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Effect of temperature and substrate surface texture on wettability and morphology of IMCs between Sn–0.7Cu solder alloy and copper substrate

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Abstract In the present work, the effect of soldering temperature (270 and 298 °C) and substrate surface texture (0.02 and 1.12 μm) on wetting characteristics and morphology of intermetallic compounds (IMCs) between Sn–0.7Cu lead-free solder on copper substrates was investigated. It was found that increase in temperature and substrate surface roughness improved the wettability of solder alloy. However, the effect of surface roughness on wettability was significant as compared to that of temperature. The spreading of solder alloy was uniform on smooth substrate, whereas spreading of the alloy on rough substrate resulted in an oval shape. The morphology of IMCs transformed from long needle shaped to short and thick protrusions of IMCs with increase in surface roughness of the substrate. Needle shaped and thick protruded intermetallics formed at the solder/Cu interface were identified as Cu_6Sn_5 compounds. The formation of Cu_3Sn IMC was observed only for the spreading of solder alloy at 298 °C which contributed to improvement in the wettability of solder alloy on both smooth and rough substrate surfaces.

1 Introduction

Sn–Pb solders (eutectic and near eutectic) have been used extensively in electronics packaging industry for the assembly of components, because they possess advantages like ease of handling, low melting temperatures, good workability, ductility, excellent wetting on general base materials like Cu and its alloys [1]. The presence of lead (Pb) contributes to many of the desired properties of solders such as lower cost and better performance. However, its toxicity towards humans and wild life has warranted the elimination of Pb from solders [2]. Waste of Electrical and Electronic Equipment (WEEE) and Restriction of the use of Hazardous Substances (RoHS) directives have banned the use of lead from electronic solders for sustaining green environment [3]. These directives have lead to the development of new lead free solders like Sn–Cu, Sn–Ag, Sn–Zn–Bi, Sn–Ag–Bi, Sn–Bi and Sn–Ag–Cu for electronic applications in which Sn is a major element [2, 3]. Among them eutectic Sn–0.7Cu has been considered to be attractive, due to its excellent physical and mechanical characteristics [4]. It is lower in cost compared to other lead free solders and this has made it attractive for soldering in electronic applications. Eutectic Sn–Cu solder alloy is extensively used in wave soldering in electronic packaging field since 1998 [5].

Reactive wetting of liquid solder alloy on substrate is an important parameter to be considered for electronic packaging applications because it plays a vital role in bond formation for improvement in the bond strength. However, the wettability of solder alloy depends upon surface roughness of the substrate and soldering temperature [6, 7].

Zuruzi et al. [8] studied about the roughness evolution of the Cu_6Sn_5 IMCs during the soldering reaction of Sn–40Pb alloy on Cu substrate and its wettability, for extended soldering times up to 24 h. It was found that R_{rms} (root mean square) roughness, λ_a (average distance between asperities) and the average thickness of the total intermetallic layer have a parabolic dependence on soldering time. The average inclination of the Cu_6Sn_5 intermetallic morphology was greater than the apparent contact angle that

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was observed during the wetting of the solder on Cu substrates.

Chun and Hsiao [9] investigated the effect of substrate surface roughness on solder droplet bouncing and concluded that decrease in surface roughness reduces the potential for droplet bouncing. Mayappan et al. [10] carried out experiments on surface roughness and temperature effect on wettability of Sn–9Zn solder alloy and concluded that wetting time decreases when the reaction time increases. However, surface roughness above 0.62 µm resulted in improvement in the wettability of solder alloy. It clearly indicates that higher surface roughness is sometimes advantage for improving the wetting of solder. But according to Chen and Duh [11], solder wettability degrades as substrates become rough for Sn–Bi solders on Cu/Al_2O_3 substrates. Lin and Lin [12] also investigated the wetting behavior of Sn–37Pb and Pb-free solder on electroplated Cu substrate having varying surface roughness. It was concluded that, by controlling the deposition current density and the deposition time, the contact angle between solder and Cu plating decreases with the increase in surface roughness. Molten metal flow over flat surface and through the micro grooves of substrates was investigated by Zhao et al. [13] using a real time cinematography in situ and concluded the spreading over a flat surface is more sluggish than the spreading through the grooves. The rough surface has a positive effect, but sometimes a negative one. But, theoretically, the contact angle on the rough surface will be decreased [11]. According to Nalagatla [14], change in surface roughness of Cu substrate had no significant influence on the spreading behavior of Sn–0.7Cu solder. In our earlier study, [15] comparison of wetting behavior of Sn–0.7Cu solder on smooth and rough Cu was made and the study showed that Sn-Cu solder atoms dissolve into the rough Cu substrate in the time period of 200–600 s which was absent for smoother Cu surface.

