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TECHNICAL PAPER

Wettability, Interfacial Intermetallic Growth and Joint Shear Strength of Eutectic Sn–Cu Solder Reflowed on Bare and Nickel-Coated Copper Substrates

Mrunali Sona[1] · Sanjay Tikale[1] · Narayan Prabhu[1]

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Abstract In the present study, wettability, interfacial intermetallic growth and shear strength of Sn–Cu eutectic solder solidified on bare as well as nickel-coated copper substrates were examined. Sn–0.7Cu solder was reflowed over the substrate for reflow times ranging from 10 to 500 s at 270 °C. Samples were cooled by quenching in water. The wetting behavior was similar on both the substrates. The corresponding time period to the end of gravity zone (T_{gz}) was measured from the relaxation curve obtained from wetting studies. T_{gz} was found to be 25 s for Sn–0.7Cu on bare and 50 s on Ni-coated copper substrates. The intermetallic compound layer thickness was fitted to a growth model to study the growth kinetics. The integrity of solder/substrate joint was assessed by performing ball as well as single-lap joint shear tests. The shear strength was found to be maximum at T_{gz} for all solder/substrate systems.

Keywords Contact angle · Wettability · Gravity zone · Intermetallic compound · Joint strength

✉ Narayan Prabhu
knprabhu.nitk@gmail.com

Mrunali Sona
mrunalisona@gmail.com

Sanjay Tikale
Sanjaytikale@gmail.com

1 Metallurgical and Materials Engineering Department, National Institute of Technology Karnataka, Surathkal, Mangalore 575025, India

1 Introduction

The quality and performance of each circuit in an electronic assembly are exceedingly influenced by the wettability of solder alloys. An effective wetting is reliant on the alloy composition, flux, substrate, reflow time and reflow temperature [1]. In some of our earlier works, the impact of reflow time on spreading characteristics and mechanical properties of hypoeutectic Sn–Ag–Cu (SAC) solders reflowed on bare as well as Ni-coated Cu substrate (labelled as NcCs hereafter) has been discussed, and the importance of T_{gz} on joint strength has been brought out [2, 3]. In the present study, the eutectic Sn–Cu (Sn–0.7Cu) has been used being eco-friendly and cost effective due to the absence of expensive silver [1, 4]. Cu present in the Sn-based materials decreases the thermal cycle fatigue and increases the solder wettability and promotes the formation of Cu_3Sn and Cu_6Sn_5 IMC at the solder/substrate joint interface. The use of Sn–Cu solder alloy is limited by the coarse precipitation of Cu_6Sn_5 phase and inherent brittleness associated with it. Ni plating over the substrate hinders the quick reaction of molten solder with copper base metal and also provides desired flat surfaces maintaining a good wettability. Ni reduces the coarse precipitation of IMC and stabilizes high-temperature hexagonal Cu_6Sn_5 phase by forming $(CuNi)_6Sn_5$ [5, 6]. A significant research work has already been conducted on the effect of Ni addition in varying amount to Sn–0.7Cu alloy [7, 8], but none of the previous research works discuss the importance of T_{gz} on the reliability of eutectic Sn–Cu/substrate system.

This study deals with the wettability, microstructure and joint strength of Sn–Cu eutectic solder reflowed on bare copper and NcCs. This is an extension of the former work where similar tests were conducted on furnace-cooled Sn–

0.7Cu/Cu samples [9]. In the current work, quench cooling method was adopted as it could arrest the microstructure at desired reflow time and the mechanical properties were assessed. Lap joint test was conducted in addition to ball shear test, as it replicated the state of joint failure in electronic components.

2 Experimental Details

Spherical balls (0.080 g) of commercial Sn–0.7Cu solder alloy (Multicore Manufacturers, UK) were prepared using a solder station. Cu substrates of dimension ϕ12 mm X 8 mm were polished to the smooth surface finish. NcCs were prepared by electroplating a layer of Ni (15 µm thickness) on the Cu substrate. The surface roughness (arithmetic mean roughness, R_a) of substrate was assessed with the help of Form Talysurf 50 surface profilometer. Both Cu and NcCs showed the R_a values of 0.01 ± 0.006 µm and 0.04 ± 0.008 µm, respectively. Wetting behavior was investigated using dynamic contact angle analyzer. After covering the substrate surface with the flux, the solder ball/Cu substrate assembly was placed inside the heating chamber of the analyzer. A reflow temperature of 270 °C was maintained inside the chamber throughout the experiment. Samples were then cooled by quenching in water. The solidified solder/substrate sample was sectioned, polished and etched with 5% nital solution and analyzed under scanning electron microscope (SEM). The different phases observed in the microstructure were characterized using energy dispersive spectroscopy (EDS). The joint shear test for reflowed solder sessile droplets was performed using the solder bond shear tester (Nordson DAGE 4000Plus). Shear height and speed of the tool were fixed at 1 µm and 200 µm/s, respectively. Fractured surfaces obtained from the ball joint test were observed under SEM for the failure mode analysis.

