RESEARCH ARTICLE OPEN ACCESS

Effect of Rare Earth Elements on Lead Free Solder Alloys

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ABSTRACT
Sn-Pb solders have been widely used as interconnecting material in electronic packaging and assembly. However, due to environmental and health concern we need to eliminate the usage of Pb bearing solders due to the inherent toxicity of Pb which has led to the development of Pb free solders. Researchers found that the properties of Pb free solders have been improved by doping it with trace amounts of rare earth (RE) elements. This work aims to summarize the effects of addition of RE elements on the wettability, mechanical properties, melting behaviour and microstructure of lead free solder alloys.

Keywords – Sn-Pb, lead free solder, wettability, mechanical properties, melting behavior, microstructure, rare earth elements

I. INTRODUCTION

Environmental related resolutions such as restriction of certain hazardous substances (RoHS) and the waste electrical and electronic equipment (WEEE) have been introduced by many countries [1] [2]. However, legislation that mandates the removal of lead from electronics was introduced by countries such as japan and those in the European Union during the last 15 years. As cited by Environmental Protection Agency (EPA), Pb and Pb containing compounds is one of the top 17 chemicals causing negative impacts to both environment and human body due to which a major change in direction of research into science and engineering of soldering has taken place [3] [4] [5]. 1 July 2006 has been officially designated as the date when the directive on the restriction of hazardous substances in electrical and electronics equipment will require "the use of lead, cadmium, mercury, hexavalent chromium and halogenated flame retardants" be phased out [6]. Electronic manufacturers now have two choices either attaining 100% recycling of Pb or using lead free solder alloys. Recycling rate of electronic devices is very low due to high cost of recycling processes especially for high technology products such as computers so the other alternative is to develop lead free solder alloys [2] [7]. For developing a new solder alloy, one needs to think of various properties such as melting temperature, wettability, mechanical properties, microstructure, cost, availability and reliability of solder joint [8] [9]. Researchers developed a large number of lead free solder alloys. These solders have been tin rich ones with various alloying elements such as Bi, Ag, Cu, In, Zn and Sb. Binary lead free solders such as Sn-Ag, Sn-Cu, Sn-Zn, Sn-Bi and Sn-In cannot fulfill the requirements in electronic packaging and assemblies, additional alloying elements were added to enhance the performance of these alloys. So this led to the development of ternary and even quaternary lead free solders [10] [11] [12] [13]. RE elements has been considered as "vitamins" of metals which means that trace amounts of these elements can significantly improve the properties of metals. In this paper the effects of addition of RE elements on various properties of lead free solder alloys has been summarized.

II. STATE OF ART

2.1 Effects of RE addition of Sn-Bi and Sn-Bi-Ag lead free solder alloys

On addition of trace amounts of RE elements to Sn-Bi and Sn-Bi-Ag has significantly improved the wettability of the solder [16]. The spreading area increases by approximately 50% on addition of RE elements to the solder alloys as shown in Fig. 1.

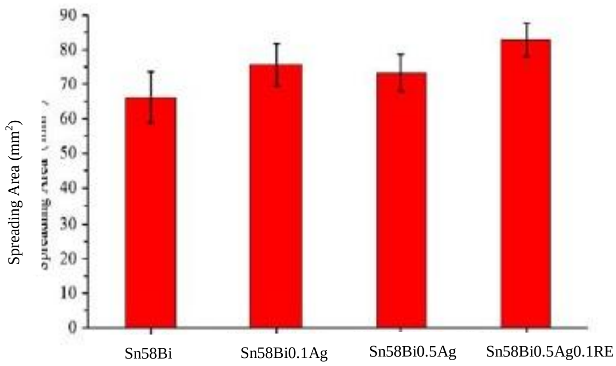


Fig 1: Spreading area of Sn-58Bi based solder alloy

Shear strength of the solder joints increases on addition of RE elements and Ag in both as reflowed condition and after thermal aging. Shear strength of all the solder joints decrease after high temperature aging for 168 hrs. (Aging temperature is 80°C). After aging shear strength of the RE doped solder joints decreased only slightly (less than 2%) as compared to the joints without RE doping (reduced by 7%) as shown in Fig 2.

