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Polytherms of Angles of Aluminum and Aluminum—Lithium Alloy Wetting by Tin-Based Melts

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Abstract—The results of an experimental study of the surface properties of the eutectic tin—aluminum alloy are presented in this work. The temperature dependences of the wetting angles for plates of aluminum and aluminum—lithium alloy wetted by tin and tin—aluminum eutectics are studied. Wetting thresholds at temperatures above 765 K are found.

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INTRODUCTION

Solders based on the Sn—Al eutectic with additions of nickel [1] and Sn—Al—Zn peritectic [2] are successfully applied for the flux-free bonding of aluminum and its alloys with ceramic plates of integrated circuits. In contrast to known solders, they do not contain precious metals and toxic components. Finding new ways for the low-temperature bonding of aluminum requires reliable data on the surface tension in Al—low-melting-point metal systems. One of the first works on experimental determination of the surface tension (ST) of Sn—Al alloys is [3] where it was shown that the surface tension of Al decreases with an increase in the Sn content (the measurements were carried out in a bounded region up to ~7% of tin in aluminum). The ST polytherm of the Sn—Al system at $T = 1273$ K was presented in [4]. There is a large gap in experimental data, and no data are available for a rather wide range of compositions (especially in the region of small tin concentrations).

In [5], the Auger spectra of Al—Sn alloys with 0.14, 0.2, 0.3, 0.58, 2.1, and 2.6% concentration of tin in aluminum at 973 K were studied. Strong segregation of tin was pronounced on the surface due to the size effect and the repulsion of atoms of different types.

In [6], the large drop method was used to study the ST of the Al—Sn double system in the region of small tin concentrations at temperatures up to 1673 K. The ST polytherm of the Al alloy with a Sn content of 0.4 at % appeared to have a zero temperature coefficient; the ST polytherms of alloys with a Sn content of 1.2 and 2.5 at % pass through a maximum near 1473 K, i.e., the ST temperature coefficient of these alloys changes its sign from positive in the region of 873—1473 K to negative in the region of 1473—1673 K. In alloys that are richer in tin, one can observe linear ST polytherms with positive or negative values of the ST temperature coefficient.

In [7], based on measurements of the speed of ultrasound within the context of free-volume theory, surface-tension isotherms were calculated for eight liquid-metal aluminum systems. According to calculations, the Al—Sn system has a surface-tension isotherm with a zero deviation from additivity at 973 K. In [8], the experimental isotherms of aluminum nitride wetting by Ge—Al and Sn—Al melts were presented, as well as the density and surface tension of the aforesaid alloys in the entire concentration range. Thorough consideration of the capillary characteristics of a melt in the study was carried out by taking into account available data on the thermodynamic activity of melt components. Tin more strongly decreases the surface tension of aluminum than germanium. This is caused not only by the lower ST value of pure tin as compared to germanium but also by the higher thermodynamic activity of tin in the aluminum melt.

Thus, most studies of ST in the Sn—Al system were performed in a region that is rich in aluminum because such alloys are often used as babbits for the car industry. In this work, in connection with the lack of experimental data on the ST in the aluminum-rich region, the polytherms of density ρ and surface tension σ of the melted Sn—Al eutectics are measured by the sessile-drop method and polytherms of wetting angles θ of Al and Al + 4 at % Li alloy wetted by Sn and $(\text{Sn–Al})_{\text{EUT}}$ melts are studied in a wide range of temperatures.

