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Wetting Behavior of Reactive and Non–Reactive Wetting of Liquids on Metallic Substrates

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***Abstract*—**Wetting characteristics of reactive (Sn–0.7Cu solder) and non– reactive (castor oil) wetting of liquids on Cu and Ag plated Al substrates have been investigated. Solder spreading exhibited capillary, gravity and viscous regimes. Oils did not exhibit noticeable spreading regimes. Solder alloy showed better wettability on Ag coated Al substrate compared to Cu plating. In the case of castor oil, Cu coated Al substrate exhibited good wettability as compared to Ag coated Al substrates. The difference in wettability during reactive wetting of solder and non–reactive wetting of oils is attributed to the change in the surface energies of Al substrates brought about by the formation of intermetallic compounds (IMCs).

***Keywords*—**Wettability, contact angle, solder, castor oil, IMCs.

I. Introduction

WETTING is one of the important properties of liquid/fluids to spread over a solid substrate [1]. Wetting a solid by a liquid is of great technological importance. Painting, printing, lubrication, coating, cleaning, soldering, brazing and composite processing are few examples among the innumerable fields utilizing the phenomenon of wetting. Some applications require a good wetting between liquid and substrate surface (for example soldering, printing etc) whereas some others demand poor wetting or repellency (for example painting and solar panels). Wetting can be broadly classified into two categories, viz., reactive wetting and non–reactive wetting [2], [3]. Spreading of liquid metals on a substrate is a case of reactive wetting. A liquid spreading on a substrate with no reaction/absorption of the liquid by substrate material is known as non-reactive or inert wetting [2]. Spreading of water on a lotus leaf is the best example of non–reactive wetting. Contact angle is a measure of the degree of wetting or wettability of a surface by a liquid [4],[5],[6].

No significant work has been carried out on reactive and non–reactive wetting of fluids. The present study is devoted to the comparison of the spreading behavior of solder and castor oil on silver (Ag) and copper (Cu) coated aluminum (Al) substrates. Eutectic Sn–Cu lead free solder alloy is a promising candidate material for electronic applications and castor oil is widely used as a lubricant in industrial applications. Hence, in the present work, Sn–0.7Cu is chosen as a reactive liquid and castor oil as the non–reactive fluid. Al has lower density than copper. Moreover, thermal and electrical conductivities are comparable to Cu. Al can replace Cu as substrate material in electronics technology.

The objective of the present work is to compare the wetting behavior of reactive (solder) and non-reactive (castor oil) liquids on Ag and Cu coated Al substrates.

II. Experimental

The solder spheres were prepared from the solder rod supplied from Hybrid Metals Pvt. Ltd, Bangalore (solder rod was first drawn into wires and cleaned using ultrasonic vibrator with acetone before preparing solder balls). A soldering station KLAPP 962D was used to prepare solder balls of weight 0.080 gm. The solder balls were then used for wettability study by measuring the contact angle on substrate surfaces after coating it with flux (Inorganic acid, Alfa Aesar, USA). Cu and Ag coated Al substrates (Ø12.5mm X 8mm) were used as substrate materials. Coatings on Al were carried out at Modern Electroplaters (Mangalore, India). The coating thickness of Cu was about 30µm and Ag was around 10 –12 µm. The surface profiles of the coated substrates were assessed using Form Talysurf 50 surface profiler. The roughness values (R_a) for Cu coated substrates were found to be 0.015 ± 0.003 µm whereas for Ag coated substrates 0.023 ± 0.007 µm respectively. Contact angle measurements were carried out using FTA 200 dynamic contact angle analyzer. The experiments were carried out at a temperature of 270°C for solder and room temperature for castor oil. The spreading process is recorded for approximately 2000 s for solder and 100s for castor oil because, in non–reactive wetting true equilibrium is often achieved, whereas in the case of reactive wetting, true equilibrium is rarely achieved due to the complexity involved. The captured images were analyzed using FTA 32 Video 2.0 software to determine the wetting behavior of solder and oil. To study the interfacial region of solder/substrate region, 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 30–60 s. The solder/substrate interfacial region was microexamined using scanning electron microscopy (SEM, JEOL JSM 6380LA) with energy disperse spectroscopy (EDS) in Back Scattered Electron (BSE) mode.

