Study of Reactive Wetting of Sn–0.7Cu and Sn–0.3Ag–0.7Cu Lead Free Solders during Solidification on Nickel Coated Al Substrates

Satyanarayana, and K.N. Prabhu

***Abstract*—**Microstructure, wetting behavior and interfacial reactions between Sn–0.7Cu and Sn–0.3Ag–0.7Cu (SAC0307) solders solidified on Ni coated Al substrates were compared and investigated. Microstructure of Sn–0.7Cu alloy exhibited a eutectic matrix composed of primary β-Sn dendrites with a fine dispersion of Cu_6Sn_5 intermetallics whereas microstructure of SAC0307 alloy exhibited coarser Cu_6Sn_5 and finer Ag_3Sn precipitates of IMCs with decreased tin dendrites. Contact angles ranging from 22° to 26° were obtained for Sn–0.7Cu solder solidified on substrate surface whereas for SAC0307 solder alloy contact angles were found to be in the range of 20° to 22°. Sn–0.7Cu solder/substrate interfacial region exhibited faceted $(Cu, Ni)_6Sn_5$ IMCs protruding into the solder matrix and a small amount of $(Cu, Ni)_3Sn_4$ intermetallics at the interface. SAC0307 solder/substrate interfacial region showed mainly $(Cu, Ni)_3Sn_4$ intermetallics adjacent to the coating layer and $(Cu, Ni)_6Sn_5$ IMCs in the solder matrix. The improvement in the wettability of SAC0307 solder alloy on substrate surface is attributed to the formation of cylindrical shape $(Cu,Ni)_6Sn_5$ and a layer of $(Cu, Ni)_3Sn_4$ IMCs at the interface.

***Keywords*—**Lead-free solder, wetting, contact angle, intermetallics.

I. Introduction

THE research in development of lead free solders increasingly become important for the past ten years as the legislations restrict the use of Pb in solder alloys [1]. Among the new lead free solders (Sn–Cu, Sn–Ag, Sn–In, Sn–Ag–Bi and Sn–Ag–Cu), eutectic Sn–0.7Cu is considered to be most promising candidate especially for wave soldering and it is equally attractive as Sn–37Pb solder in performance. Moreover, it costs 1.3 times higher than the conventional Sn-Pb solders [2]. Unfortunately, Sn–0.7Cu alloy showed poor joint fillet shape and its higher melting temperature deteriorate the board materials [3]. It is also reported that, Sn–Cu exhibited somewhat inferior mechanical properties and wettability compared to Ag containing lead-free solder alloys [4]. Zeng et al. [4] reviewed the effects of alloying elements (Ni, rare earths, Zn, Co, Ga, In, Bi, secondary particles etc.) on melting behavior, wettability, microstructure, interfacial reactions, mechanical properties and reliability of Sn–Cu solders. It was reported that, certain content of Ni improved the comprehensive properties of Sn–Cu alloy and a suitable alloying elements X can take effect on lowering the melting temperature, improving wettability, stabilizing and refining microstructure, and preventing the formation and growth of IMC layer [4]. Presence of silver (Ag) in Sn–Cu solders increases the creep resistance, mechanical strength and decreases the eutectic temperature of the alloys effectively [5]. However, higher amount of Ag in the alloy (example eutectic SAC alloy) can form large primary Ag_3Sn precipitates, which can deteriorate the ductility of the joints [5]. At present, research is diverting towards low Ag solder alloys because cost of Ag is increasing day by day. Among low Ag solder alloys Sn–0.3Ag–0.7Cu (SAC0307) gained more attraction because of its superior performance and much lower in cost than higher Ag content Sn–Ag–Cu solder alloy [6], [7]. Cheng et al [8] reported that, SAC0307 and Sn–1.0Ag–0.5Cu (SAC105) are the promising alternate candidates for Sn–3Ag–0.5Cu (SAC305) as the second-generation lead-free solders. In addition, studies related to low Ag bearing solders are limited. In the present work, experiments were carried out to study the microstructure, wetting behavior and interfacial reactions formed between Sn-0.7Cu and Sn-0.3Ag-0.7Cu lead free solders solidified on Ni coated Al substrates.

