Materials Performance and Characterization

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DOI: 10.1520/MPC20160058

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VOL. 6 / NO. 1 / 2017

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doi:10.1520/MPC20160058 / Vol. 6 / No. 1 / 2017 / available online at www.astm.org

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Manuscript received April 26, 2016; accepted for publication November 28, 2016; published online February 21, 2017.

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Reference

Tikale, S., Sona, M., and Narayan Prabhu, K., "Effect of Cooling Rate on Joint Shear Strength of Sn-9Zn Lead-Free Solder Alloy Reflowed on Copper Substrate," *Materials Performance and Characterization*, Vol. 6, No. 1, 2017, pp. 46–54, http://dx.doi.org/10.1520/MPC20160058. ISSN 2165-3992

ABSTRACT

Reliability of the solder joint largely depends on mechanical strength, fatigue resistance, coefficient of thermal expansion, and intermetallic compound formation. Cooling rate significantly affects the physical properties of an alloy and influences the mechanical behavior of solder joints. In the present study, Sn-9Zn lead-free solder alloy was solidified on Cu substrate under furnace cooling (0.04°C/s), air cooling (0.16°C/s), and water cooling (94°C/s) conditions. The effect of varying cooling rates on the intermetallic compound (IMC) formation at the interface and the resulting joint shear strength was studied. A microstructure study revealed the presence of Cu_5Zn_8 and $CuZn_5$ intermetallic compounds at the solder-substrate interface. The IMC layer thickness at the interface increased with a decrease in the cooling rate. The joint shear strength increased with an increase in the cooling rate. The air and furnace cooling resulted in the formation of a thick IMC layer. The IMC obtained from the furnace cooling was associated with micro-cracks leading to a decrease in the joint shear strength.

Keywords

Lead-free solder, intermetallic compound (IMC), cooling rate, joint shear strength

Introduction

The toxic effects of lead on environment and human health creates the concern about the applicability of Sn-Pb solders in electronic packaging. Legislative concerns over the use of Sn-Pb solders have stimulated the research and development for lead-free solders [1,2]. In response to the substantial efforts of the electronics industry for environment-friendly electronics, researchers have come up with many lead-free alternatives. The lead-free alternatives are mostly Sn based binary and ternary alloys. Sn-9Zn eutectic solder alloy with low melting temperature (198°C), high strength, and cost effectiveness compared with other lead-free solders has been recognized as one of the promising alternatives to replace the conventional Sn-Pb solder [3].

Soldering involves reactive wetting resulting in the formation of intermetallic compounds (IMCs) at the interface. IMCs are the reaction products of the molten solder and substrate. The reaction between the molten solder and a metallic substrate plays a major role in determining the microstructure and strength of the solder joint [4,5]. Investigations carried out by Huang and Lin [6] showed that Sn-9Zn solder formed Cu_5Zn_8 and $CuZn_5$ IMCs at solder-Cu substrate interface. IMCs are basically brittle in nature and lead to the sudden failure of the joint under stressed conditions. The cooling rate greatly affects the IMC morphology at the interface. Furnace and air cooling produced a thicker and rougher IMC than the water-quenched condition [7]. A smooth and continuous IMC at the interface indicates the good metallic bonding between solder and substrate. An optimum thickness of an IMC enhances the joint strength. However excessive growth of an IMC may degrade the bond strength. Overgrowth of an IMC creates the mismatch in physical properties such as the coefficient of thermal expansion and the elastic modulus between the IMC and bulk solder. This leads to the formation of micro-cracks in the IMC and also causes void formation at the interface, which weakens the solder joint under stressed conditions [5,8,9].

Prabhu et al. [10] observed finer and uniformly distributed needle shaped Zn flakes throughout the Sn matrix with an increase in the cooling rate in their study. A study done by Maveety et al. [11] on Sn, Sn-0.7Cu, Sn-3.5Ag, and Sn-37Pb solders showed an increase in ultimate tensile strength (UTS) of the alloy with an increase in the cooling rate. The investigation carried out on microstructure and microhardness of Sn-Cu and Sn-Ag solders by Seo et al. [12] suggested that both composition and cooling rate can significantly affect the Sn grain size and hardness in Sn-rich solders. The cooling rate directly affects the formation and growth of an intermetallic which in turn significantly influences the mechanical behavior of the joint [13]. The solidification rate of the solder alloy largely affects the microstructure and diffusion processes. Hence an understanding of the effect of cooling rate on microstructure, growth of intermetallic compounds, and mechanical behavior of the solder joint is very essential.

