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Factors affecting wettability and bond strength of solder joint couples*

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Abstract: The paper discusses the scientific understanding of the role of interfacial phenomena in joining of dissimilar materials using liquid-phase-assisted processes. From the example of the Sn-alloy/Cu system, it is demonstrated that interaction in the liquid solder/substrate couples is accompanied by a number of complex interfacial reactions leading to significant changes in the structure and chemistry of interfaces (solder/substrate, solder/environment, substrate/environment) and remaining solder layer that finally influence the mechanical properties of solder joints.

The experimental data on wetting behavior, interface characterization, and mechanical properties of different solder/metal substrate couples are analyzed in order to display the role of such factors as time and temperature of interaction, environment (protective atmosphere, flux), presence of oxide films on interfaces, alloying additions to a solder, formation of interfacial phases, and porosity.

Keywords: soldering; wettability; sessile drop test; interfaces; bond strength.

INTRODUCTION

The wetting of solid metal substrates by metal melts, accompanied by the formation of interfaces and resulting in the creation of bonding between dissimilar materials, belong to high-temperature phenomena of fundamental importance for improving industrial liquid-phase-assisted joining processes such as soldering.

The degree of wetting is usually estimated by the value of contact angle θ . Considering a drop resting at mechanical and thermodynamical equilibrium on a perfectly flat surface of nondeformable solid substrate, Young determined θ from the mechanical equilibrium of the drop by equation of the horizontal force balance at the three-phase line among the liquid (σ_{lv}), the solid (σ_{sv}) and solid/liquid (σ_{sl}) interfacial tensions [1]

$$\sigma_{\rm sv} - \sigma_{\rm sl} = \sigma_{\rm lv} \cos\theta \tag{1}$$

The contact angle presents a key technological parameter in selecting materials and corresponding joining processes because a good wetting ($\theta \ll 90^\circ$) is required in order to produce high-quality solder joints, whereas solderability is optimized when θ is minimized. At the same time, following the Young–Dupré equation

$$W_{\rm a} = \sigma_{\rm lv}(1 + \cos\theta) \tag{2}$$

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the contact angle θ may be considered as a "strength-related" factor since together with σ_{lv} it directly influences the work of adhesion W_a , a quantity that characterizes the thermodynamic stability of interfaces between dissimilar materials and is widely used in practice for prediction of their potential bonding properties (low θ tends to correlate with greater W_a).

Literature data on contact angle values for most systems measured by the same sessile drop method and at the same temperature show a large scattering caused generally by differences in the substrate surface roughness and by pollution from the atmosphere, mainly oxygen, the presence of which is unavoidable in the gaseous environments of technical high-temperature processes [2–4]. It is well established that oxygen affects surface tension of such metals as Sn, Pb, and In; those alloys are commonly used as solders (e.g., at the melting point, oxygen-free Sn has $\sigma_{lv} = 598$ mNn/m, contrary to 535 mN/m for oxygen-rich Sn) [5]. Additionally, oxygen can form oxide films on metallic droplets and on metallic solid substrates, contributing to a dramatic decrease in the apparent σ_{lv} value ($\sigma_{lv} = 470$ mNn/m for an oxidized surface [6]) and increase in the apparent contact angle values by tens of degrees [3,7].

Most of the solder/substrate couples present highly reactive systems in which wetting phenomena are accompanied by the dissolution of the substrate in molten solder and by complex interfacial reactions leading to the formation of intermetallic compound (IMC) layers. It results in significant changes in the structure and chemistry of interfaces and solder itself, thus finally affecting both the solder wetting behavior and mechanical properties of solder joints.

This study reviews the current state of knowledge on the role of interfacial phenomena in joining of dissimilar materials using liquid-phase-assisted joining process such as soldering of electronic materials. New experimental results on the effect of processing parameters on the relationship between wetting, interface structure, and mechanical strength of Sn-based solder/Cu couples are discussed in order to demonstrate such effects as the presence of oxide films on a solder and Cu substrate surfaces, time and temperature of interaction, environment, alloying additions to a solder, and the formation of interfacial phases and porosity.