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III. RESULTS AND DISCUSSION

The typical relaxation curves for spreading of Sn–0.7Cu solder and castor oil on substrate surfaces are shown in Fig. 1a and 1b. The relaxation behavior of solder and inert liquid are similar characterized; High spreading rate at the beginning and slower rates at final stages. However, relaxation periods were significantly different. Time to approach equilibrium values were 30 s in the case of oil whereas it was more than 200 s in the case of solder, which was roughly 5 to 6 times longer. Solder exhibited equilibrium contact angles of 29° ± 3° on Cu coated Al substrate, and 8° ± 2° on Ag coated Al substrate. Castor oil showed good wettability on Cu coated Al substrate (7° ± 1°) compared to Ag coated Al (10°± 1°) substrate. From the above results, it was observed that, there is a large scatter in the obtained contact angle values. For oil wetting, the scatter was due to the extensive spreading of oil. In the reactive wetting this can be attributed to various factors like formation of IMCs and the residue left by the flux poses problems in angle measurements; especially when there is extensive spreading. In addition, the solder does not form exact spherical shape in most of the cases making the measurement difficult.

Fig. 2a and 2b show the ln (D) Vs ln (t) plot of solder and oil spread on substrate surfaces. Solder exhibited three regimes namely capillary, gravity and viscous regimes during spreading on both the substrates but the oil did not exhibit clear transition from one wetting regime to another. Solder spread on Ag coated Al showed a longer capillary regime than Cu coated Al. Fig. 3a shows the successive images of Sn–0.7Cu solder reflowed on Ag coated Al substrate substrates respectively. Fig. 3b shows the images of spreading of castor oil on Ag coated Al substrate indicating that, castor oil had taken less time to attain equilibrium contact angle earlier than solder. This is because of the lower viscosity of castor oil than the solder. Even at higher temperature, castor oil will exhibit lower viscosity than the solder.

This difference in wettability of oil and solder can be explained by two factors viz., formation of intermetallic compounds (IMCs) in case of solder and the surface energy of metal substrates being used for the oil. In reactive wetting, formations of IMCs lead to additional surface energy due to the interfacial reactions.

In the case of Cu coated Al, wettability by castor oil was better and on the other hand, the solder showed poor wettability. Since, the surface energy of Cu (1830 mJ/m^2) is higher than the Ag metal (1250 mJ/m^2) used. Therefore, oil wetted better on Cu coated Al substrate. The formation of oxide layers formed over the metal surface during heating might have reduced the surface energy of metal surface resulting a decreasing in wettability of solder.