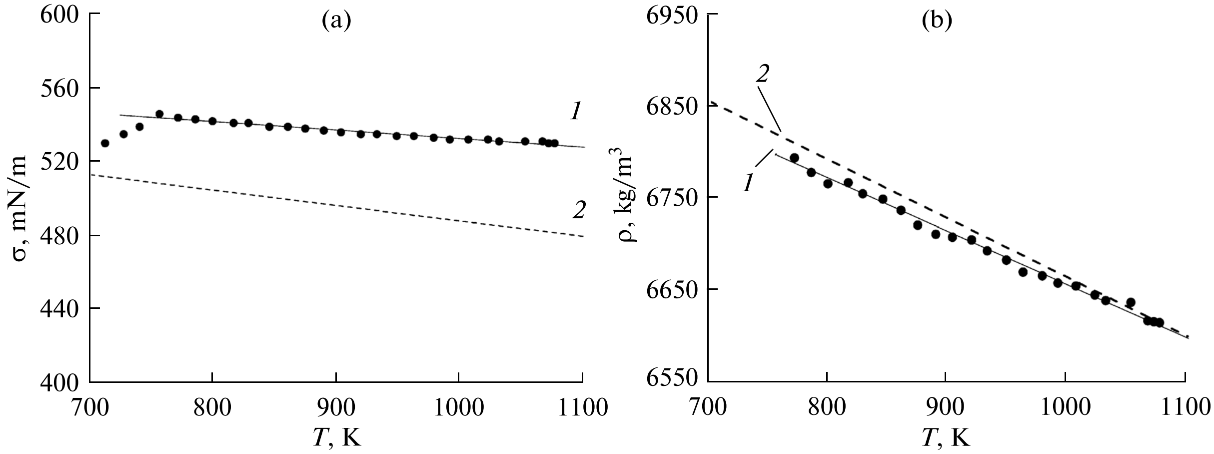

Fig. 1. Polytherms of (a) surface tension and (b) density for the eutectic melt (*1*) Sn-99.5–Al-0.5 wt % and (*2*) pure tin [11].

Such investigations are also necessary in connection with the development of technologies for tin–aluminum resistance-reaction soldering [9] and for revealing the general regularities of the relationship between the surface properties and parameters of contact melting [10].

MEASUREMENT TECHNIQUE

The eutectic Sn–Al alloy was prepared from tin and aluminum (99.9995 and 99.995 wt % purity, respectively) in glass ampoules in a helium atmosphere. During the process of melting, the melt was intensively mixed and then crystallized. The obtained ingot was then used to prepare the samples. Measurements of ρ and σ were carried out using a graphite cup to which a drop of the studied substance was delivered via a quartz funnel with an extended capillary tube. Before the beginning of the experiments, helium was introduced into the working chamber of a high-temperature installation with a water-cooled casing; then, the chamber was evacuated to a pressure of 0.01 Pa. The drop was kept at the given temperature for 5 min; the interval between successive images was 1–2 min.

The digital image of the drop profile obtained in the experiment was processed using a PC via a high-speed software package [11] which permitted one to process and perform the optimization procedure for determining the surface tension of the liquid by different methods. The measuring procedure lies in the implementation of three blocks in the form of an application for the Windows operating system. The image-processing unit reads out graphic files containing images of the equatorial cross section of the drop and separates the drop profile. In the computational unit, the thermophysical properties of the liquid are calculated using linear models. The output unit forms a report file of the experimental data processing.

Applying this technique allows simultaneous determination of ρ and σ with errors of 1% and 2%, respectively. The wetting was studied using 15 × 15 mm^2 substrates preliminarily polished and washed in alcohol and distilled water. Measurements of θ were carried out in a vacuum chamber with a residual pressure of 0.01 Pa. The wetting angle was determined using IMAGEJ free software [12] by averaging values of θ over the "left" and "right" halves of the drop with an error of about 1%.

RESULTS

Experimental data testify that the density and surface tension of the eutectic alloy of the tin–aluminum system decrease with an increase in temperature. The results are well described by linear equations (Fig. 1): $\rho = 7240.56 – 0.58\ T$ for the density and $\sigma = 579.9 – 0.046\ T$ for the surface tension. Approximating coefficients for these equations are also presented in the table where the corresponding coefficients for pure tin [11] are presented for comparison. The data on pure tin [11] well agree with recommended values. It is seen from Fig. 1 that a small addition of aluminum to tin increases its surface tension by ~30 mN/m.