The single-lap-solder joint was designed as per GB/T151n-94. Bare (R_a 0.03 ± 0.008 µm) and Ni-electroplated copper plates (R_a 0.04 ± 0.007 µm) of dimension 50 mm × 6 mm × 1 mm were used for the preparation of test specimens. The thickness of Ni coating was about 15 µm on bare copper substrate. Sn–0.7Cu alloy plate of dimension 5 mm × 5 mm × 0.5 mm was sandwiched between the isometallic plates and reflowed in a tubular furnace sustained at 270 °C. The substrate/Sn–0.7Cu/substrate system was cooled by quenching in water after the completion of reflow time. Pull test of single-lap-shear joint samples was performed under Instron 5967 tensile tester at a strain rate of 0.2×10^{-3} s^{-1} at room temperature. Fractured surfaces were evaluated under SEM for the failure mode analysis.

3 Results and Discussion

3.1 Wettability of Eutectic Sn–Cu Solder on Bare and Ni-Coated Copper Substrate

Relaxation curves obtained from the spreading analysis of eutectic Sn–Cu on bare as well as NcCs are shown in Fig. 1. In Fig. 1, three regimes, capillary (non-reactive), gravity (reactive) and viscous zones, are observed during spreading of molten solder over the substrate. Regimes are recognized by the rate of change of contact angle (θ) with respect to reflow time (s). Relaxation rates in capillary, gravity and viscous zones of Sn–0.7Cu/Cu systems are 2.71 ± 0.81°/s, 3.7 ± 0.2°/s and 0.01 ± 0.005°/s, respectively. Similarly, for Sn–0.7Cu/NcCs system, they are 0.98 ± 0.57°/s, 2.15 ± 0.35°/s and 0.02 ± 0.003°/s, respectively, in the corresponding zones. Relaxation rates are 63% and 41% lower in the capillary and gravity zones for Sn–0.7Cu/NcCs system when compared with Sn–0.7Cu/Cu system. This confirms the action of Ni as a diffusion barrier for the metallurgical reaction at the interface. Comparing the results with previous work, it can be observed that SAC alloys have taken about 37% and 43–50% more time to accomplish gravity zone on bare and NcCs, respectively. The presence of Ag in SAC alloys has reduced the relaxation rate. As the solder/substrate interface gets reactively bonded in the gravity zone, the relaxation rate decreases to a greater extent in the viscous region. The solder/substrate systems are once again prepared by reflowing for average times beyond the end of gravity zone. T_{gz} for eutectic Sn–Cu solidified on bare Cu and NcCs are found to be 25 s and 50 s, respectively. The contact angle, θ_{gz} at T_{gz} obtained for Sn–0.7Cu on bare Cu and NcCs, are 35.24° and 33.53°, respectively. Sn–0.7Cu shows good and comparable wetting on both type of substrates. Ni does not affect the wettability by reducing the relaxation rate. However, SAC solders have shown slightly lower wettability when compared with Sn–0.7Cu solders at T_{gz} on Ni-coated copper substrate [2, 3]. The presence of Ag hinders the wettability and also spreading rate of solder on the substrate.

3.2 Solder Joint Interfacial Microstructure

Joint interfacial microstructure for eutectic Sn–Cu on bare copper and NcCs systems is represented by SEM micrographs in Figs. 2 and 3, respectively. EDS analysis confirms the formation of Cu_6Sn_5 at the Sn–0.7Cu/Cu interface and $(CuNi)_6Sn_5$ at the Sn–0.7Cu/NcCs interface, respectively, as the major IMC layer. Initial morphology of Cu_6Sn_5 IMC at the interface is observed as a rounded scallop. The rise in reflow time above 100 s results in the

