Preparation, hardness studies and characterization of 88 Sn-7.5Zn-2.5Al-2In and 88 Sn-7 Zn-2Al-2.5 In lead free soldering alloys

D Arthur Jebastine Sunderraj¹, D Ananthapadmanaban², K Arun Vasantha Geethan³

¹Department of Mechanical Engineering, St.Joseph’s Institute of Technology, Chennai-119
² Department of Mechanical Engineering, SSN College of Engineering, Kallavakkam
³Department of Mechanical Engineering, St.Joseph’s Institute of Technology, Chennai-119
1 arthurjebastine@gmail.com,2 ananthapadmanaban@ssn.edu.in,
3 kavgeeth@gmail.com

Abstract: Soldering uses lead as one of its alloying elements because of the low melting point of lead. Recent research has focused on lead free solders as lead is seen as a poisonous element. In this work, two lead free alloys, namely 88 Sn-7.5Zn-2.5Al-2 In and 88 Sn-7Zn-2 Al-2.5 In were prepared using induction melting method in an argon atmosphere. Melting points of the alloys were 203.7 Celsius and 201.6 Celsius as determined by Differential Scanning Colorimetry (DSC). Vickers hardness tests were conducted. Hardness values were found to be higher than normal lead based soldering alloys. The lead free solders were characterized using Energy Dispersive X-Ray Spectra (EDS). Microstructural studies were also done to study changes in microstructure with Indium.

1. Introduction

Lead has been replaced by Sn as the major constituent of the alloy and Zn as the major alloying element. Sn-Zn solder is less expensive, non-hazardous and possesses nominal mechanical properties. However, the properties of binary Sn-Zn solders are unable to meet the requirements for applications in electronics industries. This being the case, ternary and quaternary Sn-Zn solders have been researched upon.[1,2,3.] Addition of Aluminium in Sn-Zn alloys were found to improve the wetting property and some mechanical properties.[4] Researchers have developed a large number of binary alloys such as Sn-Zn,Sn-Cu,Sn-Ag,Sn-Bi,Sn-Sb and Sn-In in recent times. Sn-9Zn has a melting point of 198 Celsius, which is close to lead tin eutectic melting temperature of 183 Celsius. In addition, it has low cost, is non-toxic.[5,6,7] The wettability of Sn-Zn solders has been an issue and these alloys have a poor oxidation resistance.[8,9,10] Indium has been found to improve ductility, wettability and fatigue strength.[11] Lead free alloys containing Sn, Ag and Indium have been prepared and patented.[12] Weight % age of Indium has been varied from 2.6 to 3.3 %. These alloys have low melting temperature and relatively low mushy range.

2. Experimental Work
2.1 Preparation of alloy
Sn-Zn and Sn-Zn-Al solders were prepared from granulated Sn,Zn ,Al foils and In dust. Tin, Aluminium, Zinc and Indium (purity 99.%) were taken and melting was carried out in a crucible in tubular furnace in the presence of argon atmosphere. Tin and Indium were obtained from Indian Platinum Ltd, Mumbai, Zinc from Microfine Chemicals, Chennai and Alumina crucible for melting was obtained from Hi-tech Ceramics, Chennai. Figure 1to 4 show the process undergone by the two new alloys for specimen preparation. Figure 5 shows the polishing machine used for metallographic sample studies and Figure 6 shows the polished parts. Casting temperature is in the range 400-600 °Celsius and holding time was approximately 2 hours.

2.2 Chemical composition
Overall Chemical composition was determined using Energy Dispersive Spectroscopy (EDS).

2.3. Hardness testing
Vickers micro hardness testing method was used to determine hardness. The microhardness test procedure ASTM E-384, specifies a range of light loads using a diamond indenter.