The shear strength of the solder alloy is a measure of the ability of interconnects to be compliant to the imposed strain. When a miniature joint is subjected to the tensile load, a tri-axial stress state will be developed rather than uniaxial tensile stress. Hence it is important to investigate the mechanical properties of a solder alloy under monotonic loading in shear and in tension and also under creep and fatigue conditions [14,15]. The present work deals with the assessment of the joint shear strength of Sn-9Zn solder reflowed on the Cu substrate. Solder joints were cooled with different cooling rates to assess its effect on intermetallic compound growth and subsequently on joint shear strength.

Experimental Details

MATERIALS

The commercial eutectic Sn-9Zn solder alloy wire was melted using a solder station (KLAPP 920D) and solidified as balls of weight 0.08 gm with the average diameter of 2.5 mm. A rolled round bar of EC grade copper (99.9 % purity) was used for making copper substrates (Ø12.5 mm by 8 mm). Substrates were polished using SiC papers of different grit sizes (1/0 to 4/0 grade) followed by a velvet cloth disc polish using diamond-lapping compound to obtain a smooth surface finish. The surface profiles of the substrates were assessed using the Form Talysurf 50 surface profiler. The roughness (Ra-value) of copper substrate was maintained in the range of 0.03–0.04 μm in this study.

JOINT SHEAR TEST

The solder ball was kept on a polished substrate coated with flux (Inorganic acid from Alfa Aesar, USA) and then reflowed for a reflow time of 100 s. From the earlier study, a reflow time of 100 s has shown higher mechanical properties among 10, 100, 500, and 1000 s reflow times for Sn-9Zn solder alloy [16]. Hence a reflow time of 100 s has been adopted for the present work. A vertical tubular furnace setup as shown in **Fig. 1** was used for the specimen preparation. The average ramp rate of 0.33°C/s was used to achieve the reflow temperature (≈TMelt + 50°C) and a holding time of 100 s at 250°C (reflow time) followed by cooling with water (94°C/s), air (0.16°C/s), and furnace (0.04°C/s), respectively, was used as the thermal profile for this study. The spreading process of the solder on the substrate was monitored from the top opening of the furnace. The shear test was performed on a solidified solder droplet specimen by using bond tester (Nordson DAGE 4000plus). The shear tool height was kept 1.0 μm ([<20 % of drop height) above the substrate base and the

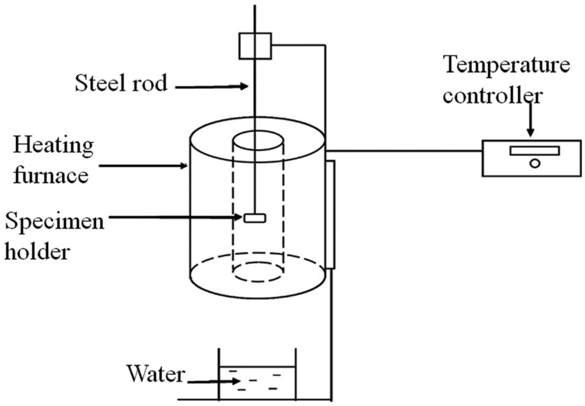


FIG. 1 Experimental setup for cooling rate effect analysis on the solder joint.

tool speed was set at 200 μm/s. The force versus displacement graphs were recorded for the shear test.