Understanding the influence of surface roughness and soldering temperature on morphology of intermetallics at the interface between solder and substrate is important as it is widely recognized that roughness and soldering temperature have an effect on wettability of liquid metal. Despite the large number of studies on effect of temperature on wettability of solder, there is not much of literature is available on the combined effect of temperature and surface roughness on evolution and morphology of intermetallics during soldering and its relation to wetting behaviour. In the present work, experiments were carried out to study the effect of operating temperature and surface texture on wettability and morphology of intermetallic compounds during wetting of Sn–0.7Cu solder alloy on copper substrates.

2 Experimental

The commercial eutectic Sn-0.7 wt% Cu solder alloy (Multicore Manufacturers, UK) was used in the present study. The procured solder rod (Ø 6 mm) was drawn into solder wires having a diameter of about 1.4 mm. Solder wire was melted using solder station (KLAPP 920D) and solidified as balls of weight 0.080–0.090 g. Rolled round bar of EC grade copper (99.9% purity) procured from Hi Tech Sales Corporation, Mangalore was used for making copper substrates having 12.5 mm diameter and 8 mm height. The solder balls were then used for wettability study by measuring the contact angle on copper substrates having two different surface roughnesses (smooth and rough). The surface profiles of substrates were determined using Form Talysurf 50 surface profiler. Contact angle measurements were carried out using FTA 200 dynamic contact angle analyzer. The initial heating rate obtained with the chamber is about 3–4 °C/min which eventually reduce as the chamber temperature approaches the set value. Spherical balls of solder alloy (weighing approximately 0.080 g) were kept on the substrate and the solder/substrate system was kept inside the environmental chamber after coating the substrate surface with flux (Inorganic acid, Alfa Aesar, USA). The chamber was heated to a preset temperature (above the liquidus of solder alloy) and maintained at that temperature during the entire process of spreading. The experiments were carried out at temperatures of 270 and 298 °C. Images were captured at regular time intervals after spreading has started. Initially the images were captured at a rate of 0.0167 fps (frames per second) and then the time of interval of image change is incremented by 0.5%. The spreading process is recorded for approximately 2,414 s. The captured images were analyzed using FTA software (FTA 32 Video 2.0) to determine the wetting behavior of solder.

The solder drop bonded to the substrate was sectioned along the axis and polished using SiC papers of different grit sizes. The final polishing was carried out on velvet cloth disc polisher using diamond lapping compound and then etched with 5% nital (a mixture of C_2H_5OH and Conc. HNO_3 in the ratio of 95:5) for about 3–5 s. Zeiss stereomicroscope (Stemi 2000-C) was used for macroscopic view of the sessile drop of solder and Zeiss Axio Imager optical microscope (Imager. A1m) was used for microstructural study. The solder/substrate interfacial region was microexamined using JEOL JSM 6380LA scanning electron microscope (SEM). X-ray diffraction (XRD) study was carried out to identify and characterize the IMC at the solder/substrate interface. A JEOL JDX-8P-XRD system was used for this purpose.

3 Results and discussion

A typical micro-topology of the smooth and rough copper substrate surfaces prior to spreading experiments are presented in Fig. 1.

The typical relaxation curves for spreading of Sn–0.7Cu solder on Cu substrates with varying surface roughnesses and temperatures are presented in Fig. 2 and Fig. 3. Each experiment was repeated atleast two times for approximately 2,414 s. Beyond this period the change in the equilibrium contact angle is negligibly small (<0.01°/s). For smooth as well as rough substrate surface textures decrease in contact angle relaxation of solder alloy was sharp at the beginning upto a time of about 100 s and then the spreading of the solder ceased.

For the operating temperature of 270 °C, equilibrium contact angle values of about 35° were obtained on Cu substrates having very smooth surface texture and for rough surface texture the contact angle was reduced to 23°. The authors reported [15] similar behavior for the solder spreading at 298 °C. On smooth surfaces, the values of equilibrium contact angles were found to be 30° and the corresponding values on rough surfaces were reduced to 19° at 298 °C. Equilibrium contact angle values obtained under different surface texture and temperature of solder on

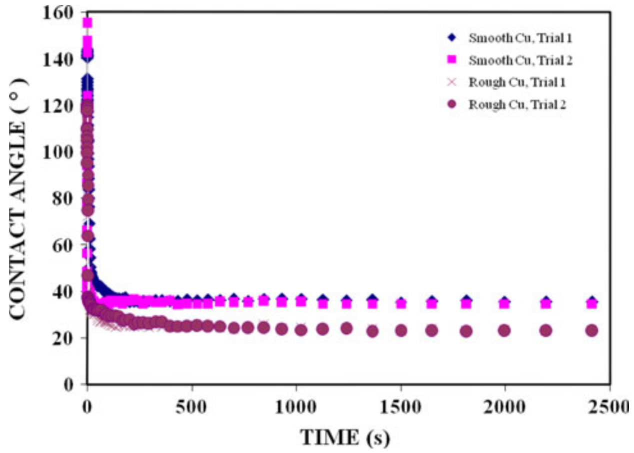

Fig. 2 Relaxation behavior of Sn–0.7Cu solder on smooth and rough copper substrates at 270 °C

