

# Grain Boundary Wetting Phase Transition and Analysis of the Energy Characteristics of Grain Boundaries in the $\text{Sn}_s-(\text{Zn}/\text{Sn})_l$ System

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**Abstract**—Regularities of the interaction of tin grain boundaries (special  $\Sigma 5$  and general  $\Sigma 17$   $\langle 001 \rangle$ ) and a Sn–Zn melt of equilibrium composition were studied. The grain boundary wetting phase transition temperature was determined; for  $\Sigma 5$  and  $\Sigma 17$ , it is 216°C. More than 90% of the general grain boundaries were completely wetted by the melt over a range of temperatures, from the eutectic melting temperature to the tin melting temperature. It was shown that the anisotropy of interphase energy at the solid tin–Zn–Sn melt interface is  $64 \pm 10 \text{ mJ m}^{-2}$  at 216°C. The energies of the  $\Sigma 5$  and  $\Sigma 17$  grain boundaries in the range of 201–216°C were obtained on the basis of the experimental dependence of the dihedral angle on temperature.

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## INTRODUCTION

The functional properties of modern materials (especially micro- and nano-crystalline, heterophase, and composition materials) are to a large extent determined by the phase distribution topology and properties of their interphase and intergranular boundaries. More than 50 years ago, it was shown [1] that the equilibrium structure of two-phase polycrystalline samples is to a large extent determined by the ratio of the grain boundary energy of the main phase  $\sigma_{\text{gb}}$  and the energy of the main phase–inclusion interface. If the sample is annealed at a temperature higher than the inclusion melting point, the interphase energy is the melt–solid tension  $\sigma_{\text{sl}}$ . If the condition  $\sigma_{\text{gb}} < 2\sigma_{\text{sl}}$  is satisfied, the dihedral angle  $\theta$  is formed along the contact line of the liquid phase and the individual grain boundary; the value of this dihedral angle is determined by the ratio between  $\sigma_{\text{gb}}$  and  $\sigma_{\text{sl}}$ ,

$$\cos\left(\frac{\theta}{2}\right) = \frac{\sigma_{\text{gb}}}{2\sigma_{\text{sl}}}. \quad (1)$$

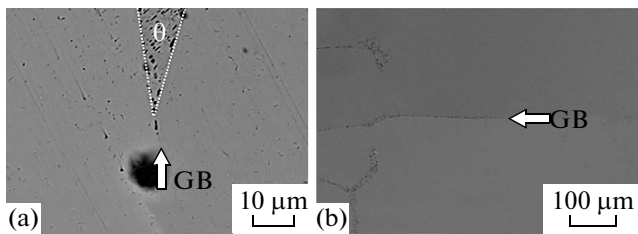
Expression (1) does not take into account the dependence of intergranular and interphase energy on interphase orientation with respect to crystallographic axes and can be used if the anisotropy of the interphase energy is not high. In the case  $\sigma_{\text{gb}} \geq 2\sigma_{\text{sl}}$ , the formation of the thin liquid phase layer replacing the grain boundary (wetting transition) is observed. Detailed analysis of morphology of binary metallic systems equilibrated at different temperatures above the eutectic temperature showed that the transition from the non-zero angle  $\theta$  (grain boundary etching) to com-

plete wetting is observed if a certain temperature  $T_w$  is reached. This is because the interphase energy usually decreases faster than the intergranular energy with increasing temperature, and the condition  $\sigma_{\text{gb}} > 2\sigma_{\text{sl}}$  starts to be satisfied at  $T > T_w$  [2].

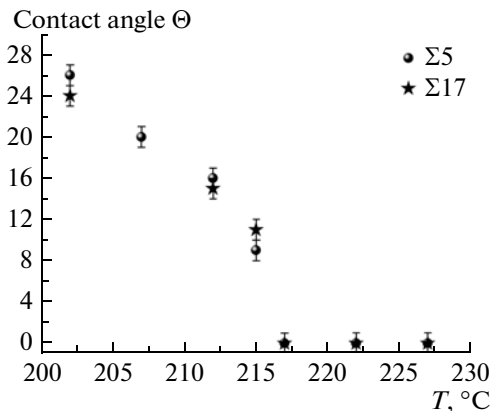
The objective of this study was to determine the conditions of the grain boundary wetting phase transition and to analyze the energy characteristics of the interfaces in the interaction of tin grain boundaries with a saturated Zn–Sn melt. The choice of the system was determined by the following factors: first, the importance of materials based on Sn and Zn in the development of lead-free soldering alloys [3, 4]. In this case, a large number of compositions tested as soldering alloys is essentially enriched by tin, i.e., is morphologically close to the samples studied in this paper. While the wetting conditions of special [5] and general [6] grain boundaries have been studied earlier for Sn–Zn alloys enriched by Zn, the wetting phase transition for tin grain boundaries contacting a zinc-based melt is studied here for the first time.

