.2	
b	31.4	15.8	11.2	14.4	13.6	
с	31.7	17.8	14.1	14.0	13.8	
d	30.6	14.5	13.3	13.3	13.5	
e	31.3	11.2	14.1	14.0	13.8	
f	31.5	13.1	14.1	13.7	14.0	
g	33.1	15.2	12.3	14.5	13.9	
h	29.8	16.7	15.0	13.2	13.2	
i	32.0	18.6	14.3	13.4	13.2	
j	31.0	16.9	15.4	13.3	13.5	
				$\bar{\Gamma}$ = (13 ± 1.0)	< 10 ⁻⁸ Km	

$$\Delta S_{\rm f} = \frac{(1 - C_{\rm S})(S_{\rm A}^{\rm L} - S_{\rm A}^{\rm S}) + C_{\rm S}(S_{\rm B}^{\rm L} - S_{\rm B}^{\rm S})}{V_{\rm S}} \tag{6}$$

where S_A^L , S_B^S , S_B^L and S_B^S are partial molar entropies for A and B materials and C_S is the concentration of solid phase. Since the entropy terms are generally not available, for convenience, the undercooling at constant composition may be related to the change in composition at constant temperature. For a solid sphere of radius *r* [23]

$$\Delta C_{\rm r} = \frac{2\sigma_{\rm SL}V_{\rm S}(1-C_{\rm L})C_{\rm L}}{rRT_{\rm M}(C_{\rm S}-C_{\rm L})} \tag{7}$$

where *R* is the gas constant, $T_{\rm M}$ is the melting temperature and $V_{\rm S}$ is the molar volume of solid phase. For small changes

$$\Delta T_{\rm r} = m_{\rm L} \Delta C_{\rm r} = \frac{2m_{\rm L} \sigma_{\rm SL} V_{\rm S} (1 - C_{\rm L}) C_{\rm L}}{r R T_{\rm M} (C_{\rm S} - C_{\rm L})} \tag{8}$$

where $m_{\rm L}$ is the slope of liquidus. For spherical solids, the curvature undercooling is

$$\Delta T_{\rm r} = \frac{2\sigma_{\rm SL}}{r\Delta S_{\rm f}} \tag{9}$$

From Eqs. (8) and (9), the entropy of fusion for an alloy is written as

$$\Delta S_{\rm f} = \frac{RT_{\rm M}}{m_{\rm L}V_{\rm S}} \frac{C_{\rm S} - C_{\rm L}}{(1 - C_{\rm L})C_{\rm L}} \tag{10}$$

The molar volume, $V_{\rm S}$ is expressed as

$$V_{\rm S} = V_{\rm c} N_{\rm a} \frac{1}{n} \tag{11}$$

where $V_{\rm C}$ is the volume of the unit cell, $N_{\rm a}$ is the Avogadro's number and n is the number of atoms per unit cell. The molar volume of solid Pb solution is $1.82 \times 10^{-5} \text{ m}^3$ [13]. The values of the relevant constant used in the determination of entropy of fusion per unit volume were obtained from the phase diagram [20] and are given in Table 3.

Comparisons of thermo-physical properties of solid Pb phases in the different binary systems at their eutectic melting temperature are given in Table 3. As can be seen from Table 3, the value of entropy of fusion for solid Pb solution in the Pb–Sb system agrees with the values of entropy of fusion for Pb solution in the different binary systems except the value of entropy of fusion for Pb solution in the Pb–Sn eutectic system. The error in the determination of entropy of fusion per unit volume is estimated to be about 5% [24].

3.3. Evaluation of the solid-liquid interfacial energy

If the values of Γ and $\Delta S_{\rm f}$ are known, the value of solid–liquid interfacial energy, $\sigma_{\rm SL}$ can be evaluated from Eq. (3). The solid–liquid interfacial energy of the solid Pb solution in equilibrium with the Pb–Sb eutectic liquid (Pb–17.5 at.% Sb) was evaluated to be $(50 \pm 6.1) \times 10^{-3}$ J m⁻² by using the values of Γ and $\Delta S_{\rm f}$. The experimental error in the determination of solid–liquid interfacial energy is the sum of experimental errors of the Gibbs–Thomson coefficient and the entropy change of fusion per unit volume. Thus, the total experimental error of the solid–liquid interfacial energy evaluation in present work is estimated to be about 12%.

3.4. Grain boundary energy

If the grains on either side of the grain boundary are the same phase then the grain boundary energy can be expressed by

$$\sigma_{\rm gb} = 2\,\sigma_{\rm SL}\cos\theta \tag{12}$$

where $\theta = \frac{\theta_A + \theta_B}{2}$ is the angle that the solid–liquid interfaces make with the *y* axis. 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. According to Eq. (12), the value of σ_{gb} should be smaller or equal to twice of solid–liquid interfacial energy, i.e. $\sigma_{gb} \leq 2\sigma_{SL}$.

The value of the grain boundary energy for the solid Pb solution was found to be $(99 \pm 13.0) \times 10^{-3}$ J m⁻² by using the values of the $\sigma_{\rm SL}$ and θ into Eq. (12). The estimated error in determination of θ angles was found to be 1%. Thus the total experimental error in the resulting grain boundary energy is about 13%.

As mentioned above, interfacial energy anisotropy is considered to play a critical role in many phase transformations. The determination of effects of anisotropy on the interfacial energy is difficult. In literature, there are no theoretical and experimental available data for anisotropy of interfacial energy of the solid Pb phase. Thus the solid–liquid interfacial energy is assumed to be isotropic.