Figure 2 presents polytherms of wetting angles for substrates of aluminum and Al + 4 at % Li alloy (which is widely used in the aviation industry) wetted by tin and Sn–Al eutectic melt. A pure aluminum substrate is not wetted by liquid tin (θ = 147°) up to a temperature of T = 855 K above which the wetting angle

Coefficients A, B and A^*, B^* of linear approximations of density $\rho = A - BT$ and surface tension $\sigma = A^* - B^*T$ in the tin–aluminum system

Substance	A, kg/m^3	B, kg/(m^3 K)	A^*, mN/m	B^*, mN/(m K)
Tin	7308.68	0.64	572.7	0.084
Eutetic	7240.56	0.58	579.9	0.046

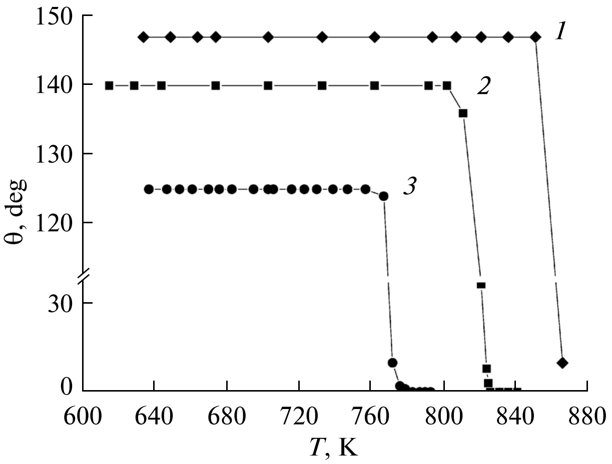

Fig. 2. Temperature dependence of the wetting angles for (*1*) pure aluminum and (*2*) aluminum Al + 4 at % Li alloy wetted by tin. (*3*) Wetting of the substrate of the Al + 4 at % Li alloy by the $(\mathrm{Sn{-}Al})_{\mathrm{EUT}}$ melt.

sharply decreases almost to zero (curve *1*). Introducing 4 at % Li into the Al substrate results in a decrease in the angle of wetting by tin by 7° ($\theta = 140°$) up to temperatures of $T = 810$–820 K, which is followed by a drop in the wetting angle to zero (curve *2*). When the Al + 4 at % Li alloy is wetted by the Sn–Al eutectic melt, the wetting angles appeared to be even smaller ($\theta = 125°$); however, at $T = 765$ K, as in the two previous cases, the wetting threshold is observed again (curve *3*). Drop melting is accompanied by intense interaction with the substrate (reaction wetting) with the formation of craters. At higher temperatures, the drop of the studied substance completely spreads over the substrate, $\theta \to 0$ (Fig. 2).

When etching the crystallized solder in a hydrochloric-acid solution, acicular structures were revealed (Fig. 3); their formation probably suppressed the wetting of the studied substrates during the initial stage. In addition, the wetting of Al and Al + 4 at % Li plates was suppressed by oxide films on the surface of the drops and substrates. It is the destruction of these films in vacuum that is followed by a sharp decrease in the wetting angle. Fragments of a partially destroyed oxide film on the surface of the aluminum plate in the case of wetting by pure tin that were found in one of the parts of the substrate when studying using a PHENOM scanning microscope are presented in Fig. 4.

To reveal the cause of the appearance of the wetting threshold, aluminum substrates with a solidified drop were studied by electron microscopy. Preliminary (before threshold) wetting along trenches formed by grain boundaries was found on the substrate. Atoms located at these boundaries possess excess energy; therefore, intergrain melt boundaries along which the tin melt preliminarily spreads can be dissolved more intensively at high temperatures.

