A COMPARATIVE STUDY ON THE AGEING BEHAVIOUR OF SOLDER ALLOY-Cu JOINT ASSEMLY USING LEAD FREE SOLDER AND Sn-Pb EUTECTIC SOLDER ALLOY

M. Ghosh*, A. Kar, S.K. Das, R. N. Ghosh and A.K. Ray

Material Science & Technology Division, National Metallurgical Laboratory (CSIR), Jamshedpur – 831007, Jharkhand, India, ghosh_mnk@yahoo.com

Abstract
In the present investigation, Sn-Ag-In ternary alloy was used to join Cu substrate (SAI-Cu) and compared with conventional Sn-Pb eutectic solder alloy–Cu assembly (SP-Cu). The melting point of the alloys was found to be 192±1°C and 184±2°C respectively. The re-flowing was carried out above +30°C of the melting point of the respective alloys for 30secs. Both the joints were aged at 100°C for 50-200hrs at a step of 50hrs. Subsequently, structural characterization and mechanical property evaluation of the joints were performed. In re-flowed condition, the shear strength of the SAI-Cu joint (~64MPa) is higher than SP-Cu joint (~55MPa). The diffusion zone of the former is decorated with Cu_6Sn_5 intermetallic phase, whereas the latter contains both Cu_6Sn_5 and Cu_3Sn. The width of the reaction zone is more in case of SP-Cu joint with respect to SAI-Cu joint. Isothermal aging of the solder assembly leads to deterioration of joint shear strength accompanied by structural change in the diffusion zone. After 200hrs of aging the shear strength of SAI-Cu joint is ~44.6MPa and the same becomes ~34.5MPa for SP-Cu joint. In both the cases, formation of Cu_6Sn_5 and Cu_3Sn has been observed which causes lowering of bond strength. Indium plays a vital role in controlling the chemical reaction at the interface during reflowing and ageing. Hence, it is responsible for betterment in mechanical properties.

Key Word: *solder alloy, shear strength, intermetallic phases, diffusion zone, aging*

1. Introduction
Sn-Ag solder alloy and its derivatives have been widely received attention globally as a potential substitute of conventional Sn-Pb solder owing to its non-toxic nature, satisfactory wettability and adequate mechanical properties [1-3]. For its acceptance as a Pb-free solder, two phenomena are important; the first one is process requirement and the other is reliability. Process requirement refers to the melting point of the alloy for the ease of manufacturing techniques as well as to reduce the fabrication cost. Reliability is emphasized by structural role of solder joints as mechanical support to components apart from traditional function of providing electrical contacts. In micro electronic components, hybrids and microsystems thermal fatigue is one of the important effects for degradation of solder joint quality [4-5]. It has been explored by several researchers that, Sn base solder alloys when joined with Cu substrate forms Cu-Sn intermetallics, which are brittle in nature [6-7]. The joint assembly appears as multilayered material consisting of solder alloy, intermetallic compounds and substrate having different physico-chemical characteristics. Under service exploitation, with the miniaturization of components thermo-mechanical stress on solder joint increases and a heterogeneous distribution of the same has been observed through the transition joint. The thermal effect and differential stress distribution accompanied by interface microstructure ultimately detoriate joint quality. A number of lead free solder alloys have been developed to minimize the problems as stated above. However, most of the studies are confined in evaluating the microstructure and mechanical properties of the solder alloys itself. Information related to the behavior of soldered assembly with respect to time is scanty. Hence in the present investigation

attempts have been made to i) modify the Sn-Ag eutectic solder alloy by adding In and ii) explore the effect of In on microstructure and mechanical properties of the solder joint in reflowed and aged condition.