EXPERIMENTAL PROCEDURE

Sessile drop test

The materials were Cu substrates and several Sn-based solders containing different additions of Cu, Ag, In, Bi, Zn, and Pb (given in wt %). Directly before wettability tests, the Cu substrates were polished up to an average roughness of a few nm while the Sn alloy samples were cleaned mechanically, and next both Cu substrate and Sn-alloy samples were cleaned ultrasonically in acetone.

The contact angles θ were measured by the sessile drop method described in [2]. The wettability tests were carried out in different environments (dynamic vacuum, air, colophony-based flux) under various testing conditions. Two improved procedures were employed for heating the solder/substrate couples:

- 1. Fast contact heating (CH) with a rate of ~20 °C min⁻¹ was achieved by introducing the solder/Cu couple into the furnace preheated to the experimental temperature T_{exp} while the time of drop/substrate contact was measured from the moment of visually estimated melting of a solder as described in [8]; this procedure is more suitable for investigation of reactive systems since it allows one to reduce the time of contact during heating a couple to T_{exp} , contrary to the widely used procedure of slow CH when a couple of materials being in contact are first placed in the furnace and then long-time heated from room temperature to the test temperature with a rate of ~1 °C min⁻¹ (Fig. 1a);
- 2. *Capillary purification* (CP) [4], in which the substrate and the metal were heated separately under vacuum, the metal in a graphite syringe. At the test temperature, a droplet of the metal is mechanically squeezed out of the graphite syringe and brought in contact with the preheated sub-

strate (Fig. 1b). Compared to CH, this procedure has two important advantages: (a) separate heating of the metal and the substrate eliminates chemical interactions that would occur during CH to the test temperature and (b) the extrusion of the liquid out of the syringe forms droplets free of oxide film, thus establishing true substrate/metal physical contact.

After wettability tests, depending on environment used, the couples were cooled either in air by removing them from the furnace or under vacuum by moving the couples to a cold part of the experimental chamber as described in [8]. The measurements of contact angles were done from the image of a solder drop reordered at $T_{\rm exp}$. For wettability tests with flux, the contact angles were measured on solidified samples at room temperature after removal of the remaining amount of flux.



Fig. 1 Schematics of testing methods and procedures: (a) CH: contact heating in classical sessile drop method; (b) CP: capillary purification in improved sessile drop method; (c) push-off shear test; (d) push-out shear test.

Droplet push-off shear test

Sutton [8] proposed a first simple yet elegant approach to relate θ to bond strength of a couple of dissimilar materials by utilizing the sessile drop samples for measuring the shear stress τ (applied parallel to the substrate) required to debond a droplet from a substrate. This test, known as the *droplet push-off shear test*, was employed in early studies [9–12] on different metal/oxide ceramic couples and demonstrated a methodological limitation due to the difficulty in applying a shear stress to thin droplets with $\theta < 90^{\circ}$. Future improvement of Sutton's approach, as proposed in [13] (Fig. 1c), allows shearing of both non-wetting ($\theta > 90^{\circ}$) and wetting ($\theta < 90^{\circ}$) couples because the solidified droplet/substrate couple is bisected perpendicular to the interface at the mid-plane of the contact circle, and one-half of the bisected droplet is used for bond strength measurement. The other half may be used for microstructural examination of the joint or for thermocycling treatment after which it is also tested for interface structure and strength. For the shear test, a load is applied to the flat end of the bisected couple at a constant rate (1 mm min⁻¹), and the load *P* vs. displacement *l* data are recorded until failure under shear occurs.

By enabling the measurement of θ and τ_{max} (shear bond strength) on each individual test specimen, the improved push-off shear test allows one to get maximum experimental data on wetting and

bonding properties, structure and chemistry of the interface in the *same* test coupon. The authors applied this test to a wide group of metal/ceramic systems [13–18] and demonstrated its convenience and usefulness in investigation of interfacial phenomena with pure Al, Cu, and Ni and Al-alloys.

Taking into account the practical importance of information about shear properties of solder joints (the strain in electronic interconnects is mostly shear due to coefficient of thermal expansion (CTE) mismatch between the solder and the substrate) as well as the fact that in the wettability tests the specimens are produced under repeatable and well-controlled conditions, the sessile drop couples might be used as model solder/substrate joints, for which mechanical properties can be easily estimated by the proposed improved push-off shear test. The first attempt of its application reported in [8] also confirmed the usefulness of the push-off shear test for investigation of the solder/Cu couples.