II. Experimental

The commercial Sn–0.7 wt% Cu (Multicore Manufacturers, United Kingdom) and hypo eutectic Sn–0.3Ag–0.7Cu (Alpha Electronics Manufacturers, United Kingdom) solder alloys were used in the present study. The procured solder rod of Sn–0.7Cu (Ø 6mm) was drawn into solder wires having a diameter of about 1.4mm and the other solder alloy procured was already in the form of wire (1.25 mm). Solder wires were melted using solder station (KLAPP 920D) and solidified as balls of weight 0.080 gm. The solder balls were then used for wettability study by measuring the contact angle on nickel-plated aluminum substrates (Ø12.5mm X 8mm). Nickel plating on Al was carried out at Modern Electroplaters (Mangalore, India). The coating thickness was about 10 –12 μm. The surface profiles of the coated substrates were assessed using Form Talysurf 50 surface profiler. The arithmetic mean roughness parameter (R_a) of the Ni-plated Al substrates was in the range of 0.02–0.08 μm. Contact angle measurements were carried out using FTA 200 dynamic contact angle analyzer. The system can capture both static and dynamic spreading phenomena. The initial heating rate obtained with the chamber is about 3–4°C/minute, which

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eventually reduce as the chamber temperature approaches the set value. Spherical balls of solder alloy 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 temperature of 270°C, which is higher than the liquidus temperature of solder alloy and maintained at that temperature during the entire process of spreading. Images were captured at regular time intervals after spreading has started. Initially the images were captured at a rate of 0.0167 fps and then the time of interval of image change is incremented by 0.5%. The spreading process is recorded for approximately for 40mins. The captured images were analyzed using FTA software (FTA 32 Video 2.0) to determine the wetting behavior of solder. Zeiss stereomicroscope (Stemi 2000-C) was used for macroscopic view of the sessile drop 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 for Sn–0.7Cu solder and 1min for SAC0307 solder alloy. The solder/substrate interfacial region was microexamined using scanning electron microscopy (SEM, JEOL JSM 6380LA) with energy disperse spectroscopy (EDS) in Back Scattered Electron mode

III. Results and Discussion

Optical microstructures of the as-received solder alloys are shown in Fig. 1. The microstructure of binary eutectic Sn–0.7Cu consists of a eutectic matrix composed primary β-Sn dendrites with a fine dispersion of Cu_6Sn_5 intermetallics (Fig. 1a). The solid solubility of Cu in Sn at eutectic temperature is only 0.006 wt.% or 0.01 wt.% and the intermediate phase corresponds to 44.8 to 46% Sn, remaining Cu [1]. The presence of 0.3wt % Ag to Sn–0.7Cu solder caused significant change in the microstructure of the solder alloy. It decreased the grain size of Sn and promoted the formation of Ag_3Sn intermetallics. Ag_3Sn is likely to be formed even with addition of 0.1%Ag [9]. Microstructure of SAC0307 alloy (Fig. 1b) shows coarser and finer precipitates of IMCs. Coarser precipitates were composed of Cu-Sn elements and the finer is Ag-Sn. The typical relaxation curves for spreading of Sn–0.7Cu and SAC0307 solders on Ni coated Al substrates are shown in Fig. 2. Each experiment was repeated atleast two times for about 40mins. For both the solder alloys, decrease in contact angle relaxation was sharp at the beginning and then the spreading of the solder ceased.

The contact angle of solder alloys exhibited significant variation with time on the substrate surfaces (Fig. 2a and 2b). Equilibrium contact angle values of about 22° – 26° were obtained on substrates for Sn–0.7Cu solder and for SAC0307 solder the contact angles were found to be 20° –22°.