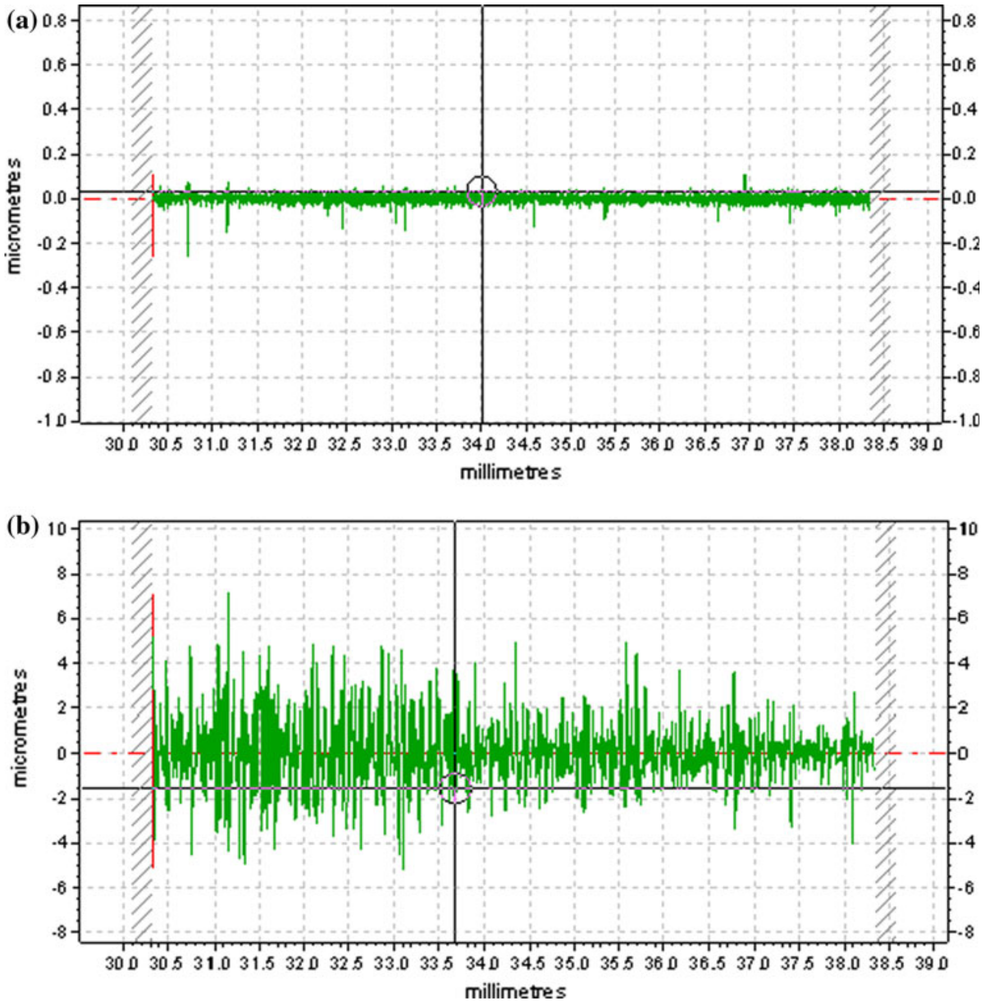

Fig. 1 Surface morphology of Cu substrate using Form Talysurf 50 surface profiler measurement system: **a** smooth Cu substrate ($R_a = 0.015$ µm), **b** rough Cu substrate ($R_a = 1.0337$ µm)

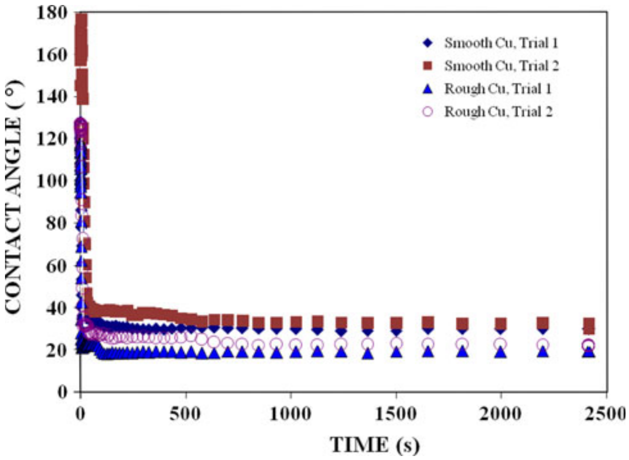

Fig. 3 Relaxation behavior of Sn–0.7Cu solder on smooth and rough copper substrates at 298 °C