MICROSTRUCTURE STUDY

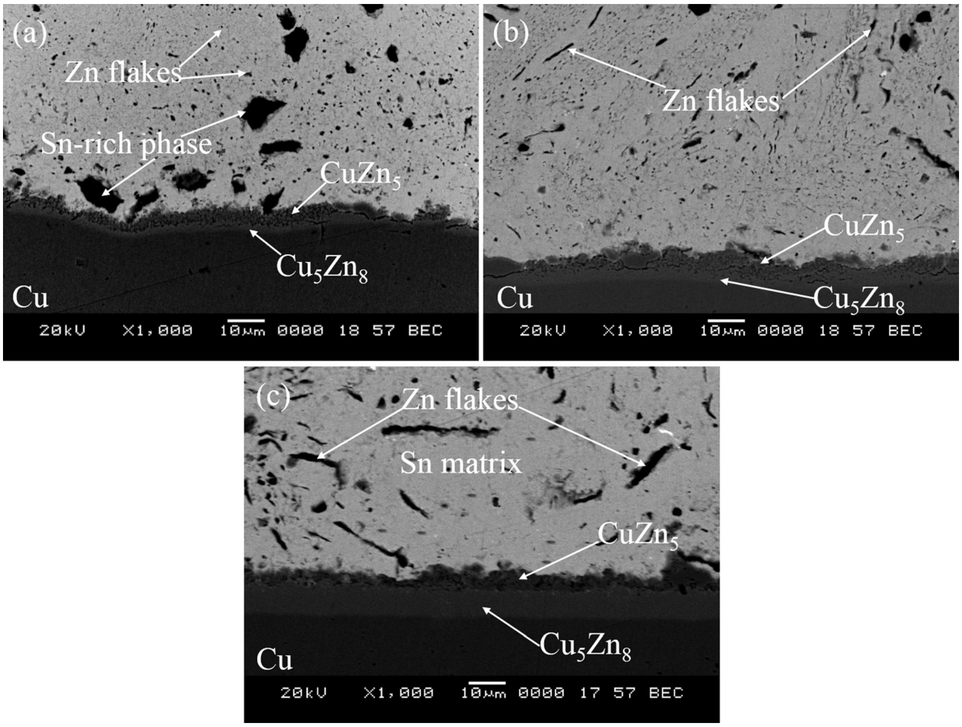
The solder drop bonded samples were sectioned along the central axis. The sectioned samples were polished by following a standard metallographic procedure and the polished surfaces were etched with a 5 % nital solution [mixture of ethanol (C_2H_5OH) and concentrated nitric acid (HNO_3) in the 95 + 5 volume ratio] for about 1 to 2 s. Scanning electron microscopy (SEM, JEOL JSM 6380LA) was used to study the microstructure at the solder-substrate interface. Energy-dispersive X-ray spectroscopy (EDS) was used to characterize the phase compositions in the microstructure. The surfaces of the sheared samples were analyzed for fracture characteristics using a Stemi 2000-C stereo-microscope. Elemental investigation of the sheared surface was done with the help of SEM and EDS analysis.

Results and Discussion

EFFECT OF COOLING RATE ON IMC GROWTH

SEM micrographs of Sn-9Zn solder-Cu substrate interface for different cooling rates are shown in **Fig. 2**. SEM and energy-dispersive X-ray spectroscopy (EDS) confirms the formation of Cu_5Zn_8 and $CuZn_5$ IMC layers at the interface as reaction products of solder and Cu substrate. Zn has very limited solubility in Sn and hence the

FIG. 2 SEM micrographs of Sn-9Zn solder-Cu substrate interface for samples cooled in (a) water, (b) air, and (c) furnace.



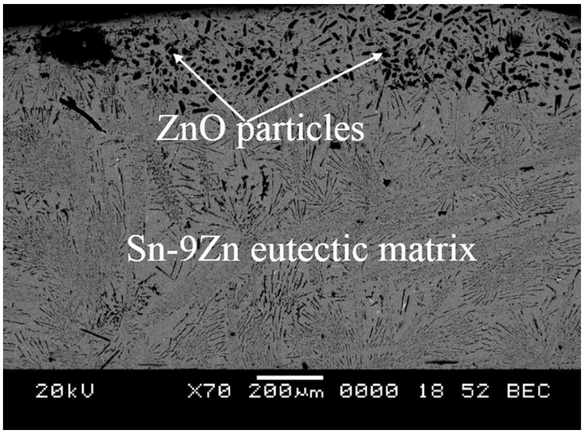


FIG. 3
SEM micrograph of Sn-9Zn solder drop solidified on Cu substrate showing ZnO particles.

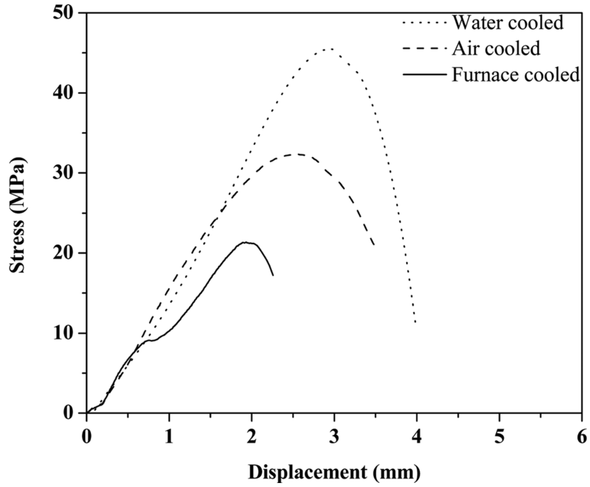
microstructure of eutectic Sn-9Zn solder alloy appears as Zn flakes distributed in the Sn matrix. With an increase in cooling rate, it is observed that the Zn flakes got finer and were distributed more uniformly in the Sn matrix, whereas with a decrease in the cooling rate long needle shaped Zn flakes were observed non-uniformly distributed in the matrix.