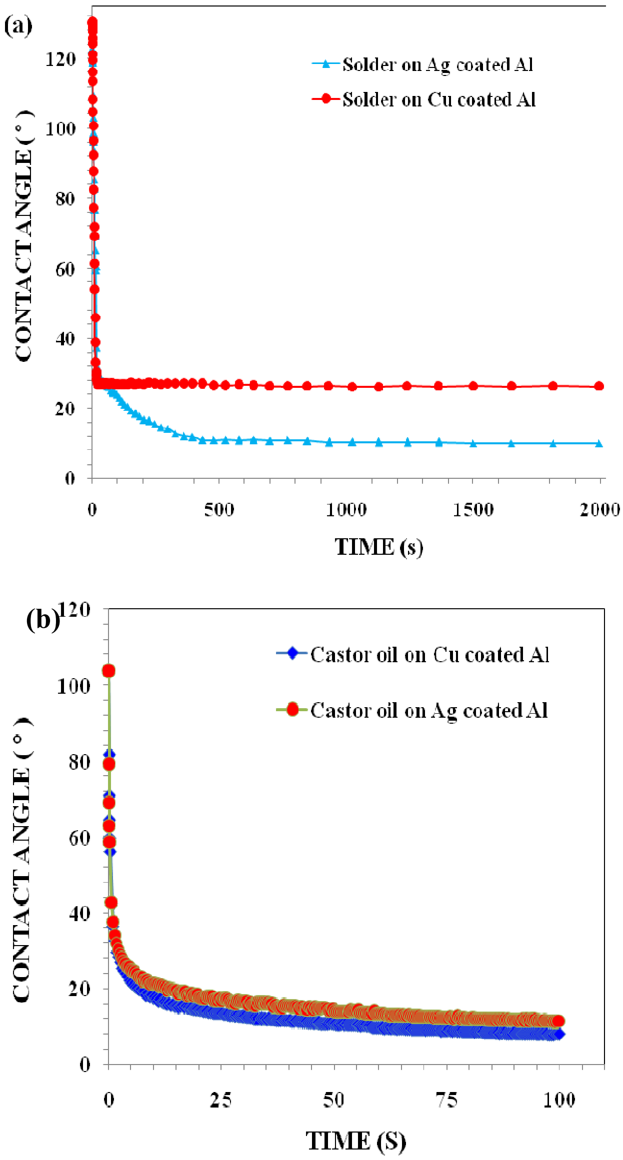

Fig. 1 Relaxation behavior of (a) Solder (b) Castor oil on substrate surfaces

In the reactive wetting of solder, the IMCs formed between solder and Cu coated Al substrate were in tube (or needle) shape and have orientation in random directions, protruding from the substrate into the bulk of the solder. Similar growth of IMCs was observed inside the bulk of the solder. Fig. 4a shows the SEM photomicrograph of solder/Cu coated Al substrate interfacial region. Energy–dispersive X–ray spectroscopy analysis (EDAX) revealed that the composition of the needle-type IMCs as shown in Fig. 4a corresponds to Cu_6Sn_5 intermetallics with small amounts of Ni and Al elements dissolved in it. One more IMC reported in literature, which is Cu_3Sn, was not observed. Fig. 4b shows the SEM photomicrograph of interfacial region of solder/Ag coated Al substrate. Ag dissolves rapidly into the liquid solder. Ni_3Sn_4 IMC was observed only at the interface, on top of this layer a layer of ternary IMCs of Cu, Ni and Sn was observed.

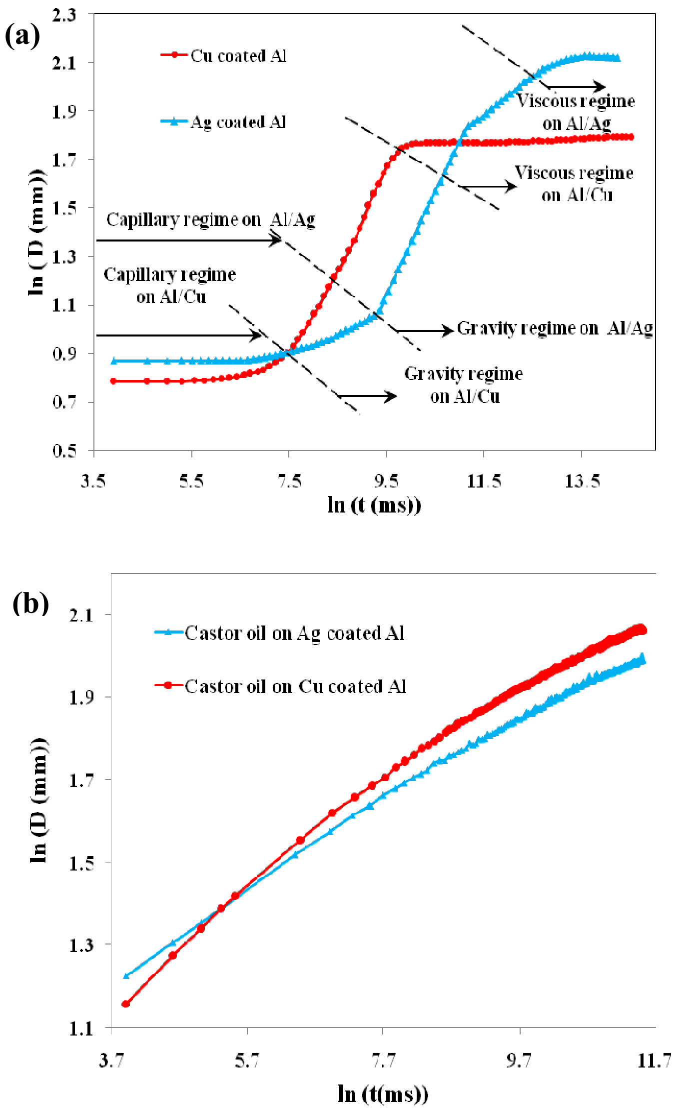

Fig. 2 Plot of ln (D) vs. ln (t) for (a) Solder alloy (b) Castor oil on substrate surfaces