Cu substrates are given in Table 1. It was found that increase in soldering temperature, affected marginally the wetting behavior. However, surface roughness has a significant effect on wettability of Sn–0.7Cu solder alloy. According to Rizvi et al. [16] for the solder alloy, by increase in solder bath temperature, wettability can be enhanced. No-clean (NC), non-activated (R) and water soluble organic acid (WS) fluxes were used for the experiments. In the present study, inorganic acid flux is used and substrate texture is considered as a variable. This also implies that, the effect of temperature on equilibrium contact angle is dependent on the type of flux used.

The macroscopic images (top view) of stabilized droplets of Sn–0.7Cu solder specimens after the spread test obtained by varying temperature and surface textures on copper substrates are shown in Figs. 4 and 5.

It was observed that the spreading of molten solder on smooth Cu substrate occurred uniformly in the radial direction whereas on rough substrate the spreading was oval in shape. Smoother surface texture resulted in uniform asperities (valleys) on substrate [17]. Therefore, liquid solder spreads fast and wets easier. Due to rapid spreading of solder alloy on smoother surface a small amount of atoms from the substrate was dissolved into the molten solder. For this faster dissolution of copper atoms into liquid solder, the liquid solder will saturate with Cu sooner, leading to a formation of sharp needle like IMCs at the interface as shown in Fig. 6a. The average size of needle shaped IMCs were found to be 89 µm in height and 3 µm thick. These IMCs grew into the solder field from the interface. The chemical composition of IMCs revealed that needle shaped IMCs were composed of Cu and Sn atoms. The atomic percentage of Cu decreases as measured from root to tip of the IMCs. Energy-dispersive X-ray spectroscopy (EDAX) analysis revealed that the composition of the needle-type IMC as shown in Fig. 6a corresponds to Cu_6Sn_5. Elemental composition of the region marked ‘A’ in Fig. 7a are given in Table 2 and it revealed that IMCs were made of Cu_6Sn_5.

Table 1 Effect of temperature and substrate surface texture on the equilibrium contact angle of Sn–0.7Cu solder on Cu substrate

Nature of polished surface	Temperature (°C)	Roughness (µm)	Equilibrium contact angle (°)
Mirror finished	270	0.0182	34.78
		0.019	35.45
Belt polished	270	0.9183	23.15
		0.932	23.95
Mirror finished	298	0.015	30.13
		0.016	30.67
Belt polished	298	1.0337	19.48
		1.2058	21.85

An increase in temperature resulted in increase in growth of needle shaped IMCs (Fig. 6b). This is due to the dissolution of more amount of Cu atoms into the molten solder at 298 °C as compared to 270 °C. The average size of needle shaped IMCs were found to be 277 µm in height and 6 µm thick. It is well known that at higher temperature the diffusion process of solder atoms at the solder/substrate interface becomes more active because flowability of liquid solder increases [18].

According to Suh et al. [19], the Cu_6Sn_5 scallop IMCs tilt easily because IMCs are surrounded by liquid solder, and it does not provide any physical restriction. Cu_6Sn_5 intermetallics were identified at the interface of solder substrate region for the operating temperature of 270 °C, because Cu_6Sn_5 is the closest intermetallic phase to eutectic temperature compared with other Cu–Sn IMCs such as Cu_3Sn, $Cu_{10}Sn_3$ and $Cu_{41}Sn_{11}$ [20]. Solder alloy spread at 298 °C exhibited Cu_6Sn_5 and Cu_3Sn intermetallics at the interface as shown in Fig. 7b. Since Cu_3Sn intermetallic formation requires higher activation energy and temperature than Cu_6Sn_5, the thickness of Cu_3Sn IMC found to be 2.4 µm. The elemental compositions of regions marked ‘P’ and ‘+’ indicated in Fig. 7b are given in Table 3 which confirms the formation of Cu_3Sn and Cu_6Sn_5 IMCs at the interface. According to Park et al. [21], only in the absence of sufficient supply of Sn, the Cu_3Sn will grow at the expense of Cu_6Sn_5 phase reacting with copper. Fig. 8a shows the XRD pattern obtained for Sn–0.7Cu solder on smooth Cu at 270 °C indicating the formation of Cu_6Sn_5 IMCs at the interface and Fig. 8b confirms the formation of Cu_3Sn and Cu_6Sn_5 IMCs at the interface for the soldering temperature of 298 °C.

According to Mayappan et al. [10] by increasing the roughness of the base metal, additional surface area can be introduced, which causes an increase in its surface energy.

