Contact angle and reactive wetting in the SnPb/Cu system

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Wetting with a low contact angle is a prerequisite for reliable solder connections. However, the contact angle is only an indirect measure of adhesion energy. To quantify this energy, we measured wetting angles of solder droplets as well as surface tension of SnPb solders under systematic variation of composition. From the data, the effective interface energy is evaluated. Although surface tension and wetting angle depend continuously on solder composition, the adhesion tension reveals distinguished plateaus which are related to different reaction products.
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Solder connections play a significant role in electronic packaging. Usually during reflow different intermetallic compounds are formed between the solder and the base metal. In industrial practice, the macroscopic contact angle is used to assure the quality of the connection. However, this angle is only an indirect measure for the adhesion energy. Even worse, the theoretical basis of correlating the correct interface energy to the wetting angle is still unclear in the relevant case of reactive wetting. In non-reactive wetting, the contact angle α is well understood by triple line equilibrium in Young's equation

$$\sigma_S = \sigma_{SL} + \sigma_L \cos(\alpha) \tag{1}$$

in which the constants σ_S, σ_L and σ_{SL} denote surface tensions of substrate and of liquid solder, and the specific interfacial energy between solder and base metal, respectively. However, if a chemical reaction takes place at the interface, the nature of the relevant interfacial energy σ_{SL} gets unclear. Yost and Romig [1] extended the triple line equilibrium by the chemical driving force of phase formation, which modifies Eq. (1) to

$$\sigma_S = \sigma_{SL} - g_V \cdot w + \sigma_L \cos(\alpha) \tag{2}$$

with g_V denoting the Gibbs energy of phase formation and w the thickness of the reaction product. In experimental soldering studies, Tu [2] investigated the correlation between contact angles of selected SnPb solders with measurements of surface tensions reported in the literature [3]. Tu interpreted his results as confirmation of Eq. (2), but had to postulate a rather small and constant phase thickness w to achieve quantitative agreement. As a major limitation of the previous study, surface tension and wetting angle were measured in two different flux environments, which limits the validity of the comparison.

More recently, Eustathopoulos [4] investigated wetting of ceramic substrates by liquid metals. Eustathopoulos suggested that at microscopic scale the product phase will always spread a bit farther than the liquid droplet at the triple line (see the sketch in Fig. 3 for illustration). As a consequence, the contact angle of reactive wetting is merely controlled by the interfacial tension between the topmost reaction product and the liquid. Since this interfacial tension is usually smaller than that with the initial substrate, a decrease in contact angle appears.

In this work, we present model experiments with SnPb solders and Cu base metallization aimed at clarifying the nature of the contact angle. In this case, Cu_3Sn and Cu_6Sn_5 may be formed as reaction products at the interface. We measure contact angle and surface tension under variation of the solder composition (0–100 at.% Pb). Pb does not take part in any reaction. As a solvent, it just controls the chemical potential of Sn and could be replaced by other metals, e.g. Bi. Therefore, the present study is presumed to be of relevance to other lead-free soldering systems, too.

A blank circular disk-shaped piece of Sn_xPb_{1-x} solder, 3 mm in diameter and ≈250 μm in thickness, is placed on top of a glass or Cu substrate for measurement of surface tension or contact angle, respectively,

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and inserted into a vacuum furnace. In order to reduce oxide contamination, the vacuum chamber is flooded with a mixture of nitrogen and formic acid. A constant, rather high reflow temperature (350 °C) was selected so that Pb-rich solders could also be melted. The heating rate of the furnace was approximately 50 K min^{-1}. Using an optical microscope and a charge-coupled device camera, soldering was observed in situ.

After melting and equilibration of the droplet on top of the glass substrate, projection images were recorded and analysed according to the sessile drop method by a plug-in of the ImageJ software developed by Stalder et al. [5]. In the sessile drop method, one has to consider the Young–Laplace equation, which describes the correlation between the surface curvature and surface tension, and the pressure difference between a liquid and its environment:

$$\Delta P = \sigma \cdot \left(\frac{1}{R_1} + \frac{1}{R_2} \right) \tag{3}$$

R_1 and R_2 are the principal radii of curvature of the drop surface, σ denotes the surface tension and ΔP is the pressure difference across the surface. At the apex of an axis-symmetric drop, one may simplify Eq. (3) to $\Delta P^{apex} = \frac{2\sigma}{R^{apex}}$. In hydrodynamic equilibrium, the pressure difference between the apex and any other point of the surface must fulfil $\Delta P^{apex} - \Delta P^{any} = z \cdot \Delta \rho \cdot g$. Hence, the desired surface tension is obtained by

$$\sigma \cdot \left(\frac{1}{R_1} + \frac{1}{R_2} - \frac{2}{R^{apex}} \right) = z \cdot \Delta \rho \cdot g \tag{4}$$

The parameters g, z and ρ denote the acceleration of gravity, the elevation of the apex with respect to the reference plane and the density of the molten solder. (The latter was calculated from data by Poirier [6].)