EDAX revealed that IMC was most likely to be $(Cu,Ni)_6Sn_5$. The dissolved Ag forms Ag_3Sn IMC in bulk of the solder away from the solder/substrate interface. Ag_3Sn was in the shape of plates or flakes.

It is important to note that, Cu coated Al substrate had a roughness range of 0.015 – 0.03 µm. Several investigators have reported that lower the roughness of Cu surface, higher is the contact angle [7], [8]. This may be attributed to the fact

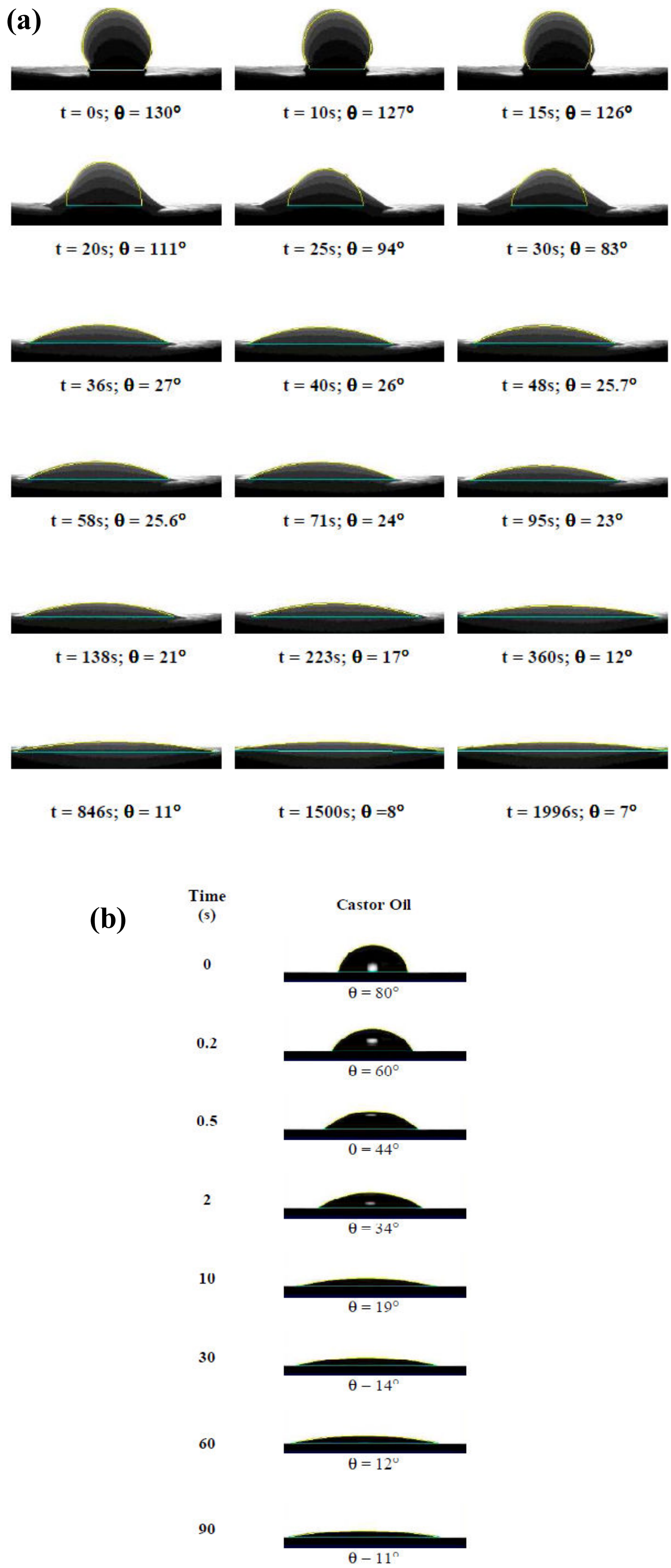

Fig. 3 Images of (a) Solder reflowed on Ag coated Al substrate (b) Castor oil on Ag coated Al substrates ('t' is the time and 'θ' is the corresponding contact angle measured)