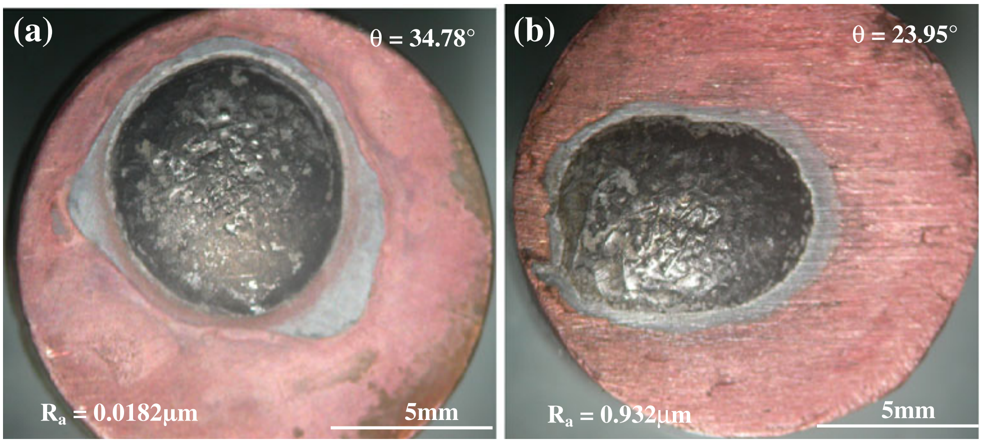

Fig. 4 Macroscopic images (*top view*) of stabilized Sn–0.7Cu solder on copper substrates at 270 °C having **a** smooth surface texture, **b** rough surface texture

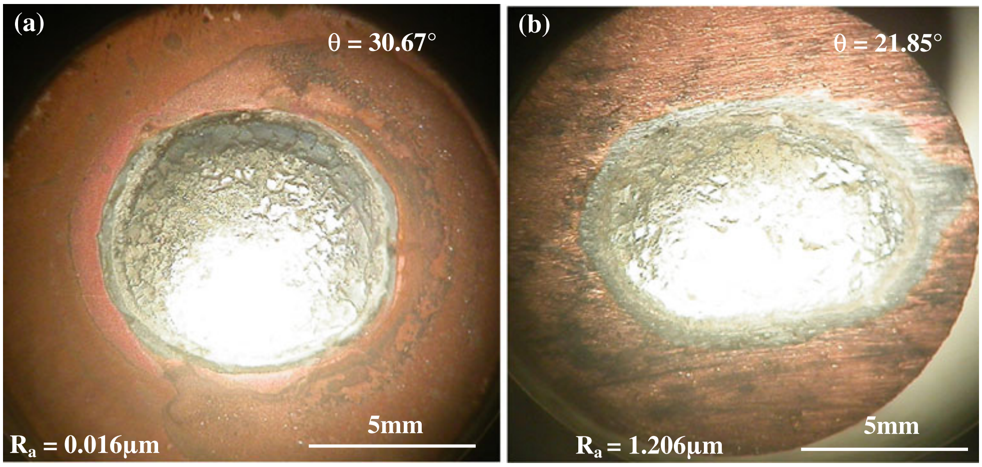

Fig. 5 Macroscopic images (*top view*) of stabilized Sn–0.7Cu solder on copper substrates at 298 °C having **a** smooth surface texture, **b** rough surface texture [15]

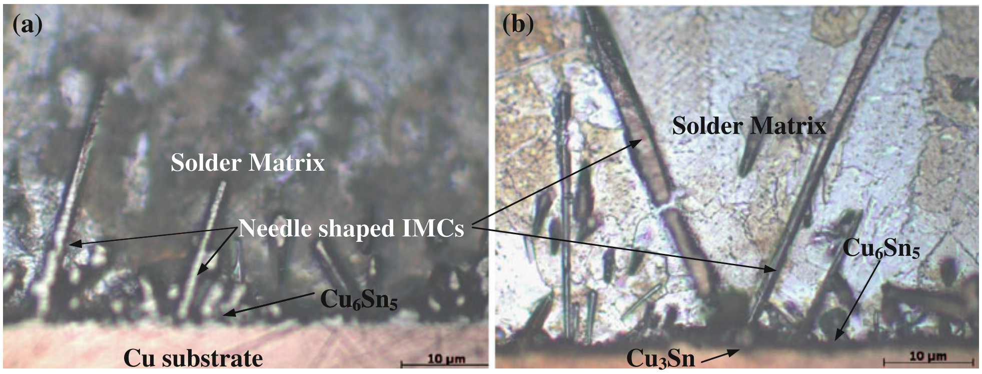

Fig. 6 Optical microstructures of Sn–0.7Cu solder on smooth Cu surface at **a** 270 °C and **b** 298 °C