Push-out shear test

A limited number of measurements were done using a push-out shear test, which is similar to that widely used for characterization of the fiber/matrix interfacial strength in fiber-reinforced composite materials [19]. The solder/Cu couples were produced from Cu rings, whose internal diameter (d = 5 mm) was comparable to the diameter of the solder droplets in the sessile drop tests. The hole in the Cu rings was filled with molten solder according to the procedure used in wettability tests with flux (230 °C, 5 min; after machining, the Cu rings were ultrasonically cleaned in acetone directly before their contact with a molten solder). The solder/Cu couples were sheared at the same constant rate as in the push-off shear tests by loading a punch of different diameters $\phi = 4.92-5$ mm (Fig. 1d).

RESULTS

Effect of oxide films

Figure 2a shows the wetting behavior in the Sn/Cu couples in different environments when the Sn droplets were produced by CH and CP procedures; the corresponding contact angles measured after 5 min interaction at 230 °C are given in Table 1. During CH in air, both the Sn droplet and the Cu substrate are oxidized, which prevents a true droplet/substrate contact and contributes to a high contact angle of 136°. In vacuum, the wetting behavior of CH couples strongly depends on the vacuum pressure *P*, lowering of which causes significant decrease in both initial (θ_0 for t = 0 min) and final (θ_f for t = 5 min) contact angles, thus resulting in transfer of the Sn/Cu system from non-wetting ($\theta > 90^\circ$) at $P = 4 \times 0^{-6}$ hPa to wetting ($\theta < 90^\circ$) at about $P = 2 \times 10^{-6}$ hPa, while at vacuum of 4×0^{-6} hPa, high value of $\theta_f = 90^\circ$ represents an apparent contact angle caused by tin oxide film around melted Sn.

This effect is related to a decrease in oxygen partial pressure P_{O_2} in a chamber when a better vacuum is produced because, for heating in vacuum, lowering P_{O_2} contributes to deoxidation of the Cu surface and prevents secondary oxidation of Sn droplet during wettability tests. Since at the test temperature the oxide film on the Sn droplet cannot be completely removed even in high vacuum, the lowest contact angle of 23° was produced by the CP procedure when both the Sn drop and the Cu substrate are oxide-free, contrary to the value of 52° recorded by CH in the best vacuum received, when the oxide film is only a few nanometers thick. A similar effect of wettability improvement takes place with Sn-alloys as shown in Table 1.



Fig. 2 Wettability kinetics in the Sn/Cu system under different environments at 230 $^{\circ}$ C (a) and shear behavior of corresponding sessile drop samples in push-off shear tests (b); (c) non-symmetric profile of Sn drop caused from local non-wetting caused due to oxidized surface.

Solder	Conditions of sessile drop tests				<i>θ</i> , °	τ _{max} *, MPa
	Method	Atmosphere	$T_{\rm exp}$, °C	Time, min		
Sn	СН	air	230	5	136	0
	СН	vac. 4×10^{-6} hPa	230	5	99	14.12
	СН	vac. 3×10^{-6} hPa	230	5	60	15.06
	CH	vac. 2×10^{-6} hPa	230	5	52	17.37
	CH	air + flux	230	5	47	18.55
	СР	vac. 3×10^{-6} hPa	230	5	23	**
SnAg4	СН	vac. 2×10^{-6} hPa	230	5	49	18.22
	CH	air + flux	230	5	40	32.31
	СР	vac. 2.6×10^{-6} hPa	230	5	18	**
SnAg3.5Cu0.9	СН	vac. 2×10^{-6} hPa	220	5	42	21.93
	CH	air + flux	220	5	40	24.08
	СР	vac. 3×10^{-6} hPa	220	5	10	**

Table 1 Effect of testing conditions on contact angle and shear strength of solder/Cu couples.

*Push-off shear test of solidified sessile drop samples.

**Impossible to shear because of a small contact angle.

The presence of oxide films on contacting metals is also responsible for a large scattering of contact angle values measured under the same testing conditions since non-symmetric profile of the drop is formed due to local non-wetting (Fig. 2c). Therefore, special attention should be taken to the sample preparation and testing conditions in order to remove primary oxides and to prevent secondary oxidation. Moreover, the comparable values of contact angles recorded at the lowest vacuum pressure of $P = 2 \times 10^{-6}$ hPa and with flux, for both pure Sn and Sn-alloys (Table 1), suggest the creation of similar conditions and related properties of interfaces in these two environments. For that reason, one may conclude that the wettability studies of the Sn/Cu couples under vacuum of about 2×10^{-6} hPa is as good as with selected flux in air.