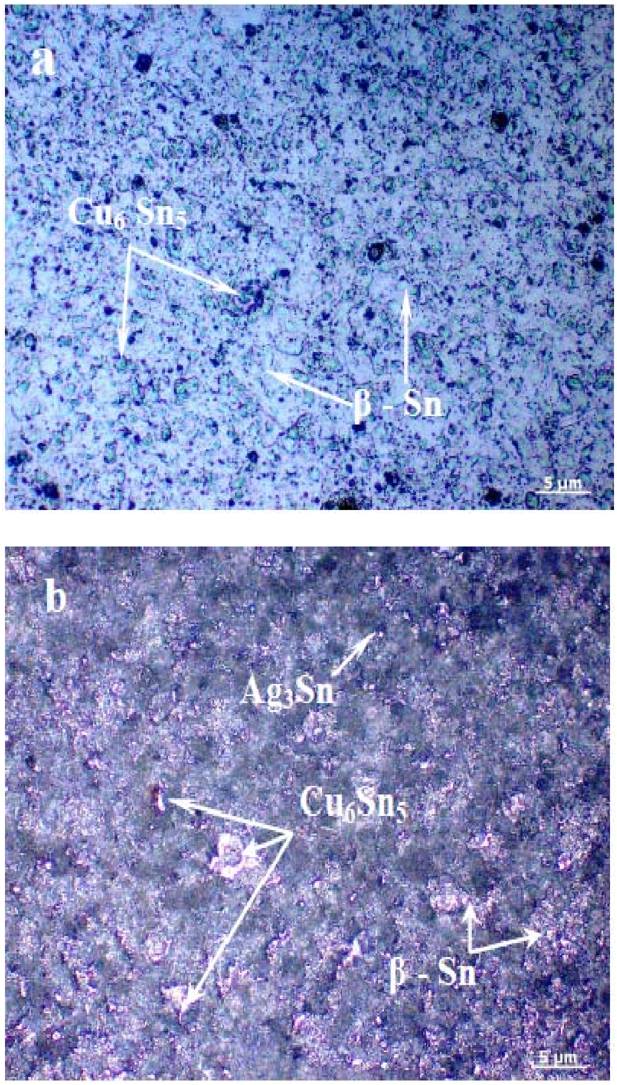

Fig. 1 Optical microstructures of as-received (a) Sn–0.7Cu (b) SAC 0307 solder alloys

The macroscopic images (top view) of stabilized droplets of solder alloys on substrate surfaces after the spread test are shown in Fig. 3.

The spreading behavior of SAC0307 molten solder on substrate surface was slightly better as compared to Sn–0.7Cu solder, though the contact angles obtained were almost similar. Solder drop area obtained for Sn–0.7Cu solder was found to be 23-27mm2 whereas for SAC0307 solder it was 30–38mm2. Since, the surface roughnesses of the substrate measured were almost same, the improvement in spreadability of solder alloy on coated substrate is due to the presence of small amount of Ag (0.3wt %) in the Sn–0.7Cu solder alloy.

