The Influence of Indium, In on Microstructure Evolution During Isothermal Aging of Sn-0.7Cu

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Abstract. This paper reports influence of isothermal aging on bulk solder and the microstructure evolution of commercial Sn-0.7Cu (Sn-0.7Cu-0.05Ni+Ge) Pb-free solder alloy with addition of bismuth (Bi) and indium (In). Sn-0.7Cu, Sn-0.7Cu-1.0Bi, Sn-0.7Cu-1.0Bi-1.0In, Sn-0.7Cu-1.0Bi-4.0In, Sn-0.7Cu-1.0Bi-7.0In solder alloys were prepared via casting process. The solder alloys were aged isothermally at 180°C for 500 hours and microstructure was compared with that of as-cast solder. Microstructure of bulk solder and melting temperatures were analysed via scanning electron microscopy, SEM and differential scanning calorimetry, DSC. The addition of In up to 7 wt% reduced the melting temperature from 231.1 to 218.5°C, and crystallisation temperature from 205.8 to 194.7°C with decreasing degree of undercooling which indicates that the In-added solder alloy had faster nucleation rate. Microstructure evaluation showed that as the amount of indium added increased to 7.0 wt%, the β-Sn grains became smaller suggesting a refinement effect with In addition. Indium addition also encouraged the formation of Sn-In and Bi-In IMC which increased as the amount of In increased. These IMCs could potentially act as blocking mechanism for deformation leading to higher strength.

1 Introduction

In electronic devices, solder alloy is critical for connecting electronic components to a substrate. For the past 50 years, electronic devices have been using Pb-containing solders in its electronic packaging due to its properties low melting temperature, good wettability, and reliability. However, despite all the benefits of Sn-Pb solders, Pb is toxic and increasing use of the electronic device in 1990s led to environmental concern on electronic devices disposal. Hence the RoHS directive was introduced in the European Union, EU in 2006 to prohibit the use of toxic and harmful elements in all electronic devices such as lead (Pb), mercury (Hg) and cadmium (Cd)[1]. As a result, researchers and the electronics manufacturing industry have focusing their efforts on developing Pb-free solder to replace Sn-Pb solder which resulting new Pb-free solders such as Sn-Zn [1], Sn-Bi [2], Sn-Cu [3] and Sn-Ag.

The Sn–0.7Cu eutectic alloy was found to be an appealing option for Pb-free solder due to its good wettability, mechanical properties, and lower cost when compared to other Pb-free solder alloys. Yet, high melting point at 227°C and rapid growth of interfacial intermetallic compounds (IMCs) observed in Sn-Cu alloy need to be overcome. One of the methods is by microalloying, i.e introduce lower melting point element that could also
impede diffusion of active elements. Reports explaining about alloying to reduce melting temperature have been published, for example alloying of Ge\(^2\), Bi \(^3\) \(^4\)and In \(^5\). Bi alloying has been reported to lower melting temperature of Sn-based solder but limited at small percentage as higher than its solubility limit, brittle pure Bi phase precipitate and would induce reliability issue \(^6\). Indium has also been reported to reduce melting point but publications on the influence of both Bi and In addition on the bulk microstructure evolution of Sn–0.7Cu during isothermal aging is limited.

This study focuses on the microstructure changes in Sn-0.7Cu-xBi-yIn solder alloy when the solder is aged at 180°C. The microstructure, thermal properties, and mechanical properties of Sn-0.7Cu-xBi-yIn were investigated. The aim is to reduce melting point of solder and observe the effect of adding Bi and In on the microstructure of as-cast and aged Sn-0.7Cu alloy for possible refinement effect. The refinement of solder will lead to higher strength, and there is also possible formation of Bi-In and In-Sn IMCs which could provide further strength increment.

2 Experimental procedures

Commercial Sn-0.7Cu solder alloy known as SN100C (Sn-0.7Cu-0.05Ni+Ge) by Nihon Superior was used. Bismuth (Bi) powder with 150μ particle size by Merck and indium (In) shot from Johnson Mattney with 99.9% purity were used as alloying element. Solder alloys were prepared by weighing Sn-0.7Cu ingot, Bi powder and In shots according to predetermined weight to achieve composition as shown in Table 1. The raw materials were then melted in a box furnace using 2-step heating at 350°C with 10 °C/min with 1 hour soaking time and re-melt at 300°C to make sure the alloy mixed homogeneously. Molten solder alloys were casted onto a mould and let to set at room temperature.

The chemical composition of the as cast solders (Table 1) was obtained using X-ray fluorescence spectroscopy, XRF. The Sn-0.7Cu portion includes existing alloying of 0.05 Ni+Ge (patented SN100C). Thermal properties of as cast solders alloy were investigated by differential scanning calorimetry, DSC; all as-cast samples were about 10mg heating from ambiance temperature to 250°C and was controlled at 10°C/min. The measurement was performed two times in nitrogen protective atmosphere. The mechanical properties were investigated by microhardness Vickers test on as cast and aged solder alloys using test load 300g and dwell time 10s with average of 10 measurement on each sample.