Second, the chosen system is a convenient model for investigating the interaction of grain boundaries with a melt. This is simple eutectic in which there are no intermetallics. Tin-based solid solution coexists with the equilibrium melt in a range of 198.5–232°C [7].

An important advantage of the system is that the energy of Sn–Zn interface is insensitive to the oxygen partial pressure in the experiment. Comparing dependences of the dihedral angle  $\phi$  on the temperature that were obtained for a system of polycrystalline Zn-satu-



**Fig. 1.** Microphotos of the interphase of a bicrystal tin  $\Sigma 5$ –zinc melt interface at 207°C.



**Fig. 2.** Temperature dependence of contact angle  $\theta$  in the interaction of tin  $\Sigma 5$  and  $\Sigma 17$ –equilibrium zinc melt interfaces.

rated Zn–Sn melt during experiments in air [8] and in a reducing atmosphere of Ar–5% $H_2$  [9], it turns out that the results agree over the studied temperature range. This considerably simplifies the experimental conditions (it is not necessary to thoroughly control the oxygen contamination) and makes this system more attractive than those containing components with high sensitivities to oxygen (Mg, Al).

## EXPERIMENTAL

To investigate the interaction of individual tin grain boundaries with an equilibrium zinc melt, bicrystal samples were put into direct contact with a Zn–Sn melt.

Tin bicrystals with  $\Sigma 5$  and  $\Sigma 17$  boundaries (rotation about the  $\langle 001 \rangle$  axis) were grown by means of directed crystallization [2]. Bicrystal samples were partially melted to the edge with grain boundaries, and zinc was introduced into the melt with stirring.

Isothermal annealings were performed in quartz ampoules (the residual pressure in the ampoules was 0.1–1 Pa) in a temperature range of 202–227°C for 15 min with subsequent quenching in water. In the course of annealing, a liquid phase of equilibrium composition interacting with the grain boundaries was formed at the edge. In the temperature range of 202–

227°C, the equilibrium zinc concentration in the melt fell from ~12 to ~1 mol % (Fig. 2).

Polycrystalline tin samples (99.999%) containing 2 wt % of zinc were also prepared to analyze the orientation anisotropy of the interphase energy and the wetting conditions of the Zn and Zn–Sn melt grain interfaces. Samples were prepared by the alloying of individual zinc and tin components at 600°C; plates with  $10 \times 10 \times 3$  mm in size were then cut and subjected to 10% deformation by cold rolling. Isothermal annealing similar to that of bicrystal samples was then performed in a temperature range of 201–215°C for 7 h with subsequent quenching in water.

For metallographic studies, the sample surfaces were polished (the bicrystals were polished in such a way that the section plane was parallel to  $\langle 001 \rangle$  plane and perpendicular to the individual boundary) in a water stream using silicon carbide sandpapers with grains of down to 2000. They were then successively polished on felt disks with diamond polishing pastes having grains of 9, 6, 3, and 1  $\mu\text{m}$ . A sample of the microstructure was studied by means of high resolution scanning electron microscopy on a LEO Supra 50 VP. Elemental analysis of the sample surface was performed using an EDAX X-ray spectral analysis pad.

## RESULTS AND DISCUSSION

Our experiments to investigate the interaction of tin interfaces  $\Sigma 5$ ,  $\Sigma 17$  (rotation about the  $\langle 001 \rangle$  axis) with an equilibrium zinc melt showed that for both types of interfaces, the contact angle ( $\theta$ ) decreases with increasing temperature. The angle  $\theta$  vanishes at the temperature of wetting phase transition ( $T_w$ ).

Figure 1 shows the microphotos of the interphase surface  $\Sigma 5$  of tin bicrystal and equilibrium zinc melt at 207°C and 222°C.

It can be seen from the microphoto in Fig. 1a that the finite angle  $\theta$  is formed upon the interaction of the zinc melt with the grain boundary at 207°C. At 222°C (Fig. 1b), a liquid metal layer of the melt is formed along the grain boundary, testifying to the complete wetting of grain boundaries at this temperature. The presence of zinc at the grain boundaries of bicrystal samples at  $T \geq 216^\circ\text{C}$  was proved by EDAX X-ray spectral analysis.