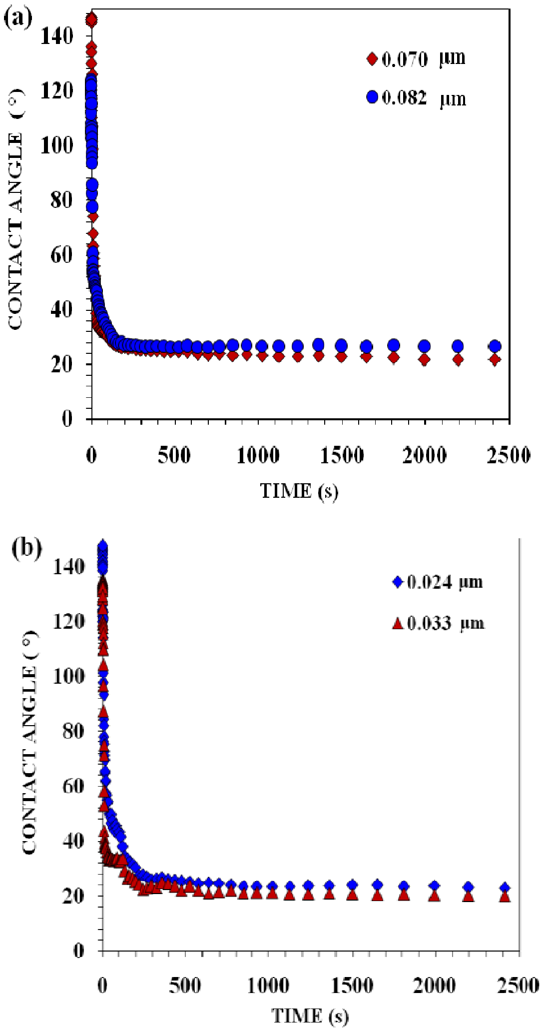

Fig. 2 Relaxation behavior of a) Sn–0.7Cu b) SAC0307 solder on substrate surface

Fig. 4a and 4b represent the SEM images with backscattered electron (BSE) mode of solder alloys solidified on substrate surfaces. Sn–0.7Cu solder/substrate interfacial region exhibited faceted $(Cu,Ni)_6Sn_5$ IMCs and $(Cu, Ni)_3Sn_4$ intermetallics precipitated at the interface at some locations whereas SAC0307 solder/substrate interfacial region showed mainly $(Cu, Ni)_3Sn_4$ intermetallics adjacent to the Ni layer and $(Cu, Ni)_6Sn_5$ IMCs in the solder matrix. Hexagonal $(Cu, Ni)_6Sn_5$ IMCs were found to be in the cylindrical shape. The mechanism behind the formation of $(Cu, Ni)_6Sn_5$ intermetallics is due to diffusion of Ni atoms from the coating layer into the Cu_6Sn_5 IMCs which were already present in the solder matrix whereas, $(Cu, Ni)_3Sn_4$ forms when Cu atoms from the solder diffused into the Ni_3Sn_4 intermetallics.

The literature review suggests that, when the Cu concentration exceeds 0.5 wt.%, the IMC will be $(Cu, Ni)_6Sn_5$ only [10], [11]. In the present study, both $(Cu,Ni)_6Sn_5$ and $(Cu, Ni)_3Sn_4$ intermetallics were observed. This could be due to the spreading time chosen for the solder alloys on substrate is longer (40 min) than that reported in the literature review.

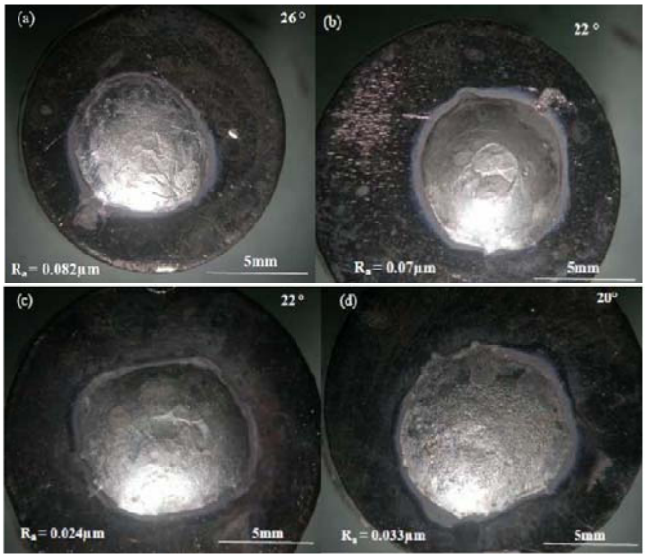

Fig. 3 Macroscopic images (top view) of stabilized alloys on substrate surfaces a – b) Sn–0.7Cu solder and c – d) SAC0307 solder