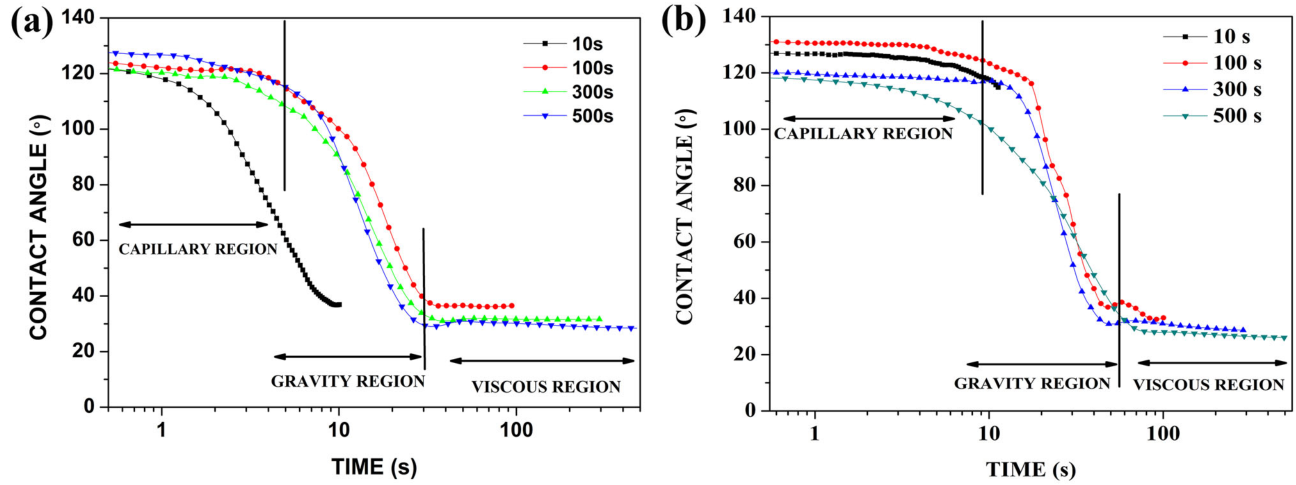

Fig. 1 Relaxation behavior of eutectic Sn–Cu reflowed on **a** bare Cu and **b** NcCs at 270 °C for varying reflow time

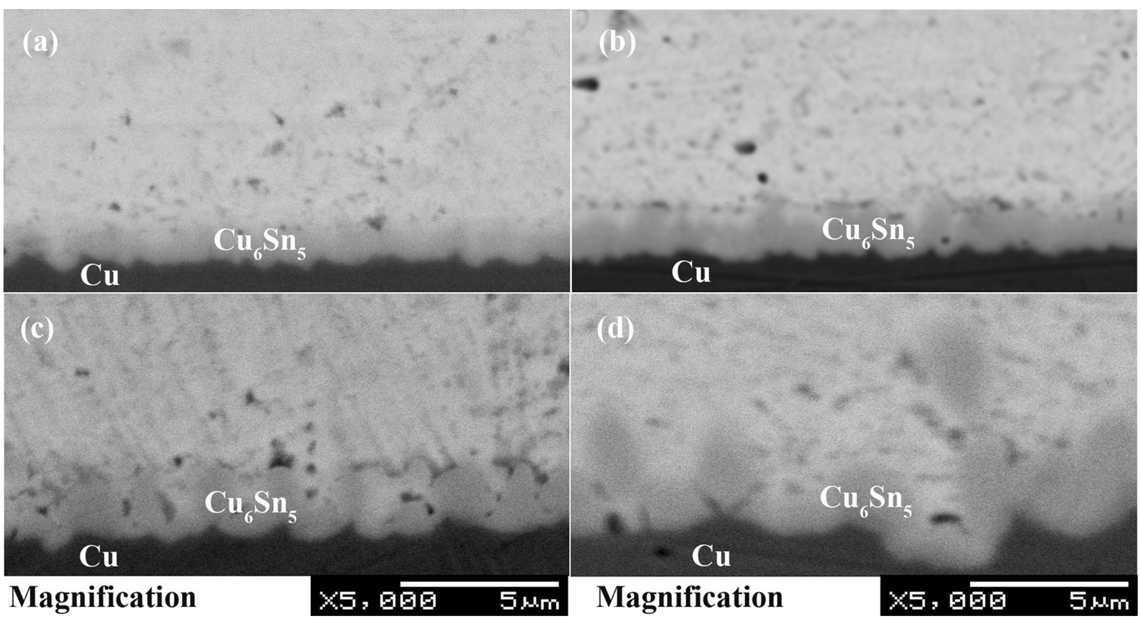

Fig. 2 SEM images of the interface of reflowed eutectic Sn–Cu/Cu system for **a** 10 s, **b** 25 s, **c** 100 s and **d** 500 s