2.4. Differential Scanning Calorimetry
DSC is a technique used to determine temperature at which phase changes take place, melting, boiling temperatures, latent heats, glass transition temperature, curing temperature etc. The technique uses changes in specific heat with change in temperature. In our work, DSC Curves were used to find out the solidus and liquidus temperatures .Between the liquidus and the solidus temperatures, the alloy exists in a mushy state. The mushy zone can be deduced as- Liquidus- Solidus temperature. Figure 7 & 8 shows the Differential Scanning Calorimeter. All DSC analyses were performed between 25 and 250 Degree Celsius .Heating and cooling rates used were 10 Degree Celsius.
3. Results and Discussions

Overall chemical composition as determined by EDS is given in Table 1

Table 1. Shows composition of the two new alloys

| Sample | Sn | Zn  | Al  | In  |
|--------|----|-----|-----|-----|
| 1      | 88 | 7.5 | 2.5 | 2   |
| 2      | 88 | 7   | 2   | 2.5 |

3.1 DSC Results

DSC curves are shown below. Melting range can be deduced from the DSC Curves

Figure 7. Showing DSC of 88Sn-7.5Zn-2.5Al-2In.

Figure 8. Showing DSC of 88 Sn-7 Zn-2Al-2.5.
From the DSC curves, it can be deduced that the melting range of 87Sn-7Zn-3Al-3In is 11 Celsius and of 88Sn-7Zn-2Al-2.5In is 6.2 Celsius. It is seen that decrease in Indium % age combined with a slight increase in Tin content decreased the melting range of the alloy. This could be because the above mentioned combination increases solubility of the phases in the matrix.

3.2 Hardness Results

Table 2 and 3 given below shows the results of hardness testing

| Specimen          | Hardness, Hv 0.2 |
|-------------------|------------------|
| 88Zn7Zn-2Al-2.5In |                  |
| Diagonal 1        | 22.42            |
|                   | 22.46            |
|                   | 24.32            |
|                   | 19.92            |
|                   | 20.53            |
| Diagonal 2        | 22.42            |
|                   | 19.19            |
|                   | 25.21            |
|                   | 16.89            |
|                   | 19.5             |

| Specimen          | Hardness, Hv 0.2 |
|-------------------|------------------|
| 88Sn-7Zn-2.5Al-2In|                  |
| Diagonal 1        | 17.5             |
|                   | 20.9             |
|                   | 22.42            |
|                   | 22.52            |
|                   | 21.9             |
| Diagonal 2        | 18.6             |
|                   | 21.6             |
|                   | 21.6             |
|                   | 22.41            |
|                   | 22.2             |

Further, a microhardness survey (average of 5 readings taken) done on the precipitates gives an average value of 103 Hv in the first new alloy. The same procedure, repeated in the second new alloy gives an average value of 107 Hv. The higher hardness compared to the average hardness of the matrix is probably because of the hard 2nd phase precipitates which occur due to the presence of Indium. Small additions of Indium have been shown to improve the microhardness and also produce considerable changes in the microstructure.[13] Small amounts of Indium addition have been found to refine grain size and improve hardness.[14,15]

3.3 Micro structural & EDAX Analysis

Microstructures taken at different locations in the prepared solders showed variations and the detailed analysis of the microstructures is given below.

Figure 9. Shows Spectrum 1 Electron Image.  
Figure 10. Shows Spectrum 1 EDAX graph.
Figure 9 shows the microstructure and Figure 10 the corresponding EDAX Line spectrum. In the Aluminium peak (2nd from left in EDAX) WT % Sigma phase is 0.6%, in the Zn peak (first from left), wt % is 1.55% and in the Indium peaks (seen in the middle cluster along with the cluster of Sn peaks) showed 0.23 % Sigma phase. Sigma phase is a hard, brittle phase and generally not desirable.

Presence of Indium seems to have decreased the amount of Sigma phase.

**Figure 11.** Shows Spectrum 2 Electron Image.  
**Figure 12.** Shows Spectrum 2 EDAX graph.

In the microstructure shown below (Figure 11 and 14), Indium peaks are absent in the EDAX image and Sigma phase is around 0.93 % in both the Zn peak (first from left) and the Aluminium peak (2nd from left). Sigma phase % age is more in this case compared to the previous microstructure.

**Figure 13.** Shows Spectrum 3 Electron Image.  
**Figure 14.** Shows Spectrum 3 EDAX graph.

In this case, the Zn peak (first from left) shows 1.91% Sigma phase, the cluster of Sn peaks (seen in the middle of the EDAX) shows 1.71 % Sigma phase. The Indium peaks (2 small peaks are seen along with the Sn peak cluster) have a Sigma wt % of 0.20 %

**Figure 15.** Shows Spectrum 10 Electron Image.  
**Figure 16.** Shows Spectrum 10 EDAX graph.
Figure 15 and 16 show the microstructure and EDAX at another location. This location shows the Zn peak (first from left) showing Sigma phase 1.50 %, Aluminium peak (2nd peak from left) showing 0.55 % Sigma phase, Indium peak (seen along with the Sn peak cluster in the middle) showing 0.1 % Sigma phase and the Sn peak cluster showing 1.42 % Sigma phase.