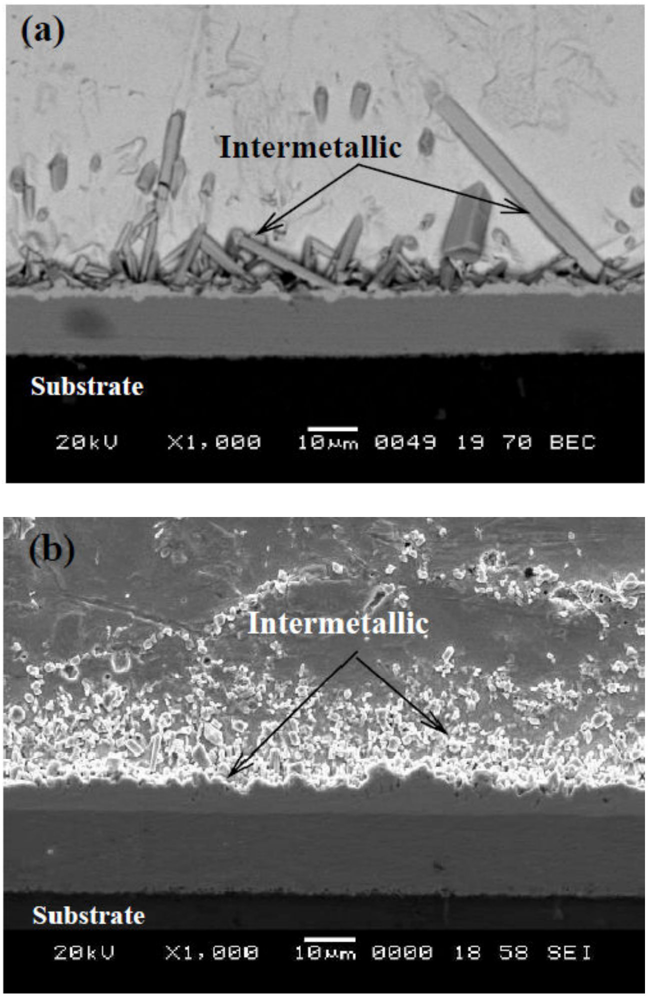

Fig. 4 BSE SEM images of IMCs formed between solder (a) Cu coated Al substrate and (b) Ag coated Al substrate

that the rod shaped IMCs formed on Cu coated Al substrate (rod or needle shaped IMC form on smoother surfaces rather than on rough surface) act as a rough surface causing pinning effect during spreading of solder. Further spreading of the liquid solder also depends on how far it wets the formed IMCs. These factors may have prevented the liquid solder from further spreading, resulting in higher contact angles. Moreover, Cu has higher tendency for the formation of oxides during spread of solder than on Ag substrate. This could be the reason for improvement in the wettability of solder on Ag coated Al substrate.

IV. Conclusion

The relaxation behavior of Sn–0.7Cu solder and castor oil are similar with high spreading rate at the beginning and slower rates at final stages. However, relaxation periods were significantly different. Time to approach equilibrium values were 30 s in the case of oil whereas it was more than 200 s in the case of solder. Solder exhibited all the three regimes (capillary, gravity and viscous) during spreading on all the substrates but oils did not show well defined regimes. Ag coated Al substrate exhibited good wettability by solder with a contact angle of 8° ± 2° than Cu coated Al (29° ± 3°). Castor oil exhibited better wettability on Cu coated Al (7° ± 1°) than Ag coated Al (10°± 1°). The difference in wettability between reactive wetting of solder and non – reactive wetting of oils was due to the change in surface energies of Al substrate, brought about by the formation of IMCs. Lower wettability on Cu coated Al by solder attributed to the needle or tube morphology of the IMC formed at the interface and higher tendency of Cu to form oxides on substrate surface.

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