transformation of round morphology to elongated scallop shape. SAC alloys have shown similar microstructures with an additional Ag_3Sn IMC in the bulk matrix [2, 3]. The interfacial IMC thickness is comparable for Sn–0.7Cu and SAC solders. Two reaction products, $(CuNi)_6Sn_5$ and $(CuNi)_3Sn_4$, have been identified by EDS analysis at the Sn–0.7Cu/NcCs interface. The formation of $(CuNi)_3Sn_4$ layer underneath $(CuNi)_6Sn_5$ is detected in the samples reflowed above 300 s with the thickness very small to be measured. Thickness of $(CuNi)_6Sn_5$ IMC increases with an increase in reflow time. The thickness of IMC layer at the solder/Ni-coated Cu interface is found to be lower than that of solder/bare-Cu interface. This clearly shows that the Ni layer hinders the rapid diffusion of the copper atoms from the substrate to the solder. The effect is more prominent at higher reflow time. A reduction of 4.3% and 15% in IMC thickness are observed on NcCs when compared to bare copper substrate for a reflow time of 10 s and T_{gz}, respectively. Samples reflowed up to 300 s show about 30% reduction and about 41% reduction for 500 s in IMC thickness growth on NcCs when compared to bare copper.

The acquired IMC thickness data are fitted to the growth model given by Eq. 1 to understand the rate-controlling process in interfacial IMC growth.

$$y = kt^n \tag{1}$$

Here, y represents the thickness of IMC layer, k stands for growth constant, t represents the reflow time and n is

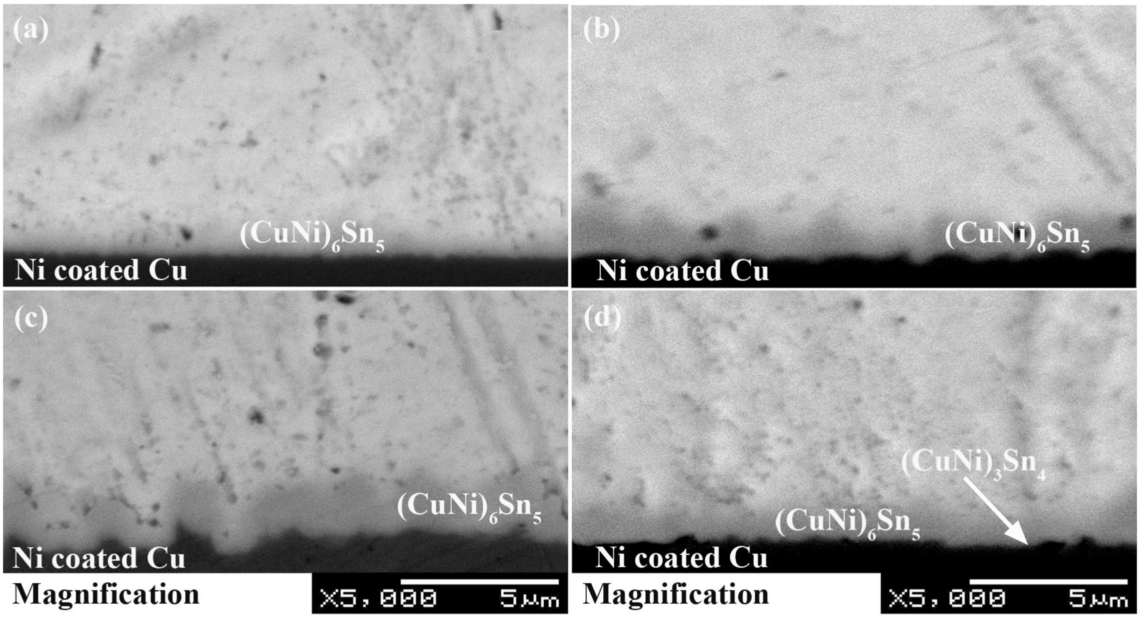

Fig. 3 SEM images of the interface of reflowed eutectic Sn–Cu/NcCs system for **a** 10 s, **b** 50 s, **c** 100 s and **d** 500 s

growth exponent. It is understood that grain boundary diffusion dominates the IMC growth process till the growth rate (n) is equal to 1/3 and volume diffusion takes over the growth process when n is equal to 1/2 [10]. The thickness values obtained are fitted to the growth model given by equation [1]. The IMC thickness versus reflow time data for eutectic Sn–Cu/Cu system results in $n = 0.34$ with a R^2 value of 0.94 and for eutectic Sn–Cu/NcCs system, $n = 0.23$ with R^2 value of 0.91. The fitting curve clearly confirms that the grain boundary diffusion is the prime rate-controlling process for the growth of IMC layer in both the systems.