The rough surfaces may act as preferable sites for reaction, diffusion, absorption and nucleation [22]. An increase in surface roughness on substrate enhances the capillary action for solder solidification, which leads to the dissolution of more amount of molten solder into the substrate. Rougher asperities have number of corners and these corners act as nucleation sites for solidification of liquid solder. Due to dissolution of molten solder in larger

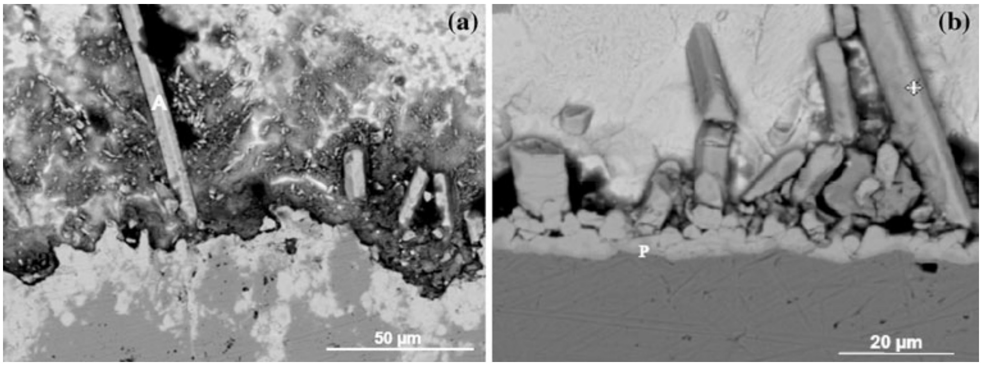

Fig. 7 SEM micrographs of Sn–0.7Cu solder on smooth Cu surface at (**a**) 270 °C and (**b**) 298 °C

Table 2 EDS analysis results of (mark 'A' in Fig. 7a) Sn–0.7Cu solder on smooth Cu substrate interface at 270 °C

Elements	Mark 'A' at %
Cu K	51.74
Sn L	48.26

Table 3 EDS analysis results of (mark 'P' and '+' in Fig. 7b) Sn–0.7Cu solder on smooth Cu substrate interface at 298 °C

Elements	Mark P at %	Mark +, at %
Cu K	74.23	52.19
Sn L	25.77	47.81

quantity at higher surface texture, the size of the IMCs becomes sufficiently thick but shorter and protruded.

Microstructures (Fig. 9a, b) and SEM micrographs (Fig. 10a, b) show the formation of short and thick protruding IMCs at solder substrate interface on rough Cu surface at 270 and 298 °C. So reactive wetting of solder leads to a sufficient reduction in the number of longer needle shaped IMCs as the surface texture changes from smooth to rough. The slower dissolution rate of Cu into molten liquid solder leaves more time for the growth of Cu–Sn IMCs at the interface on rougher surface. This spreading behavior of solder leads to oval or non- uniform in shape (Figs. 4b, 5b) as compared to that on smooth surface. However, the final equilibrium contact angle of solder alloy on rough surface was lower than the smooth surface. The transformation in the morphology of long and sharp needle shaped IMCs to short and thick protrusions of IMC occurred as the surface texture changed from smooth to rough when molten solder reacts with the substrate. The average size of these IMCs were found to be 68 μm in height and 7 μm thick on rough Cu at 270 and at 298 °C the corresponding values were 53 μm and 10 μm respectively. Mean length (H) of IMCs and their thickness (D), formed in the interfacial region of Sn–0.7Cu solder/Cu substrate at both the temperature and surface texture are given in Table 4. It was found the H/D ratio of IMCs was significantly affected by the substrate surface texture. At soldering temperature of 270 °C, the H/D ratio decreased significantly from 29.5 to 9.7 for the rougher surface. The corresponding values of H/D ratio at 298 °C were 46 and 5, respectively.