Figure 2b illustrates the shear stress vs. displacement $(\tau - l)$ curves of the sessile drop Sn/Cu couples produced at different processing conditions. Similar to wetting properties, the shear behavior in the system depends on the environment and heating procedure used for the preparation of the couples during wettability tests, i.e., the lower the vacuum pressure, the higher the shear strength (τ_{max}). As expected, for the CH test in air, both Sn and Cu are oxidized, thus, there is no bonding in the Sn/Cu couple. The shear strength of the Sn/Cu, SnAg4/Cu, and SnAg3.5/Cu0.9/Cu couples produced by CH with flux is higher than that of the couples produced under high vacuum (Table 1). However, for Sn/Cu and SnAg4/Cu, the difference in τ_{max} is small (6.3 and 8.9 %, respectively), which suggests additional evidence for creation of similar conditions in two selected environments. Quite the reverse, application of flux for the SnAg4/Cu couple results in almost two-fold increase in its shear strength accompanied by 18.4 % decrease in contact angle, compared to the couple produced under high vacuum.

Structural characterization of cross-sectioned sessile drop samples shows that, independently on chemical composition of the solders, the same IMC layers of comparable thickness are formed under vacuum and with flux. Therefore, one may suggest a lack of significant difference in the microstructure of the interfaces produced in these two environments thus expecting comparable shear strength of the couples. Our investigation of numerous solder/Cu evidenced that, generally, either sudden decrease in shear strength or unexpected shear behavior take place when the presence of gas porosity was noted to occur at or in the vicinity of the interface as it is shown in Figs. 3,4. We noted that pores tend to nucleate at the oxidized surfaces and as soon as the oxide film is detached or consumed, the pore nuclei are separated from the substrate consequently making the couple shear strength less sensitive to such struc-



Fig. 3 Examples of structural defects formed in the Sn-based solder/Cu couples.

(a)

(b)



Fig. 4 Examples of the effects of gas porosity (a–d) and non-flat interface profile accompanied with the formation of non-homogeneous thickness of IMC (e–h) on cracking at or in the vicinity of the interface during thermocycling (TC): (a,c,e,g) before TC, (b,d,f,h) after TC (magnification 200×).

tural defects. The presence of oxide films contributes also to dissimilar local structure of interfaces such as discontinuities in the IMC layers, their smaller thickness, compared to the oxide-free regions and in non-flat profile of the Cu/IMC interface. As evidenced in Fig. 4, the above mentioned structural defects located at or in the vicinity of the interface are the main source of cracking in thermocycled solder/sub-strate couples thus reducing their reliability.

Additionally, it was noted that these defects do not occur in the solder/Cu couples produced by the CP procedure, when before contact with the Cu substrate the solder drop is in situ cleaned from its primary oxide film directly in vacuum chamber. In order to demonstrate the role of oxide films in the formation of gas porosity in the solder/substrate couples, two tests were done with pure Sn on perfectly flat and smooth sapphire substrate (roughness $R_a = 0.8$ Å) under dynamic vacuum of about 2×10^{-6} hPa using CH and CP procedures. Since the transparent sapphire substrate allows the inspection of the inter-

face under magnifications of optical microscopy it was clearly evidenced that gas bubbles are nucleated at the sapphire substrate in the CH couple while there is no porosity at the interface formed with oxidefree Sn droplet in the CP test.

Note that similar effects of processing conditions and testing procedure on wetting-shear strength relationship, caused from the presence of oxide film on a droplet, were reported recently for Al [14] and Al-alloys [17,18] on different ceramics substrates.

Effect of alloying additions

To facilitate the role of alloying additions in mechanical strength of solder/Cu couples, comparison shear tests have been done with both solder alloys and solder/Cu couples, several examples of which are shown in Figs. 5–7. The solder rods of 4 mm diameter and 50 mm length were cast in a graphite mold. For each rod, two specimens were cut from the bottom (B) and upper (U) parts of each rod as shown in Fig. 5d.