It is observed that during solidification, Zn partly reacted with atmospheric oxygen to form ZnO which appears at the top portion of the solidified solder drop while some part of Zn reacts with the Cu substrate and formed IMCs. **Fig. 3** shows ZnO particles at the upper portion of the solidified solder drop. The Cu_5Zn_8 IMC layer was observed as a flat continuous layer adjacent to the substrate whereas a scallop type $CuZn_5$ IMC was observed on it. The mean IMC thickness with respect to different cooling rates is presented in **Table 1**. IMC thickness data reveals that the thickness of Cu_5Zn_8 and $CuZn_5$ IMC layers increased with a decrease in the cooling rate. Water is a severe quenching medium compared to air and furnace and resulted in a fine grain structure and a thin IMC layer at the interface. With air and furnace cooling, a coarser grain structure and a thick IMC layer was obtained at the interface. The morphological difference between IMCs and bulk solder causes the mismatch in physical and mechanical properties. Such mismatch in properties increases with the growth of IMC layers, which produce internal stresses, leads to form microcracks in the IMC and decrease the bond strength under applied stress. The diffusivity difference between Sn and Zn with respect to Cu (the intrinsic diffusivities of Zn and Sn in Cu are $D_{Zn} = 2.70 \times 10^{-10}$ cm^2/s and $D_{Sn} = 1.90 \times 10^{-10}$ cm^2/s at 102°C,

TABLE 1
Mean IMC layer thickness with respect to different cooling rates.

Cooling Media	Cooling Rate, °C/s	Cu_5Zn_8 IMC Mean Thickness, μm	$CuZn_5$ IMC Mean Thickness, μm
Water	94	1.6	1.3
Air	0.16	2.9	1.8
Furnace	0.04	7.2	4.7

FIG. 4 Shear stress versus displacement curves of Sn-9Zn solder-Cu substrate joint for different cooling medium.



respectively [5]) may lead to the formation of Kirkendall voids at the Cu_5Zn_8/Sn interface for the furnace cooled samples. However, in the present work as the specimen experienced the solid/liquid reaction for single reflow only, the cracks formation in IMC may be attributed to the difference in molar volume between IMCs and the solder and the stress generated during the processing.

FIG. 5 Stereo-micrographs showing failure characteristics for samples cooled in (a) water, (b) air, and (c) furnace.