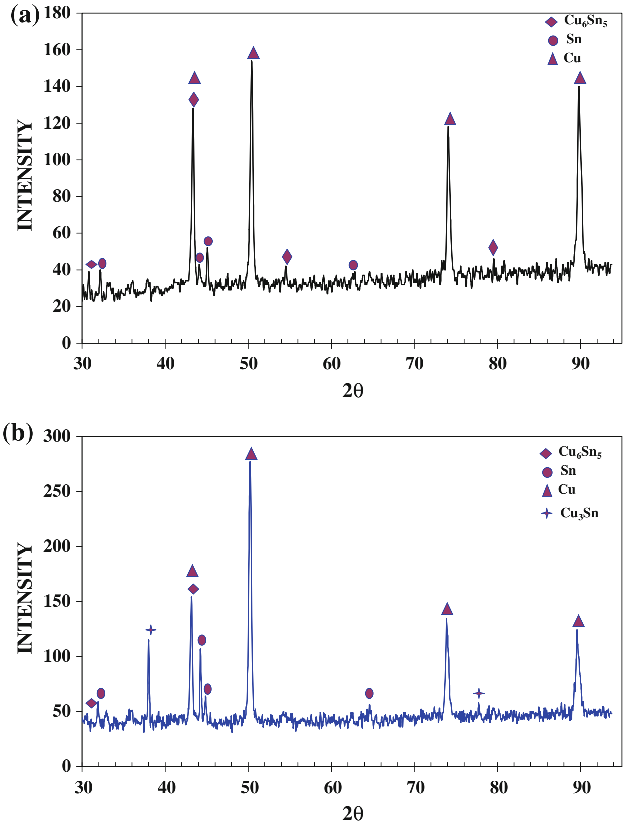

Fig. 8 XRD pattern of Sn–0.7Cu solder on smooth Cu surface at **a** 270 °C and **b** 298 °C

The formation of Cu_6Sn_5 and Cu_3Sn intermetallics at the interface were observed for solder spreading carried out

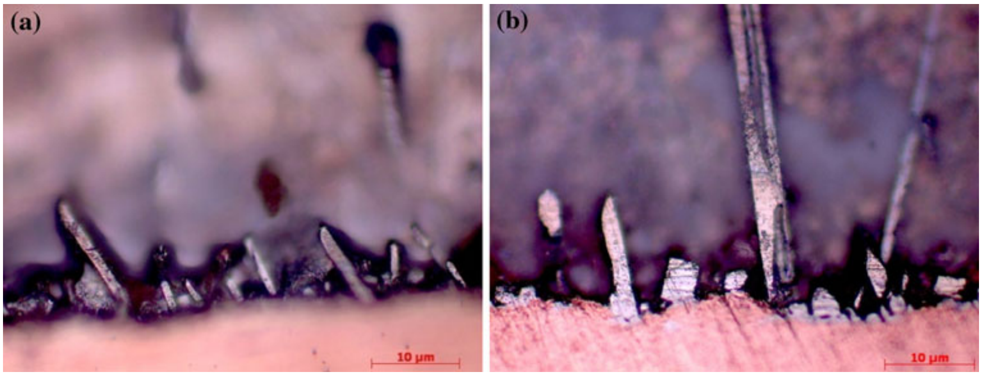

Fig. 9 Optical microstructures of Sn–0.7Cu solder on rough Cu surface at **a** 270 °C and **b** 298 °C

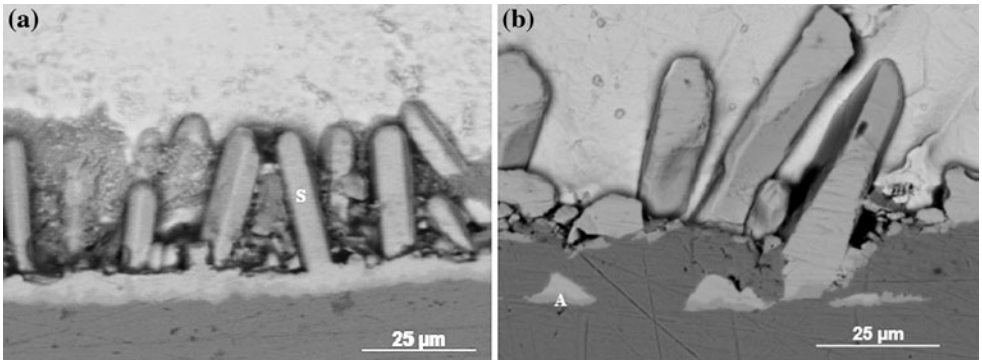

Fig. 10 SEM micrograph of Sn–0.7Cu solder on rough Cu surface at **a** 270 °C and **b** 298 °C

Table 4 Effect of temperature and substrate surface texture on length/thickness (H/D) ratio of IMCs formed between Sn–0.7Cu solder and Cu substrate

Nature of substrate surface	Temperature (°C)	Mean length (H) (μm)	Mean thickness (D) (μm)	H/D ratio
Smooth Cu	270	88.6	3	29.53
Smooth Cu	298	277	6	46.16
Rough Cu	270	68	7	9.714
Rough Cu	298	53	10	5.3

at 298 °C on rough surface. However, Cu_3Sn formation on rough Cu at 270 °C was not observed. The elemental compositions of regions marked ‘S’ and ‘A’ in Figs. 10a and b are given in Table 5 indicating the formation of Cu_6Sn_5 at 270 °C and Cu_3Sn IMCs at 298 °C. Figure 11a, b show the XRD pattern of Sn–0.7Cu solder on rough Cu surface at 270 and 298 °C. XRD pattern confirms the formation of Cu_6Sn_5 IMCs at the interface for 270 °C and Cu_6Sn_5 and Cu_3Sn intermetallics at 298 °C. The formation of Cu_3Sn IMC at the interface for the soldering temperature of 298 °C contributed to improvement in the wettability of solder alloy on both smooth and rough surfaces. It is reported that the formation of Cu_3Sn between Cu and Cu_6Sn_5 is beneficial and it improves the adhesion strength [23].