As expected, pure Sn (Fig. 5a) does not show any difference in shear behavior of the samples B and U. Alloying Sn with only 0.5 wt % Cu results in its strengthening and small changes in the B and U shear curves are caused from the alloy segregation (Fig. 5b).



Fig. 5 Shear behavior (push-off shear test) of different parts of cast solder rods and solder/Cu couples (CH, 230 °C, 5 min, vac): (a) pure Sn, (b) SuCu0.5, (c) SnAg3.95Cu0.65, (d) schematic of sample selection.



Fig. 6 Shear behavior (push-off shear test) of different parts of cast solder rods and solder/Cu couples with corresponding optical micrographs of cross-sectioned sessile drop samples under 100× magnification (CH, 230 °C, 5 min, vac): (a,c) SnIn5, (b,d) SuIn20.



Fig. 7 Shear behavior (push-off shear test) of cast solder rods and solder/Cu couples (CH, 230 °C, 5 min, vac): (a) Sn/Cu, (b) SnAg4, (c) SnAg3.5Cu0.9, (d) SnAg3.95Cu0.65.

Introduction of 3.95 % Ag and 0.65 % Cu produces the alloy of multiphase structure with corresponding highest shear strength. However, due to the highest degree of solidification segregation in the

cast rod there is the strongest effect of alloying on shear behavior of dissimilar solidified parts that is evidenced by higher τ_{max} for the bottom than the upper part of cast rod (Fig. 5c).

The reverse relationship takes place in the Sn-In alloys: less alloyed SnIn5 solder (Fig. 6a) demonstrates slightly higher shear strength in the upper part but much bigger difference in the B and U shear curves, whereas the more alloyed SnIn20 solder (Fig. 6b) has similar shear behavior of the upper and bottom parts but relatively higher τ_{max} in the bottom. From the Sn-In peritectic phase diagram [20], indicating an increase in dissolution of In in Sn with temperature decrease, both alloys should have a single-phase microstructure resulting in solid solution strengthening of the β -Sn(In) for SnIn5 and the γ -phase for SnIn20. However, due to solidification segregation, the cast SnIn5 rod is more alloyed, and consequently more strengthened, in its upper part. On the contrary, this part in the SnIn 20 rod presents the In-rich γ -phase which has lower strength compared to the Sn-rich γ -phase in the bottom part. Additionally, due to a wide solidification rate, the appearance of shrinkage porosity was noted to occur in the upper part of the SnIn20 rod. The observed effect contributing to the alloy weakening takes place also in the solder/Cu couples as illustrated in Fig. 6c.

The results reported above demonstrate that the solder shear strength is very sensitive to small changes in the materials structure and chemistry. In the case of solder/substrate couples, generally, the drop-side interface is responsible for the shear behavior of the couple. Therefore, the degree of solder alloying due to the dissolution of the substrate in the solder as well as the structure and thickness of IMC formed at the interface are the key and competitive factors, influencing the mechanical strength of a solder/substrate joint.

Under conditions used in this study, the formation of interfacial IMC layers in pure Sn/Cu couple is not critical at the same time as the dissolution of Cu in Sn results in a slight increase in τ_{max} , compared to that of cast Sn rod (Fig. 5a). Alloying with 0.5 % Cu (Figs. 5a,b) and, particularly, with 4 % Ag (Fig. 7a,b) or with both Ag and Cu (Figs. 7c,d) causes further increase in the couple shear strength. On the other hand, for the high content of alloying elements, the shear strength of the couple is much smaller compared to that of corresponding cast rod, suggesting that the interface becomes the weakest place in the joint. Similar relationships are observed in the Sn-In/Cu couples, indicating the couple weakening due to increase of In content from 5 to 20 % (Figs. 6a,b).