3.3 Shear Strength of Sn–Cu Eutectic Solder Reflowed on Bare and NcCs

Effects of reflow time and interfacial IMC growth on bond strength have been investigated by performing the shear test on reflowed solder ball specimen. The shear energy values calculated from the test are tabulated in Table 1. Sn–0.7Cu/Cu system reflowed for 25 s (T_{gz}) exhibits maximum bond strength. Samples reflowed above 25 s show a decrease in joint strength. These results validate the observations represented in our previous work on SAC alloys. SAC alloys has shown higher joint strength than eutectic Sn–Cu. The presence of Ag_3Sn IMC particles in the bulk matrix is the prime reason for improved joint strength of SAC alloys [2]. A reflow time of 50 s results in maximum joint strength for Sn–0.7Cu/NcCs system, where 50 s happens to be the approximate T_{gz} value for the same system. Solder reflowed beyond T_{gz} results in lower shear strength. The fracture analysis of sheared samples indicate ductile failure mode.

3.4 Lap Joint Shear Strength of Cu/Sn–0.7Cu/Cu and Ni-Coated Cu/Sn–0.7Cu/Ni-Coated Cu System

Single-lap-shear joint pull test is performed on samples reflowed for 10 s, T_{gz} and 100 s. The solder joint shear strength under different reflow times is tabulated in Table 2. Both the systems show maximum shear strength at T_{gz}. The eutectic Sn–Cu on bare copper shows decrease in shear strength of about 18% compared to Sn–0.3Ag–0.7Cu alloy [3] and that of 34% for Sn–2.5Ag–0.5Cu alloy [2] reflowed for T_{gz} on bare copper. However, SAC alloys show comparable results with Sn–0.7Cu alloy when reflowed over Ni-coated copper substrate. Fracture analysis of sheared surface shows elongated dimple-like structures on the fractured surface indicating a ductile mode of

Table 1 Shear energy of the joint for Sn–0.7Cu reflowed on bare Cu and NcCs

Sn–0.7Cu/Cu		Sn–0.7Cu/NcCs	
Reflow time (s)	Shear energy (kJ/m^2)	Reflow time (s)	Shear energy (kJ/m^2)
10	54.35 ± 5.99	10	54.72 ± 0.08
25	63.26 ± 8.01	50	69.24 ± 3.43
100	58.35 ± 6.08	100	56.54 ± 0.49
300	55.85 ± 8.03	300	52.57 ± 0.64
500	48.76 ± 4.44	500	42.18 ± 2.09

Table 2 Single-lap joint shear strength of Sn–0.7Cu solder

Cu/Sn–0.7Cu/Cu system		NcCs/Sn–0.7Cu/NcCs system	
Reflow time (s)	Joint shear strength (MPa)	Reflow time (s)	Joint shear strength (MPa)
10	111.04 ± 6.5	10	196 ± 9.69
25	119.62 ± 4.67	50	279.75 ± 2.47
100	94.33 ± 22.8	100	216.33 ± 27

failure, regardless of reflow time conditions, whereas SAC alloys reflowed above T_{gz} is a combination of both ductile and brittle failure at the matrix and interface [2, 3].

4 Conclusion

Based on results obtained on wettability, microstructure and joint strength of eutectic Sn–Cu on bare and NcCs, the following conclusions were drawn.

1. Ni hindered the metallurgical reaction at the interface, but did not affect the wettability of eutectic Sn–Cu on the copper substrate.
2. The time required for the completion of gravity zone (T_{gz}) for the eutectic Sn–Cu solidified on bare Cu substrate was found to be 25 s and that for NcCs was 50 s. T_{gz} values were on the lower side for the eutectic Sn–Cu solder alloy when compared to SAC alloys from the previous work.
3. Thickness of IMC at the interfacial region for the eutectic Sn–Cu alloy and NcCs was lower than at the interface on bare Cu substrate. To obtain a good joint strength, the IMC thickness should be between 1 and 1.5 µm. IMC growth rate was controlled by grain boundary diffusion in all solder/substrate combinations.
4. Solder alloy reflowed till T_{gz} yielded maximum joint strength with ball shear and single-lap-shear pull tests. While comparing the results with our previous studies, it was concluded that specimens reflowed for T_{gz} yielded maximum strength regardless of the alloy used and the presence of Ag increased the joint strength.

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