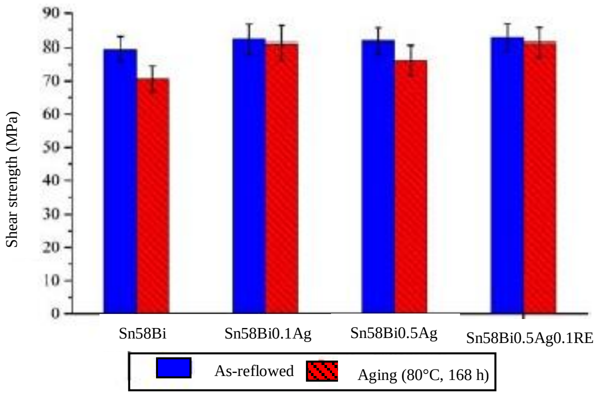


Fig.2. Shear strength of Sn58Bi based solder joints

Microstructure of Sn-58Bi solder is much coarser as compared to other three solders. Addition of trace amount of RE elements and Ag has refined the microstructure [Refer Fig. 3]. Micrographs show that addition of RE elements depressed the rate of coarsening after aging as shown in Fig. 4. Microstructure of RE doped solder is more uniform and width of eutectic colony is thinner.

Two types of intermetallic compounds Cu_6Sn_5 and Ag_3Sn were observed. Addition of RE elements refine intermetallic particles as well as decreases the thickness of interfacial intermetallic whereas high temperature aging an increase in the intermetallic thickness of the solder joint as shown in Fig.5, Fig 6, and Fig 7.

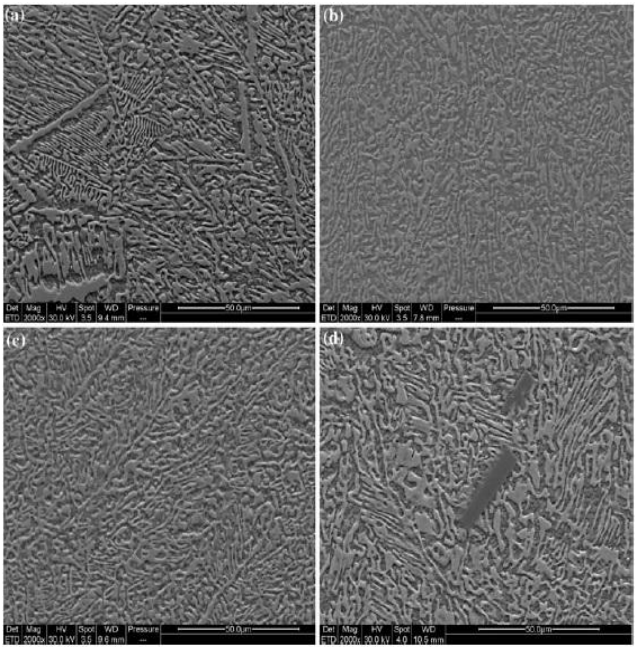


Fig.3. Microstructure of the solder alloys in the as-reflowed state: (a) Sn-58Bi, (b) Sn-58Bi-0.1RE, (c) Sn-58Bi-0.5Ag, and (d) Sn-58Bi-0.5Ag-0.1RE.