The samples for microstructure evaluation were prepared according to standard procedures by grinding using SiC paper and polished by diamond suspensions. The morphology of IMC was exposed by deep etching the bulk solder with etching solution of 2ml HCl, 5ml HNO\(_3\) and 93ml methanol at room temperature for 30s. The microstructure was observed by scanning electron microscope, SEM.

| Table. 1 Chemical Composition of Sn-0.7Cu-xBi-yIn solder alloy |
|---------------------------------------------------------------|
| **Solder composition** | **Percentage wt,%** |
| | Sn-0.7Cu | Bi | In |
| Sn-0.7Cu | 100 | - | - |
| Sn-0.7Cu-1.0Bi | 99 | 1.0 | - |
| Sn-0.7Cu-1.0Bi-1.0In | 98 | 1.0 | 1.0 |
| Sn-0.7Cu-1.0Bi-4.0In | 95 | 1.0 | 4.0 |
| Sn-0.7Cu-1.0Bi-7.0In | 92 | 1.0 | 7.0 |
3 Results and Discussion

3.1 Thermal Behaviour, DSC

The findings of DSC analysis are summarized in Table 2. The Sn-0.7Cu melting temperature, \( T_m \) was found to be 231.1°C, a bit higher comparing to conventional Sn-0.7Cu that is 227°C [7]. This is because commercial Sn-0.7Cu solder contains Ni and Ge. Addition of bismuth lowered the solidus temperature, \( T_{om} \) from 224.3°C to 221.9°C and this trend continues as In was introduced and increased in wt%. The addition of Bi and In reduced the undercooling, except for Sn-0.7Cu-1.0Bi-1.0In which had slightly higher value compared to Sn-0.7Cu-1.0Bi, and this could be attributed to minor impurity which influence the heterogeneous nucleation process. The adding of In reduced the degree of undercooling even more as more In atoms act as additional nucleating agents during the crystallisation process, causing the molten solder to solidify faster from 19.7°C for Sn-0.7Cu to 6.8°C for Sn-0.7Cu-1.0Bi-7.0In. The results showed a favourable effect of In and Bi addition on the Sn-Cu solder.

| Solder alloy     | Onset Melting Temperature, \( T_m \) | Onset Crystallisation Temperature, \( T_{oc} \) | Melting Temperature, \( T_m \) | Crystallisation Temperature, \( T_{c} \) | Degree Of Undercooling, \( T_{om}-T_{oc} \) |
|------------------|--------------------------------------|--------------------------------------|--------------------------------------|--------------------------------------|--------------------------------------|
| Sn-0.7Cu         | 224.32                               | 204.64                               | 231.11                               | 205.80                               | 19.68                                |
| Sn-0.7Cu-1.0Bi   | 221.93                               | 208.33                               | 231.42                               | 210.57                               | 13.60                                |
| Sn-0.7Cu-1.0Bi-1.0In | 218.65                           | 204.32                               | 229.38                               | 207.02                               | 14.33                                |
| Sn-0.7Cu-1.0Bi-4.0In | 214.21                           | 201.14                               | 224.88                               | 193.06                               | 13.07                                |
| Sn-0.7Cu-1.0Bi-7.0In | 204.52                           | 197.77                               | 218.53                               | 194.70                               | 6.75                                 |

3.2 Mechanical Properties

Table 3 shows measured Vickers microhardness test results for solders Sn-0.7Cu-xBi-yIn (Bi:0,1.0 wt%, In: 0,1.0,4,7.0wt%) as-cast and thermally aged for 500 hours at 180°C. The alloying of Indium increased hardness from 9.86 HV for Sn-0.7Cu to 15.17HV for Sn-0.7Cu-1.0Bi-7.0In, and this is 65% increment. It is worth noting that the Sn-0.7Cu-1.0Bi-7.0In hardness increased after aging, reaching 19.97HV compared to 15.17HV for the as-cast sample. The reason for this is discussed in next section. Similar increment is shown by solder added with 4% In, although the increment is only slightly. For the other samples, aging reduced the hardness, most likely due to grain coarsening.

| Aged Hours | Vickers hardness (HV) |
|------------|------------------------|
|            | Sn-0.7Cu | Sn-0.7Cu-1.0Bi | Sn-0.7Cu-1.0Bi-1.0In | Sn-0.7Cu-1.0Bi-4.0In | Sn-0.7Cu-1.0Bi-7.0In |
| 0          | 9.86     | 12.61         | 12.66                  | 14.33                  | 15.17                  |
| 500        | 9.32     | 11.32         | 11.21                  | 14.54                  | 19.97                  |
3.3 Microstructure of Thermal Aged Solder Alloy