4. Conclusion

Mushy range is in a moderate range for both the new alloys prepared, namely 11 and 6.2 Celsius respectively. This range is preferable for optimum results. Hardness values for the two alloys varies between 16 and 22 H. However, hardness of the precipitates was in the range 103-107 H This may be due to the presence of Indium in the precipitates. This may give longer life of solder. Presence of Indium in the microstructure reduced the amount of detrimental Sigma phase from 1.9 % in the alloy to 0.1-0.2 % in the Indium containing precipitates.

REFERENCES

[1] K N Tu, K Zeng, Tin lead(Sn-Pb) solder reaction in flip chip technology, Materials Science and Engineering R 34(1),2001,pp 1-58
[2] Anderson I E, Foley J C, Cook,Harringa J, Terpstra R L, Unal O L, Allooying elements in near eutectic Sn-Ag-Cu solder alloys for improved microstructural stability, J. Electron Mater 30(9) (2001) PP 1050-1059
[3] Cormack M Mc, Jin S, Kammlott G W, Chen H S, New Pb - free solder alloy with superior mechanical properties, Appl. Phys. Lett. 63(1) (1993) pp. 15-17
[4] Miric A Z, Grusd A, Lead free alloys, Soldering Surface Mounting Technology 10 (1) (1998) pp 19-25
[5] El- Dalya, Swilem Y, Makled M H, El- Sharaaraawy M G, Abraboh A M, Thermal and Mechanical properties of Sn-Zn-Bi lead free solder alloys, Journal of Alloys and Compounds, Volume 484(1-2), 2009, pp 134-142
[6] Song J M, Wu Z M, Effect-of-3-wt.%-25-Bi-in-Sn-Zn-solder-on-the-reaction, Scripta Material, 54 (2006) pp 1479-1483
[7] Cheng S C, Lin K L, Determination And Characterization Of Lead Free Solder Alloys, Journal of Material Transactions, 46 (2005), pp 42-47
[8] Chonan Y, Komiyama T, Onuki J, Urao R, Kimura T, Nagano T, Influence of P Content in Electroless Plated Ni-P Alloy Film on Interfacial Structures and Strength between Sn-Zn Solder and Plated Au/Ni-P Alloy, Film Material Transactions, 43 (2002) pp 1887-1890.
[9] Yu S P, Lin H J, Hon M H, Wang M C, Microstructures Variations of Sn9 Zn1 Al and Sn 8Zn 3Bi Solder Pastes with Sn3.8 Ag0.7 Cu Solder Balls on OSP PCBs after Thermal Cycling Test Journal of Materials Science, Electron 11 (6) (2000) pp 461-471
[10] N C M S Lead free solder project final report 0401RE96 National Centre for Manufacturing Sciences, Michigan (1997)
[11] Mei Z, Morris J W, Integrating technology into radiologic science education. Journal of Electron Mater, (21)1 992, pp 401-599
[12] James A. Slattery, Charles E. T. White, Lead-free alloy containing tin, silver and indium, US Patent No 5256370A
[13] Budi Dharma I G B, Hamdi M, And Ariga T, The Effects of Adding Silver and Indium to Lead-Free Solders, Welding Journal 88(4), 2009, pp45-47
[14] Shalaby R M, Effect of indium content and rapid solidification on microhardness and micro-creep of Sn-Zn eutectic lead free solder alloy, *Crystal Research and Technology*, Volume 45, Issue 4 April 2010, Pages 427–432

[15] Yi-Ta Wang; Cheng Jen Ho; Hsien-Lung Tsai, Effect of In addition on mechanical properties of Sn-9Zn-In/Cu solder, *Nano/Micro Engineered and Molecular Systems (NEMS)*, 2013 8th IEEE International Conference on Nano/Micro Engineered and Molecular Systems.