2. Experimental

Two alloys i.e. Sn-Pb and Sn-Ag-In have been chosen in the present study. Respective alloys were prepared in induction furnace in argon atmosphere taking Sn (~99.98 wt%), Ag (~99.99 wt%), Pb (~99.95 wt%), and In (~99.94 wt%). Details of alloy preparation have been described elsewhere [6]. The average concentration of chemical species in solder alloys is furnished in Table-1. The melting point of the alloys was determined using a thermal analyzer (SDT Q600, TA Instruments-USA) and found to be 184 ± 2 and $192\pm1^{o}C$ for SP and SAI respectively. The 50gms of cast ingots were rolled down to thickness of ~0.2 mm, cleaned in acetone and used for soldering. Reflow temperature during soldering of the alloys was $+30^{o}C$ above the melting point and reflow time was 20secs. Hence forth the solder joints will be indicated as SP joint and SAI joint. Transverse section of the assembly has been prepared by metallographic technique. The samples were examined in scanning electron microscope (Jeol JSM 840A) in back scattered mode (BS). The compositions of chemical species (wt%) in the reaction layer was obtained by energy dispersive spectroscopy (Kavex). The average thickness of the reaction product was determined by measuring width of the same at six different locations. Shear testing was done at room temperature using a jig mounted on a tensile testing machine (Honsfield, H10K-S, 10KN capacity) at a cross head speed of 0.1mm min^{-1}. Test was repeated to check the reproducibility of the results. The solder joints were aged at $100^{o}C$ for 50-200hrs at an interval of 50hrs. After aging treatment, both structural characterization and evaluation of mechanical properties were repeated.

3. Results & Discussion

The solder assemblies in reflowed condition are shown in Fig.1. Continuous reaction layer formation is evident within the diffusion zone. SP joints exhibits stiff concentration gradient of chemical species within the reaction product. Adjacent to Cu substrate, the zone is enriched in Cu (~70.4) and near the solder alloy the area is depleted in Cu (~27.2). Based on the binary phase diagram of Cu-Sn the chemical composition indicates that, the layer adjacent to Cu substrate is Cu_3Sn and that of near solder alloy is Cu_6Sn_5 (Fig.1a) [8]. In case of SAI joint the concentration of alloying elements remain more or less same through out the reaction zone. EDS analysis exhibits that, the reaction product contains Cu~35.4, In~1.9 and Sn~62.7. Hence the diffusion zone contains only Cu_6Sn_5 in association with some amount of In (Fig.1b). Aging leads to increment in the width of reaction layer due to diffusion of chemical species across the interface (Fig.3a). Compositional analysis of intermetallics with respect to aging time shows negligible variation for SP joint; only small quantity of Pb (~0.7) has been detected with the reaction zone. Up to 50hrs of aging, SAI joint exhibits growth of existing intermetallic layer with marginal change in composition. At and above 100hrs of aging, another reaction layer has been detected close to Cu substrate having composition Cu~73.3, In~0.7 and Sn (bal). The concentration of chemical species near solder alloy becomes Cu~35.5, In~1.8 and Sn (bal). As predicted before, the former is

Cu_3Sn and the latter is Cu_6Sn_5. Aging beyond 100hrs leads to increment in the width of reaction layer without any significant change in composition further. In reflowed condition, shear strength of SP and SAI joints are 55±3 and 64±2 respectively. With the increment in aging time, the shear strength decreases (fig.3b); after 200hrs the values become 34.5±1 and 44.6±1 respectively. Cu_6Sn_5 formation takes place at the time of solder reflow and that of Cu_3Sn during subsequent cooling to ambient temperature [9]. It has been already reported that Sn diffusion is slower than Cu, In diffusion is the fastest among the major diffusing species and Ag and Pb have negligible effect on diffusion reaction [9-10]. Thus Sn diffusion controls the reaction in the diffusion zone to form the intermetallics and is sluggish through Cu_6Sn_5. At the initial stage of bond formation In reaches the Cu surface first and creates a barrier layer for further Cu diffusion. Hence in reflowed condition the width of the reaction zone is smaller for SAI joint with respect to the SP joint [10]. With the increment in aging time the barrier layer gets softened because of low melting point of In facilitating Sn diffusion. The Sn diffusion results in increment in the width of Cu_6Sn_5 and migration of Cu through the interface promotes the reaction between Cu_6Sn and Cu to form Cu_3Sn adjacent to Cu substrate The shear strength of the joint is governed by interface microstructure. More will be the volume fraction of intermetallics in the diffusion zone, greater will be the embrittlement effect Hence, with the increase in aging time the detoriation in shear strength is at par with the growth of intermetallic phases near interface. However, comparing the mechanical properties of SP and SAI joint, it is evident that, detoriation is more for the former owing to the presence of In in the reaction zone for the latter.