The comparisons of the values of Gibbs–Thomson coefficient (Γ), solid–liquid interfacial energy (σ_{SL}) and grain boundary energy

Table 3

Comparisons of thermo-physical properties of solid Pb phases in the different binary systems at their eutectic melting temperature.

System	Pb-Sn	Pb–Sb	Pb-Pd	Pb-Pt	Pb-Bi	Pb-Ag	Pb-Au
Solid phase	Pb–29 at.% Sn	Pb solution (Pb–5.8 at.% Sb)	Pb	Pb	Pb solution (Pb–21.9 at.% Bi)	Pb solution (Pb–0.2 at.% Ag)	Pb
The value of $f(C)^{a}$ for solid phase	2.32 [13]	0.81 [20]	1.09 [20]	1.06 [20]	0.68 [20]	1.00 [20]	1.18 [20]
Eutectic melting temperature, $T_{\rm m}$ (K)	456 [13]	525.15 [20]	533.15 [20]	563.15 [20]	460.15 [20]	577.15 [20]	485.65 [20]
Molar volume of solid phase $\times 10^{-5}$ (m ³)	1.82 [13]	1.82 [13]	1.82 [13]	1.82 [13]	1.82 [13]	1.82 [13]	1.82 [13]
Liquidus slope, <i>m</i> _L (K/at.fr)	408 [13]	527.20 [20]	871.43 [20]	895.06 [20]	472.59 [20]	952.00[20]	816.50 [20]
Entropy of fusion for solid phase, $\Delta S_f \times 10^5 (J/K m^3)$	11.8 [13]	3.7	3.0	3.0	3.0	2.8	3.2

^a $f(C) = \frac{C_S - C_L}{(1 - C_L)C_L}$

Table 4

Comparisons of the values of Γ , σ_{sL} , σ_{gb} for solid Pb solution in the Pb–Sb eutectic system measured in present work with the values of Γ , σ_{sL} , σ_{gb} for solid Pb phases in the different binary systems obtained in previous works.

System	Solid phase	Liquid phase	Melting temperature (K)	Gibbs–Thomson coefficient $\Gamma \times 10^{-8}$ (Km)	Solid–liquid interface energy $\sigma_{\rm SL} imes 10^{-3}$ (J m $^{-2}$)		Grain boundary energy $\sigma_{ m gb} imes 10^{-3}$
					Theoretical	Experimental	$(J m^{-2})$
РЬ	Pb	РЬ	600.6	-	50.2 [25] 69 [26] 66 [27] 49 [28] 55 [29,6] 62 [31] 50 [31]	42.7 [32] 40±7 [33] 46 [5] 40 [34]	-
Pb-Bi	Pb	Pb-38.0 at.% Bi	460.15	14.7*	44.1 [30]	-	-
Pb-Ag	Pb	Pb-4.69 at.% Ag	577.15	19.3 [*]	53.9 [30]	-	_
Pb-Au	Pb	Pb-15.24 at.% Au	485.65	14.5*	46.6 [30]	-	-
Pb–Pt	Pb	Pb–5.29 at.% Pt	563.15	17.0*	51.2 [30]	-	_
Pb–Pd	Pb	Pb-8.40 at.% Pd	533.15	16.8*	50.5 [30]	-	_
Pb–Sn	Pb	Sn–26.1 at.% Pb	456	4 ± 0.45 [13]	52.7 [28]	56 ± 8.15 [13]	111 ± 15.61 [13]
Pb-Sb	Pb	Pb–17.5 at.% Sb	525.15	13 ± 1.0 [PW]	53 [30]	50 ± 6.1 [PW]	99 ± 13.0 [PW]

PW: Present work.

^{*} Calculated from Eq. (3) by using the values of σ_{SL} and ΔS_f .

 $(\sigma_{\rm gb})$ for solid Pb solution measured in present work with the values of Γ , $\sigma_{\rm SL}$, $\sigma_{\rm gb}$ for solid Pb phases in the different binary systems obtained in previous works is given in Table 4. As can be seen from Table 4, the resulting values of $\sigma_{\rm SL}$ and $\sigma_{\rm gb}$ for solid Pb solution in the Pb–Sb system agree well with the values of $\sigma_{\rm SL}$ and $\sigma_{\rm gb}$ determined in previous works for solid Pb phases in the different binary systems except the value of Γ for Pb solution in the Pb–Sn eutectic system. The value of Γ for solid Pb solution in equilibrium with the Pb–Sn eutectic liquid is three times smaller than the values of Γ for solid Pb solution in the Pb–Sn eutectic systems while the value of $\Delta S_{\rm f}$ for Pb solution in the Pb–Sn eutectic system is three times bigger than the values of $\Delta S_{\rm f}$ for Pb phases in the different binary eutectic system.

4. Conclusions

A radial temperature gradient on the sample was established by heating from the centre with a single heating wire and cooling the outside of the sample with a heating/refrigerating circulating bath. The equilibrated grain boundary groove shapes for solid Pb solution in equilibrium with the Pb–Sb eutectic liquid were observed from a quenched sample. Some thermo-physical properties such as the Gibbs–Thomson coefficient, solid–liquid interfacial energy and grain boundary energy of solid Pb solution in equilibrium with the Pb–Sb eutectic liquid have been determined from the observed grain boundary groove shapes. The thermal conductivities of solid Pb solution and eutectic solid phases at the eutectic temperature have also been determined.

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