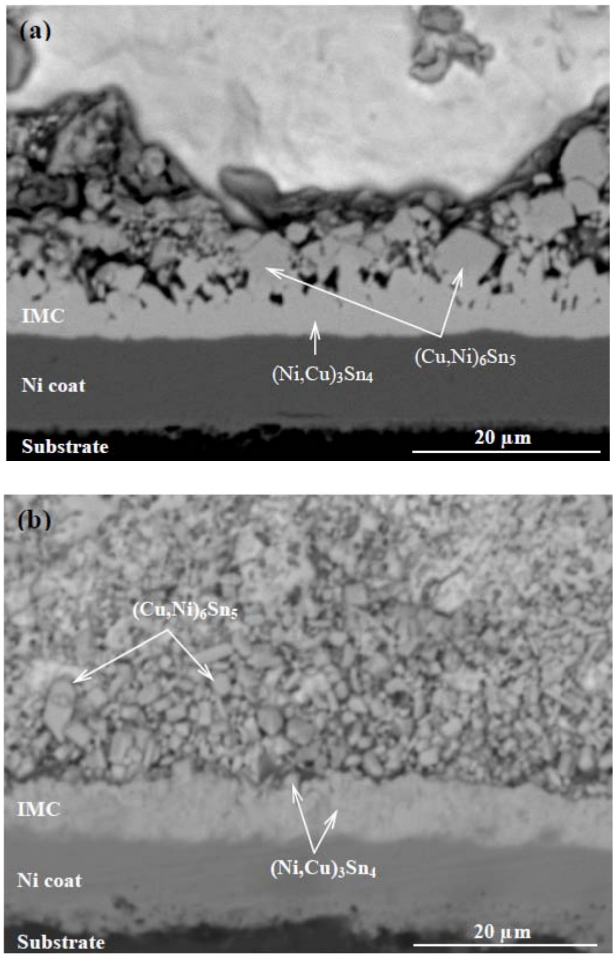

Fig. 4 SEM micrograph of a) Sn–0.7Cu solder/substrate interfacial b) SAC0307 solder/substrate interfacial regions

The faceted $(Cu,Ni)_6Sn_5$ IMCs protruded in the solder matrix, restricted the spreading of Sn–0.7Cu solder alloy on substrate surface. Such IMCs, which interlock with each other, will decrease the bond strength of the solder joints. For SAC0307 solder on substrate surface, needle shaped $(Cu, Ni)_3Sn_4$ IMCs were also observed at some locations near the interface. This was also reported by Wei et. al. [12]. This implies that, cylindrical shape $(Cu,Ni)_6Sn_5$ and layer of $(Cu, Ni)_3Sn_4$ IMCs at the interface had a significant effect on wettability and spreadability of SAC 0307 solder alloy on substrate surface. Zhang et.al [10] reported that, in the aged Sn–3.5Ag/Ni/Cu samples the formation of thick $(Ni_{1-y}Cu_y)_3Sn_4$ compounds at the interface and the coarsening of the Ag_3Sn particles reduce the shear strength of solder joints. Hence, to assess the effect of reactive wetting of solders on substrate surface under various conditions, more studies are needed to determine the bond strength of solder joints.

IV. Conclusion

The following conclusions are drawn.

1. Microstructure of Sn-0.7Cu alloy exhibited a eutectic matrix composed of primary β-Sn dendrites with a fine dispersion of Cu_6Sn_5 intermetallics whereas SAC0307 alloy exhibited coarser Cu_6Sn_5 and finer Ag_3Sn precipitates of IMCs with decreased tin dendrites.
2. Contact angles in the range of 22° – 26° were obtained for Sn–0.7Cu solder solidified on substrate surface whereas for SAC0307 solder alloy were found to be in the range of 20° – 22°.
3. Sn–0.7Cu solder/substrate interfacial region exhibited faceted $(Cu, Ni)_6Sn_5$ IMCs protruding into the solder matrix and at some locations small amounts of $(Cu, Ni)_3Sn_4$ IMCs were observed.
4. SAC0307 solder/substrate interfacial region showed mainly $(Cu, Ni)_{3Sn4}$ intermetallics adjacent to the coating layer and cylindrical $(Cu, Ni)_6Sn_5$ IMCs in the solder matrix.
5. The improvement in the wettability of SAC 0307 solder alloy on substrate surface is attributed to the formation of cylindrical shape $(Cu,Ni)_6Sn_5$ and a layer of $(Cu, Ni)_3Sn_4$ IMCs at the interface.

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