Table 5 EDS analysis results of (mark ‘S’ in Fig 10a and mark ‘A’ in Fig. 10b) Sn–0.7Cu solder on rough Cu substrate at 270 and 298 °C

Elements	Mark ‘S’ at %	Mark ‘A’, at %
Cu K	58.19	71.22
Sn L	41.81	28.78

The presence of Cu_3Sn between Cu and Cu_6Sn_5 IMCs has been reported by Arenas and Acoff [24]. But in the current study, formation of Cu_3Sn formation on smooth and rough Cu at 270 °C was not observed. It is due to the flux used in this study is different from Arenas and Acoff [24] study. According to Laurila et al. [25] Cu_3Sn layer forms just after reflow or wave soldering and this layer was clearly detected by SEM only after 64 min of contact times at 250 °C. Since the residence time of the solder alloy on the copper substrate in the current study is only 40 min, it is possible that Cu_3Sn appeared as a very thin layer, which could not be identified by the XRD and SEM.

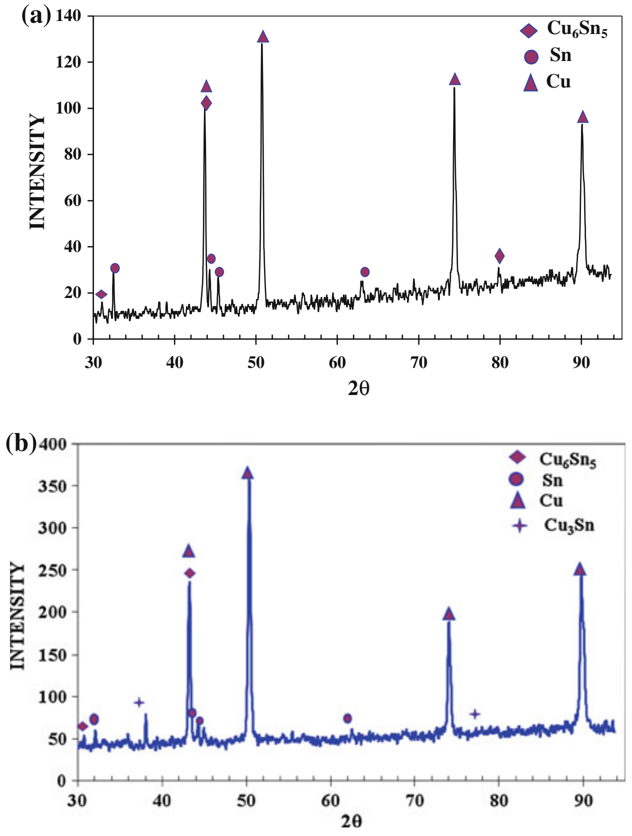

Fig. 11 XRD pattern of Sn–0.7Cu solder on rough Cu surface at **a** 270 °C and **b** 298 °C

At higher soldering temperature of 298 °C, viscosity and surface tension of the solder decreases and the final equilibrium contact angle of the solder was found to be lower. The surface tension and viscosity of Sn–0.7Cu solder at 280 °C are 402 mN/m and 2.15 mPa s. As the temperature increased to 300 °C, both will decrease to around 370 mN/m and 1.98 mPa s, respectively [26]. Hence, at higher temperature, the wettability of Sn–0.7Cu solder alloy was enhanced and the effect was more pronounced at higher surface roughness of the substrate.

4 Conclusion

It was found that increase in temperature and substrate surface roughness improved the wettability of solder alloy. However, the effect of surface roughness on wettability was significant as compared to that of temperature. At the operating temperature of 270 °C, the contact angle decreased significantly from 35° to 23° as the surface texture was changed from smooth to rough. The corresponding values of contact angle at 298 °C were 30° and 20° respectively.

The morphology of IMCs transformed from long needle shaped to short and thick protrusions of IMCs with increase in surface roughness of the substrate. The spreading of sessile drop of solder alloy on smoother surface Cu was uniform, whereas on rough Cu surface spreading of solder alloy resulted in an oval shape. It was found the length/thickness (H/D) ratio of IMCs was significantly affected by change in the substrate surface texture. At the operating temperature 298 °C, the H/D ratio decreased significantly from 46 to 5 as the surface texture was altered from smooth to rough. The corresponding values of H/D ratio at 270 °C were 29.5 and 9.7, respectively. The formation of Cu_3Sn IMC was observed only for the spreading of solder alloy at 298 °C which contributed to the improvement in the wettability of the solder alloy on both smooth and rough surfaces.

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