Thus, before the wetting threshold, the wetting of trenches along grain boundaries antecedes the destruction of oxide films on the substrate and on the

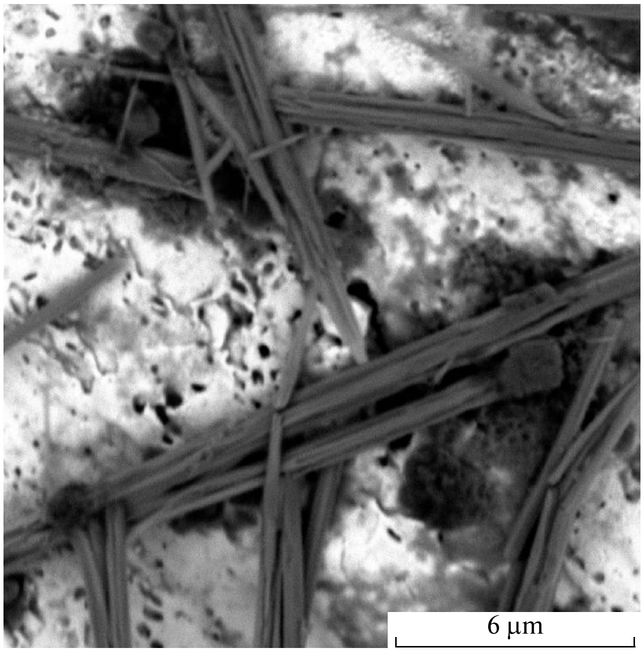

Fig. 3. Electron-microscopy images of a film of the melt crystallized on Al + 4 at % Li plate, after etching. The image was taken using a PHENOM microscope with ×15000 magnification.

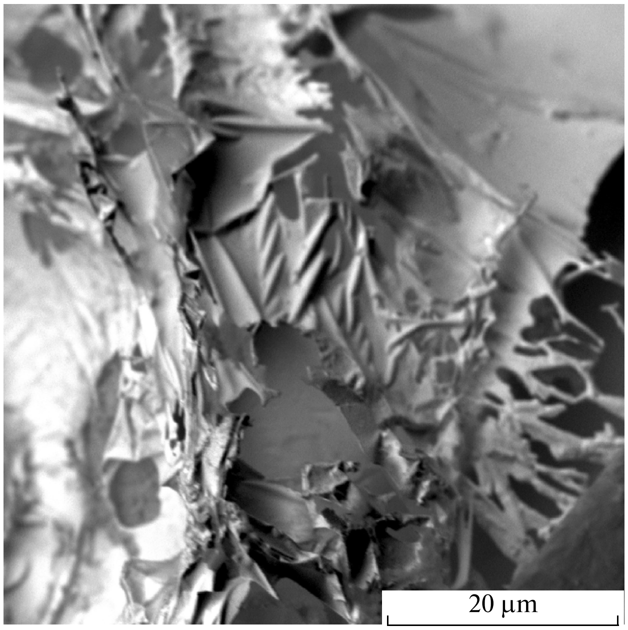

Fig. 4. Fragment of a partially destroyed oxide film in the process of wetting of aluminum by tin after etching (beginning of spread at 855 K).

drop, which makes an additional contribution to the moving force of spreading.

CONCLUSIONS

Based on the performed study, the following conclusions can be made.

The polytherms of density and surface tension of the Sn–0.5 wt % Al alloy in the temperature range of 750–1100 K are linear, with negative temperature coefficients.

Wetting thresholds were found in the polytherms of wetting angles for the Al + 4 at % Li alloy wetted by tin and $(\mathrm{Sn{-}Al})_{\mathrm{EUT}}$ at temperatures of 810–820 K and 765 K, respectively. When pure aluminum is wetted by pure tin, the wetting threshold is observed at $T = 855$ K.

When the Al + 4 at % Li alloy is wetted by the eutectic melt of the Sn–Al system, the formation of acicular structures is observed; they probably suppress wetting of the substrates during the initial stage together with oxide films on the surface of melt drops.

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