At temperatures below 216°C, Zn is not detected at the grain boundary far from the triple interface of the interphase boundaries or at the grain boundaries in the direction of the bicrystal volume. A similar situation is observed at the special boundary  $\Sigma 17$ , where the wetting phase transition takes place at 216°C. The temperature dependence of the dihedral angle  $\theta$  for grain boundaries  $\Sigma 5$  and  $\Sigma 17$  is shown in Fig 2.

Note that the observation of wetting phase transition at tin boundaries  $\Sigma 5$  and  $\Sigma 17$  at the same temperature indicates that the energies of these boundaries are close to each other.

We propose using the Gibbs–Smith equation (1) to estimate the value of the intergranular energy at the  $\Sigma 5$  and  $\Sigma 17$  tin grain boundaries. At  $216^\circ\text{C}$   $\cos(\theta/2) = 1$ , the grain boundary energy is equal to twice the interphase energy.

The possibility of ignoring the dependence of the interphase energy on the solid–melt interface orientation is proved by the experimental data obtained upon the annealing of polycrystalline Sn–Zn samples. Figure 3 shows the inclusions formed after solidification of a Zn–Sn melt inside an individual Sn grain. It is well known [9] that the equilibrium form of such inclusions, corresponding to the minimum of the excess free interphase energy at a constant volume, can be used to calculate the maximum anisotropy of interphase energy:

$$\frac{\sigma_{sl}^{\max}}{\sigma_{sl}^{\min}} = \frac{R}{r}, \quad (2)$$

where  $R$  and  $r$  are the maximum and minimum inclusion radii, respectively. It can be seen from the microphoto in Fig. 3 that the anisotropy of  $\sigma_{sl}$  is no greater than several per cent (the inclusions are virtually spherical).

The value of the solid tin–melt interphase energy can be estimated using Eq. (3), obtained by methods of statistical thermodynamics with account of the following approximations [10]:

- (i) Zn–Sn melt represents a regular solution;
- (ii) the solid–melt interphase boundary is coherent, i.e., the difference of Zn and Sn molar volumes is assumed to be negligible;
- (iii) solubility of the liquid component in the solid one is negligible;
- (iv) adsorption of the solid component on the interphase surface is negligible (this assumption cannot introduce a large error in calculation, since the melt at  $216^\circ\text{C}$   $X_{Sn}^1 = 0.95$ );

$$\sigma_{sl} = \sigma_{Sn}^0 + \frac{1}{4\Omega_0} \left( -RT \ln X_{Sn}^1 + \Delta H_{Sn}^1 \left( 1 - \frac{T}{T_{Sn}^m} \right) \right), \quad (3)$$

where  $\sigma_{Sn}^0$  is the interphase energy of solid tin at the interface with its melt,  $\Omega_0$  is the tin molar area,  $\Delta H_{Sn}^1$  is the tin melting heat, and  $T_{Sn}^m$  is the tin melting temperature.

The values of the quantities used to estimate the energy characteristics in the studied system are given in the table.

Values of quantities used for the theoretical estimation of energy characteristics upon the interaction of tin  $\Sigma 5$ ,  $\Sigma 17$ –equilibrium zinc melt interfaces

$\Omega_0 \times 10^{-7}, \text{cm}^2 \text{mol}^{-1}$	$\sigma_{Sn}^0, \text{mJ m}^{-2}$	$X_{Sn}^1 (216^\circ\text{C}), \text{mol } \%$	$\Delta H_{Sn}^1, \text{kJ mol}^{-1}$	$\sigma_{\text{surf}}, \text{mJ m}^{-2}$
59	$62 \pm 10$ [10]	0.95	7.029	688 [11]

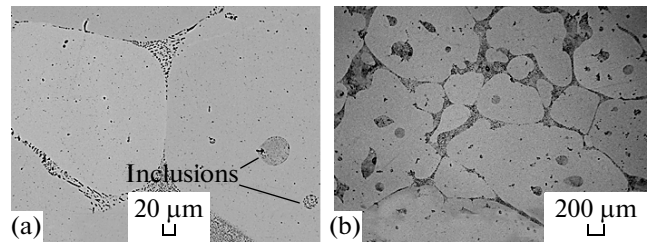


Fig. 3. Microstructure of polycrystalline Sn–2 wt % Zn samples at  $201^\circ\text{C}$ . The absence of Zn on unwetted boundaries is proved by EDAX microanalysis.