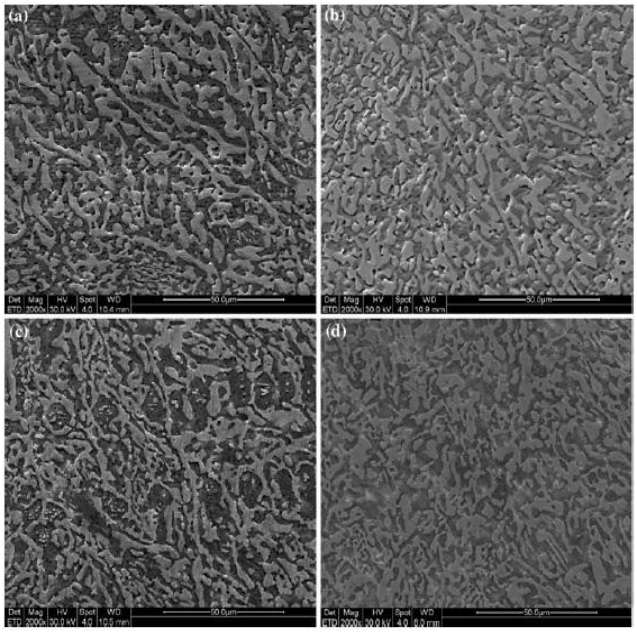


Fig.4. Microstructure of the solder alloys after aging: (a) Sn-58Bi, (b) Sn-58Bi-0.1RE, (c) Sn-58Bi-0.5Ag, and (d) Sn-58Bi-0.5Ag-0.1RE

There is little influence on melting temperature and micro hardness of the solder on addition of RE elements [16].

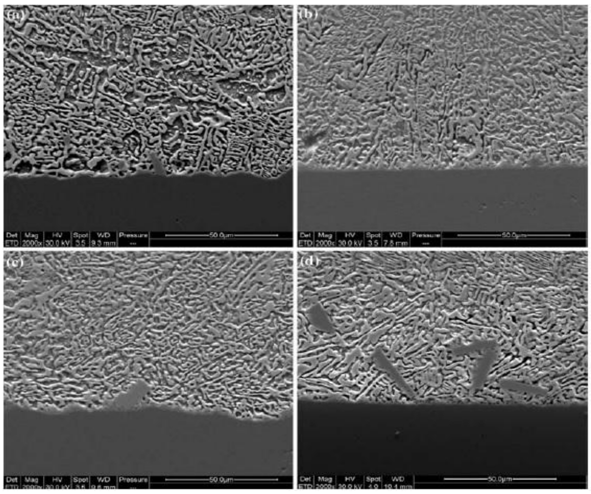


Fig.5. Microstructures at the solder/Cu substrate interface in the as-reflowed state: (a) Sn-58Bi, (b) Sn-58Bi-0.1RE, (c) Sn-58Bi-0.5Ag, and (d) Sn-58Bi-0.5Ag-0.1RE.

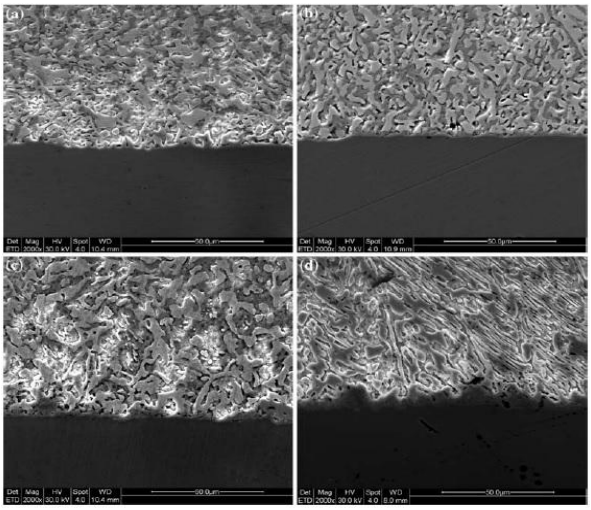


Fig.6. Microstructures at the solder/Cu substrate interface after aging: (a) Sn-58Bi, (b) Sn-58Bi-0.1RE, (c) Sn-58Bi-0.5Ag, and (d) Sn-58Bi-0.5Ag-0.1RE.