4. Conclusions

In the present study Sn-Pb and Sn-Ag-In alloys were soldered with Cu substrate. Microstructure and mechanical properties of the joints were determined in reflowed condition and after aging for different time period. The observations are as follows: i) In addition to Sn-Ag system lowers the melting point of the alloy and becomes close to Sn-Pb solder alloy. ii) Joining of the solder alloy with Cu substrate promotes formation of Sn-Cu intermetallics in the diffusion zone; for SP joint it is Cu_3Sn and Cu_6Sn_5 and for SAI joint it is Cu_6Sn_5 in reflowed condition. iii) In reflowed condition the width of the reaction layer for SAI is smaller than SP joint because of the presence of In in the reaction zone. iv) Shear strength of SAI joint is greater than SP joint owing to smaller width of intermetallics in diffusion zone. v) Aging propels the growth of reaction layer accompanied by decrement in shear strength for both the joints. In case of SAI joint, aging after a certain time period promotes the formation of Cu_3Sn adjacent to Cu substrate owing to softening of In barrier layer and further aging only leads to the growth of both Cu_6Sn_5 and Cu_3Sn.

Acknowledgement

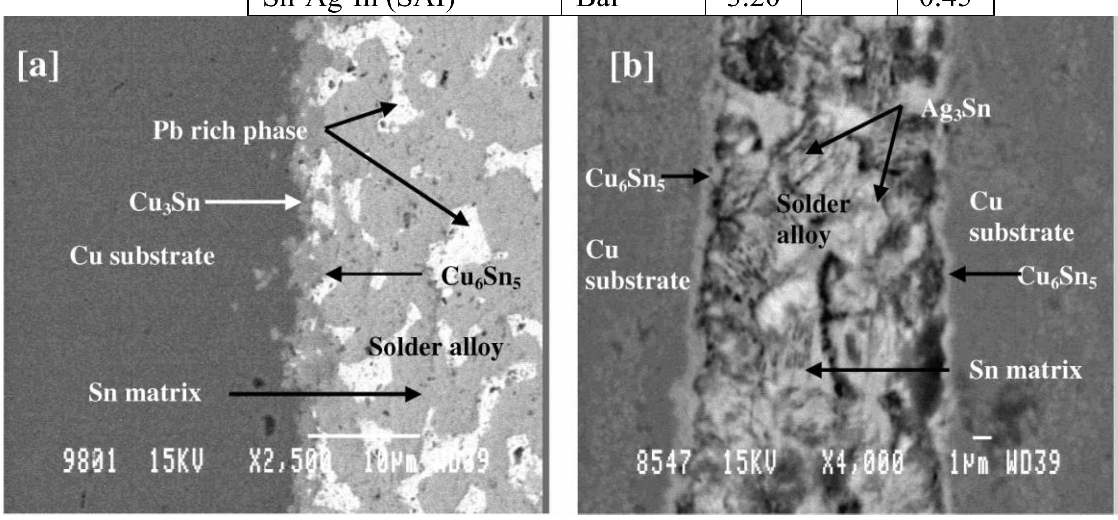
The authors wish to thank Director–National Metallurgical Laboratory for his continuous inspiration to carry out this investigation and kindly permitting to publish this work.