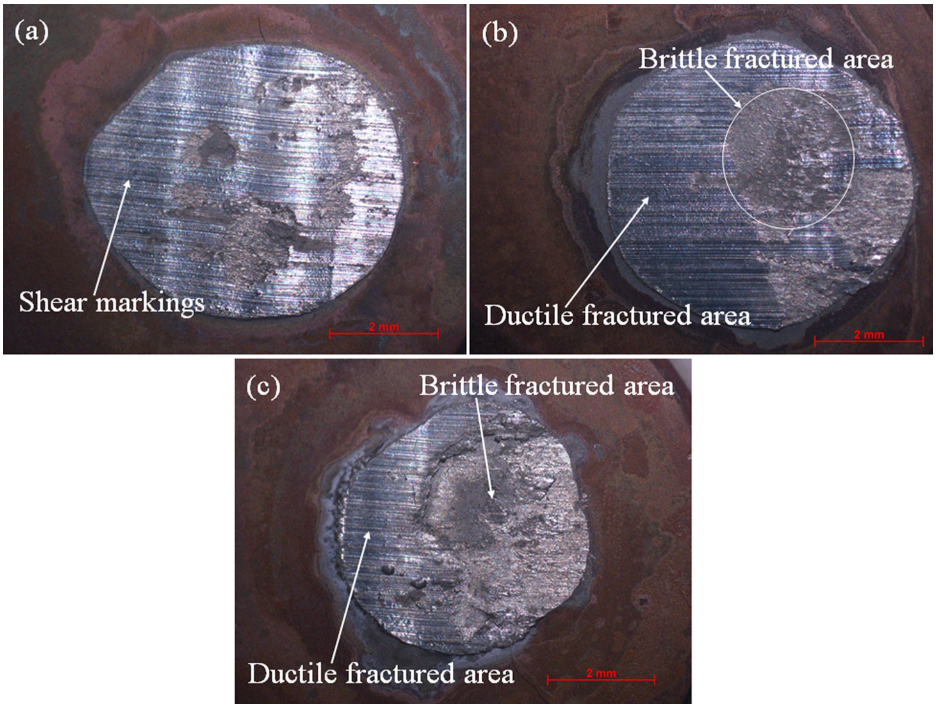


TABLE 2
Brittle to ductile fractured area ratio for samples cooled under different conditions.

Reflow Time, s	Cooling Media	Total Mean Spreading Area, mm^2	Mean Brittle Fractured Area, mm^2	Mean Ductile Fractured Area, mm^2	Brittle/Ductile Fractured Area Ratio	% Change in Brittle Fractured Area
100	Water	17	4.6	12.4	0.37	27
	Air	18	8.3	9.7	0.85	46
	Furnace	20	14.1	5.9	2.38	70

SHEAR STRENGTH

The shear strength of Sn-9Zn solder-copper joints cooled with different cooling rates were studied and shear strength data were obtained. The stress required to shear the solder joint versus displacement of the shear tool is shown graphically in **Fig. 4** for samples cooled in water, air, and furnace. The graph indicates that the shear stress value of the solder joint increased with an increase in the cooling rate.

Brittle IMCs are often stress concentration sites which initiate the crack under stress. A thin IMC layer ($<2\ \mu m$) can act as a bond strengthening agent whereas a thick IMC layer ($>3\ \mu m$) generally weakens the mechanical properties of a solder joint. The brittle nature of the IMC and the presence of micro-cracks cause the failure of the solder joint at a lower stress value. **Fig. 5** shows the stereo-micrographs of sheared surfaces showing failure characteristics of the samples cooled in water, air, and furnace media. The small voids on the sheared surfaces represent the entrapped gas bubbles in the bulk solder during solidification.

Water cooled samples showed complete ductile failure, characterized by shear markings. Air and furnace cooled samples showed ductile as well as brittle failure characteristics. From the stress versus displacement graph it is observed that the water cooled samples undergo complete ductile failure while furnace cooled samples first sheared in ductile mode and then suddenly fails in a brittle manner. The brittle to ductile fractured area ratio for samples cooled in water, air, and furnace is presented in **Table 2**. The brittle fractured region in the furnace cooled sample was more by 24 percentage points than the air cooled specimen. The irregularities in stress versus displacement graph explain the presence of voids and micro-cracks at the interface. The micro-cracks in a thick IMC assist in crack propagation during shear failure and joint fails at a lower stress value in a brittle manner. Fracture data analysis showed that, with a decrease in the cooling rate the brittle fractured area increases. The joint shear strength and the shear energy of the Sn-9Zn solder-copper substrate joint for different cooling rates are tabulated in **Table 3**. The data indicates

TABLE 3
Bond shear strength and shear energy of Sn-9Zn solder-Cu substrate joint for different cooling rates.

Reflow Time, s	Cooling Media	Cooling Rate, °C/s	Peak Shear Stress, MPa	Avg. Joint Shear Strength (τ), MPa	Avg. Shear Energy Per Unit Area, kJ/m^2
100	Water	94	45	21	67
	Air	0.16	32	18	60
	Furnace	0.04	20	14	43

that the joint shear strength and shear energy increased with an increase in the cooling rate.

Conclusion

The microstructure and mechanical properties of the Sn-9Zn solder were found to be strongly affected by the cooling rate. The microstructure of the water cooled samples consisted of uniformly distributed fine Zn flakes in a Sn matrix whereas air and furnace cooling resulted in coarser and longer Zn flakes in the matrix. The decrease in cooling rate increases the thickness of Cu_5Zn_8 as well as $CuZn_5$ IMC layer at the interface. Water cooled samples showed a higher joint shear strength compared to the air and furnace cooled specimen. The enhancement in the joint strength is attributed to the higher cooling rate. High IMC growth resulted in micro-crack formation in the intermetallic compound and affects the bond strength. The fine grain structure and thin IMC layer enhanced the joint strength while excess IMC growth and brittleness of the IMC layer were responsible for the decrease in the joint shear strength.

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