Our observations have shown that alloying additions have the strongest effect on the interface structure and their properties. For example, alloying with Cu suppresses the growth of brittle IMC layers (Cu_6Sn_5 and Cu_3Sn). Zn forms the thickest and very brittle IMC layer (Cu_5Zn_8), which grows inside the solder drop (the drop/IMC interface is moved toward the drop) that together with a tendency of Zn-containing solders to form porosity at the interface contribute to reliability decrease. Alloying with In increases the reactivity of the solder/Cu couple, and its consumption for the formation of the In-rich IMC phases significantly shifts the droplet composition to a much smaller amount of In while the IMCs formed are relatively less brittle, compared to those formed with other alloying elements. Bi as well as Pb do not react with Cu, and thus they do not affect the properties of IMCs formed. However, in their case, the consumption of Sn for the formation of IMCs with Cu results in shifting chemical composition of the solder to a higher amount of these alloying additions, especially at the solder-side interface. For high Bi content solders, it results in the formation of large Bi grains in the vicinity of the interface that may cause low resistance to thermal fluctuations and decreased solder joint reliability as explained in [21]. These observations are in agreement with the literature data reported for real solder joints (e.g., [22–26]).

Even a small amount of third alloying element or addition of solid precipitates to a solder were found to significantly affect reactivity and structure of the solder as well as the type, thickness, and morphology of interfaces formed, a few examples of which are shown in Fig. 8. However, more systematic work is needed to understand how these factors control wetting and mechanical properties of the solder/Cu couples.



Fig. 8 Examples of the effect of alloying additions (a,b) and solid particulate reinforcements (c,d) on microstructure of solder/Cu couples: (a), SnAg4, (b) SnAg3.5Li0.3, (c) paste SnAg3Cu0.5 + 10 % Cu_p; (d) paste SnAg3Cu0.5 + 10 % Ni_p (Cu_p and Ni_p are copper and nickel powder, respectively).

Effect of processing parameters

Since both the creation of continuous true solder/substrate contact and the formation of IMC layers play an important role in the reliability of solder joints, the temperature and processing time are the key processing parameters which should be optimized. Table 2 shows such an example for SnCu0.5 alloy when a small change in temperature results in a notable change in shear strength of solder/Cu couples.

Table 2 Effect of processing parameters of the sessile drop SnCu0.5/Cu couples on their shear strength before and after thermal cycling (TC) (1000 cycles from 50 to 150 °C).

Processing parameters	$ au_{ m max}$, MPa		
	Before TC	After TC	
CH: 240 °C, 5 min, vac.	10.69	8.20	
CH: 235 °C, 5 min, vac.	14.90	13.00	
CH: 230 °C, 5 min, vac.	16.14	16.39	
CH: 227 °C, 5 min, vac.	13.10	12.78	

The authors suppose also that due to certain methodological problems with the temperature measurements in the discussed low-temperature range of Sn-based solders when fast heating and cooling are required, there is no sureness that the contact angle values given in the literature always correspond to a true temperature. Furthermore, chemical reactions, accompanying the formation of IMC phases, may cause heat release and signify an additional factor for temperature fluctuation in the couple, as reported in [27].

Effect of testing procedure used for characterization of interfacial strength

In order to identify the effect of testing procedure, two sets of experiments were performed. The first one was focused on comparison studies of two halves of the same sessile drop couples using two types of testing machines with two corresponding different designs of holders for shearing sessile droplets. These tests show only a maximum 2 % difference in the shear strength measurements, thus suggesting a good repeatability and reliability of the results of push-off shear tests.

The second set of experiments was done by push-out shear test using different inner diameters of the Cu rings (Fig. 1d); those most representative results are shown in Table 3 and Fig. 8. For the Sn/Cu and SnPb40/Cu couples characterized by relatively thin layers of IMC, the size of the loading punch has no effect on the shear strength of these samples. However, their shear strength is almost two-fold higher than that of the solidified sessile drop samples examined by the push-off shear test. This effect may be caused by dissimilar testing conditions due to two effects taking place during loading and shearing of the solder part in the push-out shear test: (1) higher roughness of unpolished (only machined) inner surface of the Cu ring, (2) high ductility of Sn and SnPb40 alloys resulting in plastic deformation accompanying with additional friction (solder extrusion through a hole in the Cu ring).

Solder	SD samples		Push-out samples (\$\$ mm)			
	θ, °	$ au_{ m max}$, MPa	$\tau_{\rm max}$, MPa (push-out shear test)			
		(push-off shear test)	d = 4.92 mm	<i>d</i> = 4.95 mm	d = 5 mm	
Sn	47 ± 4	18.55 ± 2.1	34.43 ± 0.03	34.80 ± 0.8	37.51 ± 2.37	
SnPb40	16 ± 5	7.3 ± 4.4	51.13 ± 1.1	50.68 ± 0.38	50.75 ± 0.45	
SnZn13.5	53 ± 4	26.71 ± 3.65	16.39 ± 2.2	29.65 ± 0.54	46.43 ± 3.52	

Table 3 Effect of testing procedure on shear strength of solder/Cu couples (CH: 230 °C, 5 min, flux).