References

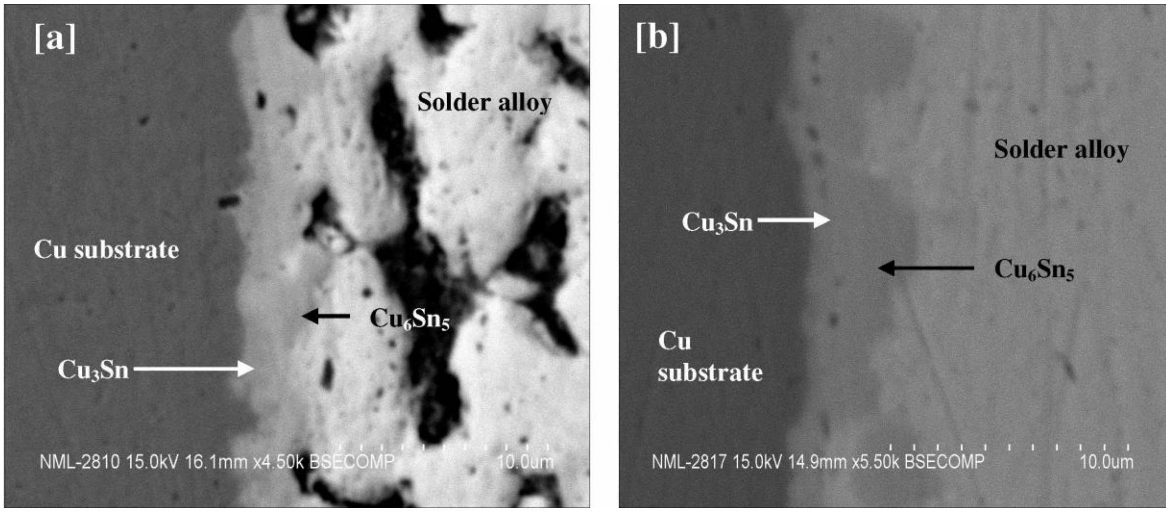
1. J. Villain, O.S. Brueller and T. Qasim, Sensors & Actuators. A99, 194-197 (2002).
2. J. Liang, N. Dariavach, P. Callahan and D. Shagguan, Mats. Trans. 47, 317-325 (2006).
3. M. He, Z. Chen and G. Qi, Acta Mater. 52, 2047-2056 (2004).
4. L. Zhang, Z. G. Wang and J. K. Shang, Scripta Mater. 56, 381-384 (2007).
5. F. Guo, J. Lee, S. Choi, J. P. Lucas, T. R. Bieler and K. N. Subramanian, J. of Electronic Mats. 30, 1073-1082 (2001).
6. Abhijit Kar, Mainak Ghosh, Ajoy Kumar Ray, Rabindra Nath Ghosh, Mats. Sci. Engg. A. 459, 69-74 (2007).
7. X. Deng, M. Koopman, N. Chawla and K. K. Chawla, Mats. Sci. Engg. A. 364, 240-243 (2004).
8. J.H. Shim, C.S. Oh, B.J. Lee and D.N. Lee, Z. Metallkde. 87, 205–212 (1996).
9. C. M. Chuang and K. L. Lin, J. of Electronic Mater. 32, 1426-1431 (2003).
10. A. Kar, M. Ghosh, B. S. Majumdar, R. N. Ghosh and A. K. Ray, Mats. Technol. 22,161-165 (2007).

Table – 1: Chemical composition of the solder alloys

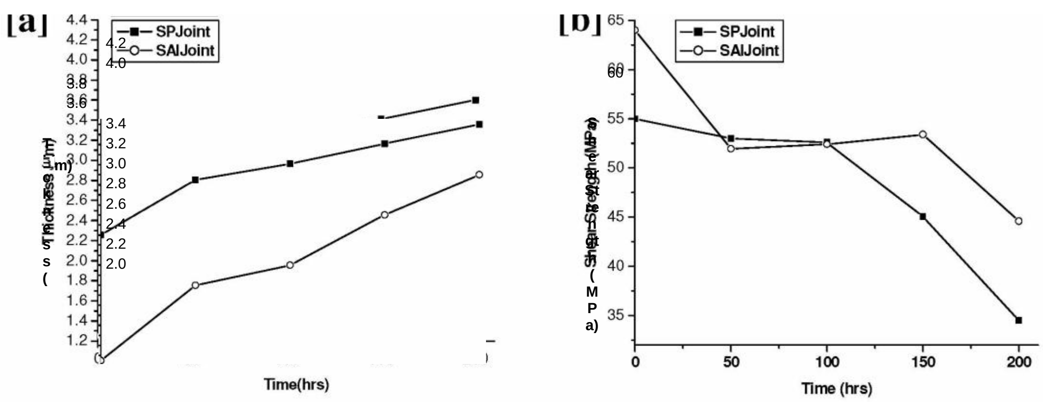
SAMPLE id	ALLOYING ELEMENTS (WT%)			
	Sn	Ag	Pb	In
Sn-Pb (SP)	Bal	-	36.4	-
Sn-Ag-In (SAI)	Bal	3.20	-	0.45



Figs. 1(a-b): SEM-BSE micrographs of solder joints in reflowed condition (a) SP joint and (b) SAI joint.



Figs. 2(a-b): SEM-BSE images of solder joints after aging at 100°C for 200hrs (a) SP joint and (b) SAI joint.



Figs.3(a-b): Effect of aging time on the solder joints (a) variation in thickness and (b) change in shear strength.

FIGURE CAPTIONS

Figs. 1(a-b): SEM-BSE micrographs of solder joints in reflowed condition (a) SP joint and (b) SAI joint.

Figs. 2(a-b): SEM-BSE images of solder joints after aging at 100°C for 200hrs (a) SP joint and (b) SAI joint.

Figs.3(a-b): Effect of aging time on the solder joints (a) variation in thickness and (b) change in shear strength.