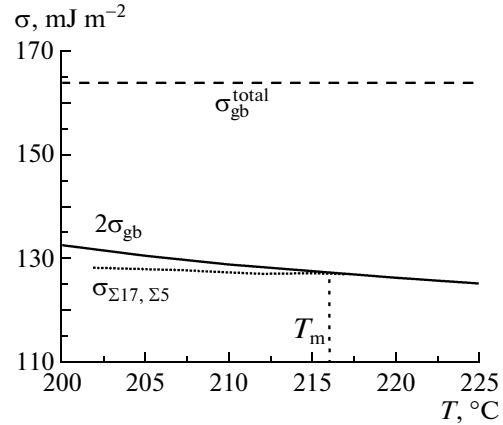


Fig. 4. Energy characteristics of tin  $\Sigma 5$ ,  $\Sigma 17$ –equilibrium zinc melt interfaces.

The value of the interphase energy calculated at  $216^\circ\text{C}$  was  $64 \pm 10 \text{ mJ/m}^{-2}$ . Note that this differs slightly from the interphase energy at the solid–melt tin interface (Table). This is because the melt contains only 5 at % of Zn and is close to pure Sn. Figure 4 shows the doubled values of  $\sigma_{sl}$  calculated using Eq. (3) in the range of  $200$ – $225^\circ\text{C}$ . At temperatures below  $T_m$ , Eq. (1) and the experimentally measured dihedral angles  $\theta$  were used to calculate the energies of special tin grain boundaries  $\Sigma 5$  and  $\Sigma 17$  (Fig. 4). At  $T = 216^\circ\text{C}$ , the energy of tin grain boundaries  $\Sigma 5$  and  $\Sigma 17$  is  $127 \pm 20 \text{ mJ m}^{-2}$ .

The obtained value is much lower than the known published estimates of general grain boundaries in Sn. In [11], it was proposed that  $\sigma_{gb}(\text{general}) = 0.24\sigma_{\text{surf}} \approx 165 \text{ mJ m}^{-2}$  be used for tin. It can be seen from Fig. 4 that the general tin grain boundaries (unlike the special boundaries with lower energy) should be wetted by

Zn–Sn melt beginning at the eutectic melting point, since  $\sigma_{gb} > 2\sigma_{sl}$ . This assumption is proven by the results obtained upon the annealing of polycrystalline tin samples containing 2 wt % of Zn (Fig. 3). At 201°C more than 90% of the grain boundaries are already wetted by the melt. A small portion of the unwetted grain boundaries is probably of a special character or is low-angular. To prove this hypothesis, we plan to determine the crystallographic characteristics of such unwetted boundaries. All of the grain boundaries in the polycrystalline samples are already wetted by the melt at temperatures above 210°C.

### CONCLUSIONS

(1) The temperature of the wetting phase transition for Zn  $\Sigma 5$  and  $\Sigma 17$  (rotation about the  $\langle 001 \rangle$  axis) and Zn–Sn melt interfaces has been determined. This temperature is 216°C.

(2) It was shown that the anisotropy of interphase energy at the solid tin–Zn–Sn melt interface is no greater than several per cent; the value of the interphase energy in the range of 200–230°C was calculated.

(3) The energies of tin grain boundaries  $\Sigma 5$  and  $\Sigma 17$  in the range of 201–216°C were calculated on basis of

the experimentally obtained dependence of the dihedral angle on the temperature.

### REFERENCES

1. Smith, C.S., *Trans. AIME*, 1948, vol. 175, pp. 15–51.
2. Straumal, B.B., *Fazovye perekhody na granitsakh zeren* (Phase Transitions at the Grain Boundaries), Moscow: Nauka, 2003.
3. Chia-Wei Huang and Kwang-Lung Lin, *J. Electr. Mater.*, 2006, vol. 35, no. 12, pp. 2135–2141.
4. Masayuki Kitajima and Tadaaki Shono, *Fujitsu Sci. Tech. J.*, 2005, vol. 41, no. 2, pp. 225–235.
5. Straumal, B.B., Gust, W., and Watanabe, T., *Mater. Sci. Forum*, 1999, vols. 294–296, pp. 411–414.
6. Passerone, A., These, INPGrenoble, 1981.
7. *Binary Alloy Phase Diagrams*, Massalski, T., Ed., ASM Int., 1990.
8. Miller, W.A. and Williams, W.M., *Canad. Met. Quart.*, 1963, vol. 2, no. 2, pp. 157–175.
9. Passerone, A. and Sangiorgi, R., *Acta Metall.*, 1985, vol. 33, pp. 771–776.
10. Eustathopoulos, N., *Int. Met. Rev.*, 1983, vol. 28, no. 4, pp. 189–210.
11. Porter, D.A. and Easterling, K.E., *Phase Transformations in Metals and Alloys*, CRC Press, 1992, p. 514.