The surface tensions of 11 different solder compositions between pure Sn and pure Pb were measured at a temperature of 350 °C. The results are presented in Figure 1a (solid symbols). With increasing lead content, the surface tension decreases continuously from ≈520 mN/m (pure tin) to ≈410 mN/m (pure lead). In view of the slightly higher melting point of Pb, this may be surprising. However, our data follow the trend observed by other groups [7], although measured under different experimental conditions. For comparison, Figure 1 also shows data by Howie and Hondros [3] measured under an H$_2$ atmosphere or organic flux at a temperature of 400 °C (open symbols). Our new data points closely match a model curve (solid line) based on Butler's equation [8,9]. This and the low scatter of the data points demonstrate that the measurement was sufficiently accurate.

To measure the contact angles, glass substrates were replaced by copper. The typical temporal evolution of the contact angle is shown in Figure 2 (open symbols) in the example of a pure Sn solder. Upon melting, a spherical droplet is formed immediately with a large contact angle in the non-wetting regime. Then, after a short incubation, the contact angle drops significantly when reaching the wetting regime. After less than a minute of reflow, the contact angle approaches a practically constant equilibrium level. It is remarkable that, even
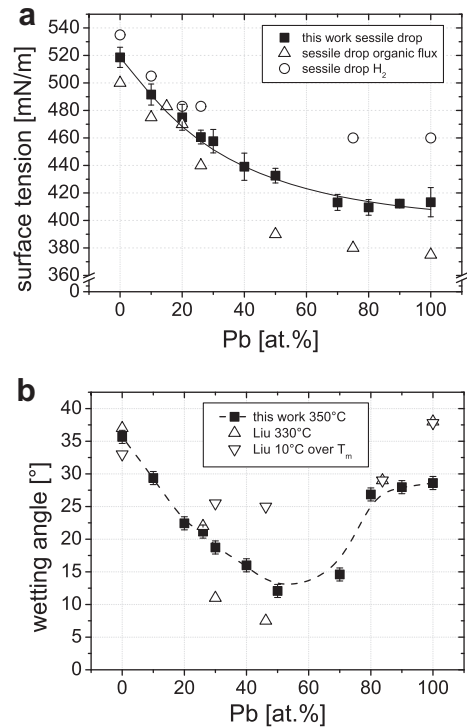

Figure 1. (a) Surface tension of different SnPb solders measured at 350 °C under formic acid in comparison to literature data [3]. (b) Wetting angle of different SnPb solders measured at 350 °C under formic acid in comparison to literature data [2].
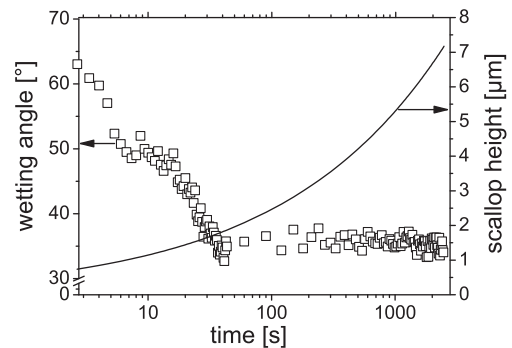

Figure 2. Temporal evolution of wetting angle during the soldering reaction of Sn on Cu (open symbols). For comparison, the thickness of the Cu$_6$Sn$_5$ reaction product (solid line) as derived from Ref. [10] is also shown.

after this steady angle has been established, the interfacial reaction product still grows significantly with time. For comparison, see in the same figure the thickness w of the intermetallic product Cu$_6$Sn$_5$ (solid line) as derived from studies by cross-sectional electron microscopy [10]. In view of Eq. (2), this observation is quite enlightening. If the energetic balance suggested by Yost and Romig [1] were valid, the contact angle could not be stable as long as significant phase growth appears.

The steady contact angle, determined after 10 min of reflow, reveals a significant dependence on solder composition, as plotted in Figure 1b (solid symbols). A minimum appears at intermediate compositions, while the contact angles of pure Sn and Pb are quite similar.