For such alloys as SnZn13.5 (Fig. 9a), which are characterized by relatively low plasticity and high reactivity with the Cu substrate (evidenced by the formation of almost two-fold thicker IMC layer than that formed with pure Sn and SnPb40), the punch diameter has a significant effect on the push-out shear strength and τ_{max} measured with d = 4.95 mm is comparable to that of push-off shear test on the solidified sessile drop sample. This effect is caused by a relatively thick IMC layer that is growing inside the solder and has nonhomogeneous thickness due to a local non-wetting accompanied by gas bubble nucleation (Fig. 9b), all contributing to decreased resistance to shear loading.



Fig. 9 Effect of the size of loading punch on shear behavior of Sn13.5/Cu samples reordered by push-out shear tests (a) and corresponding interface microstructures (b,c).

Effect of solidification phenomena

Several commonly observed unfavorable effects accompanying solder alloy solidification, such as gas porosity, shrinking voids, rough dendrite solder surface, fillet lifting, and hot tearing, which may drastically affect solder joint reliability, are extensively reported in the literature (e.g., [26]). They contributed to unsatisfied compatibility between the solder and the substrate due to microsegregation toward the solder/substrate interface and thermal mismatch of two contacting materials. Most of these defects are caused by volumetric change (mainly constriction), known as shrinkage $\beta = \beta_{l-s} + \beta_s$ ($\beta_{l-s} - solidification shrinkage at <math>T_1 - T_s$, $\beta_s - shrinkage during cooling of a solidified material from <math>T_s$ to room temperature T_r), which can be estimated from the data on materials density in solid and liquid states. The calculated values for pure metals (Table 4) show a wide range of both β and β_{l-s} due to scattering of experimentally estimated values of densities in liquid state owing to dissimilar purity of metals and methodological differences. Although such data are not available for most solder alloys, the solder solidification shrinkage can be roughly forecast from the data of pure metals, suggesting that alloying with Bi and Ga should decrease β_{l-s} . It has been confirmed experimentally by observation of solder droplet during wettability tests and further structural examination of solidified sessile drop samples.

Metal	Crystal structure	Melting point, °C	Solidification shrinkage (%)	Total shrinkage (%)
Ag	fcc	962	3.8	10.99
Al	fcc	660	$6.0 \div 7.14$	11.66
Au	fcc	1063	5.1 ÷ 5.47	11
Bi	rhomb	271	$-3.35 \div -3.32$	-2.73
Cd	hcp	321	$3.8 \div 4.7$	7.18
Cu	fcc	1083	4.1 ÷ 5.3	10.7
Ga	orthorhombic	30	-3.2	-3.05
In	fct	156	$1.98 \div 2.0$	3.8
Mg	hcp	651	$3.1 \div 4.1$	8.6
Ni	fcc	1453	5.11 ÷ 5.4	10.67
Pb	fcc	327	$3.22 \div 3.56$	8.58
Sb	rhomb	631	$-0.9 \div 0.8$	2.95
Si	diam	1410	$-9.6 \div -2.9$	-6.26
Sn	tetrag	232	$2.51 \div 2.6$	4.1
Zn	hcp	420	$4.08 \div 4.3$	7.9

Table 4	Shrinkage	of selected	metals*.
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*Calculated from data collected from [28-31].

CONCLUSIONS

The shear behavior of the solder/Cu couples depends on solder chemical composition, materials preparation, processing parameters, as well as testing method and procedure used for characterization of shear strength. The push-off shear test of sessile drop solder/Cu couples is the microstructure-sensitive method, which provides useful information for understanding mechanical behavior of solder joints and prediction of their reliability.

The results clearly demonstrate that the presence of even a few nanometers thick but continuous and tenacious oxide film on the solder droplet (formed either before introduction of the sample in vacuum chamber or due to reacting the solder with the residual oxygen in the furnace caused by degrading the vacuum level and hence presumably increasing the oxygen partial pressure) significantly affect macroscale properties of the solder/Cu couples such as wetting and shear bond strength.

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