Fig. 1 shows the microstructure of as cast a) Sn-0.7Cu, and b) Sn-0.7Cu-1.0Bi-7.0In solder alloys. It could be observed that addition of 7% In refined the β-Sn grains and there are additional IMCs, i.e Bi-In and InSn₄ present in the bulk solder. The commercial Sn-0.7Cu exhibits β-Sn dendrites and a two-phase eutectic of Cu₆Sn₅ and (Cu,Ni)₆Sn₅ phases formed by the presence of Ni, with Ni atoms doped into Cu₆Sn₅ to form the (Cu,Ni)₆Sn₅ phase. Fig 1(b) shows the solder alloy added with 7.0% wt In and it can be observed that β-Sn grains are finer. Two additional IMC phases, i.e BiIn and InSn₄ can be observed, with much smaller size compared to the Cu₆Sn₅ which appear as needle-like dark grey structure. The presence of additional IMC particles altered the hardness of the solder junction in a positive way because better able to impede dislocation motion. The microstructure of aged solder added with 7% In on the other hand, did not show the rather large needle of Cu₆Sn₅ present in as-cast sample. Instead, they were smaller in size and more equiaxed in shape. The change of structure for Cu₆Sn₅ could be due to diffusion of Sn atoms, and also possible formation of Cu₃Sn from Cu₆Sn₅ which has been reported by many researchers when Sn-based solder is aged in the presence of Cu. Cu₃Sn however, could not be clearly observed in the sample. The InSn₄ can be more clearly seen and appear as fine white particles uniformly distributed throughout the Sn matrix. This is believed to have provided the strengthening effect to the solder, as shown in the increment in hardness presented in Table 3. It is also observed that the grains in Sn100C sample coarsened after aging, resulting in reduction in hardness but the grain coarsening was not seen in In-added solder. It is possible that the presence of IMC particles impedes diffusion of atoms avoiding grain coarsening during thermal aging, and this result in hardness increment seen in 7% In-added solder.
Fig. 1. The microstructure of a) Sn-0.7Cu solder, b) Sn-0.7Cu-1.0Bi-7.0In c) Sn-0.7Cu aged at 500 hours, b) Sn-0.7Cu-1.0Bi-7.0In aged at 500 hours.

4 Summary

Several conclusions can be made from this study. The addition of Bi and In (up to 7%) in Sn-0.7Cu solder alloy reduced the melting point and lower the degree of undercooling. With lower degree of undercooling, refinement effect was observed in microstructure of In-added solder. Also, increasing amount of In up to 7% resulted in hardness increment after thermal aging at 180 °C for 500 hours and this is due to smaller particles of Cu6Sn5 and more clearly observed small InSn4 particles. Also, In-added solder did not show coarsening of Sn grains compared to SN100C after aging. The uniformly distributed IMC particles and finer grains contributed to the hardness increment of In-added solder alloys, both as-cast and after aging.

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References

1. C. M. Méndez, V. L. Scheiber, R. S. Rozicki, A. I. Kociubczyk, A. E. Ares, Arab. J. Chem. 11, 1084–96 (2018)
2. Z. Wang, Q. K. Zhang, Y. X. Chen, Z. L. Song, J. Mater. Sci. Mater. Electron. 30, 18524–38 (2019)
3. M. Zhao, L. Zhang, Z. Q. Li, M. Y. Xiong, L. Sun, Sci. Technol. Adv. Mater. 20, 421–44 (2019)
4. X. Zhang, X. Hu, X. Jiang, Y. Li, Mater. Res. Express, 6 (2019)
5. H. A. Jaffery, M. F. M. Sabri, S. M. Said, S. W. Hasan, I. H. Sajid, N. I. M. Nordin, M. M. Megat Hasnan, D. A. Shnawah, C. V. Moorthy, J. Alloys Compd. 810, 151925 (2019)
6. A. M. Erer, S. Oguz S, Y. Türen, Eng. Sci. Technol. an Int. J. 21, 1159–63 (2018)
7. S. Tian, S. Li, J. Zhou, F. Xue, R. Cao, F. Wang, J. Mater. Sci. Mater. Electron. 28, 16120–32 (2017)
8. N. R. A. Razak, M. A. A. Mohd Salleh, N. Saud, R. M. Said, M. I. I. Ramli, Solid State Phenom. 273 SSP, 40–5 (2018)
9. Anon (PDF) Sn-Bi(-Ga) TIM Alloys: Microstructure, Tensile Properties, Wettability and Interfacial Reactions
10. S. A. Belyakov, J. W. Xian, K. Sweatman, T. Nishimura, T. Akaiwa, C. M. Gourlay, J. Alloys Compd. 701, 321–34 (2017)
11. M. L. Huang, L. Wang, Metall. Mater. Trans. A Phys. Metall. Mater. Sci. 36, 1439–46 (2005)
12. A. Nabihah, M. S. Nurulakmal, 17, 803–9 (2019)
13. C. Morando, O. Fornaro, Solder. Surf. Mt. Technol. 33, 57–64 (2020)