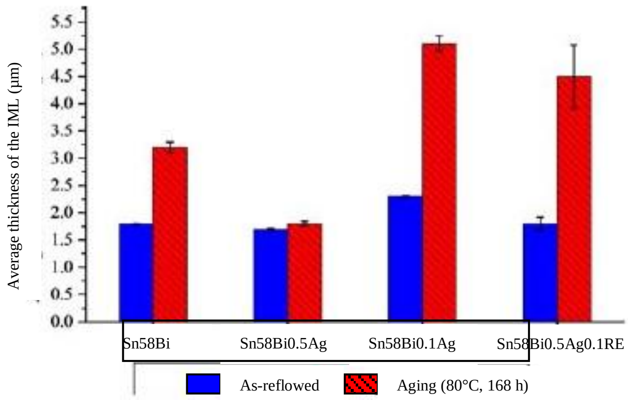


Fig.7. Average thickness of the Intermetallic layer (IML) at the solder/Cu interface.

2.2 Effects of RE on Sn-Zn lead free solder alloy

With 0.05% RE elements the coarse β-Sn grains disappear and the Sn rich phase becomes finer. Microstructure of the solder is uniform as shown in Fig 8 [17].

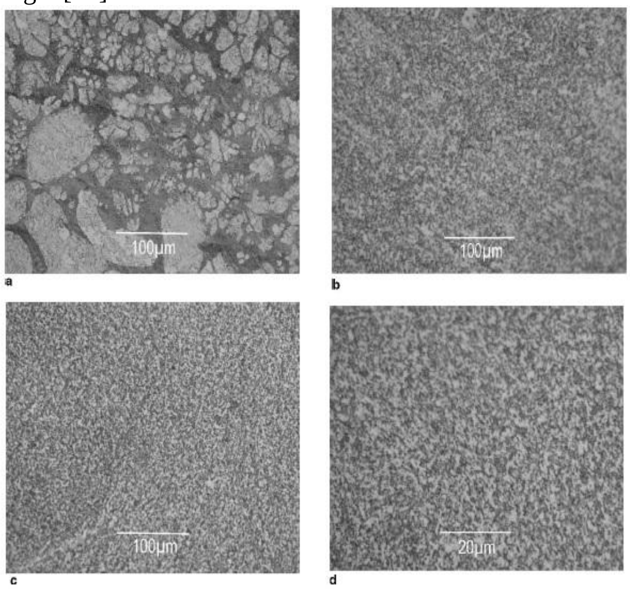
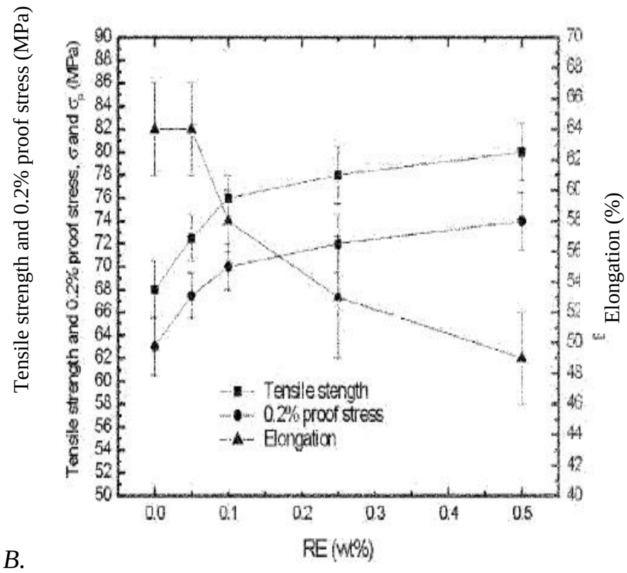


Fig.8. Optical micrographs of chill-cast samples of (a) Sn-9%Zn, (b) Sn-Zn-0.05RE, (c) Sn-Zn-0.5RE, and (d) Sn-Zn-0.5RE (high magnification).

A. On addition of 0.1% Re elements tensile strength is improved by 20% and it increases to 30% on addition of 0.5% RE to the solder alloys whereas elongation is decreased. Proof stress is improved by 0.2% in RE doped solder alloys as shown in Fig 9



B.

Fig.9. Tensile properties of Sn-Zn, Sn-Zn-0.05RE, Sn-Zn-0.1RE, Sn-Zn-0.25RE, and Sn-Zn-0.5RE alloys

With 0.05% and 0.1% RE addition the wetting properties were significantly improved with RA flux as shown in Fig 10 and Fig 11 [18].

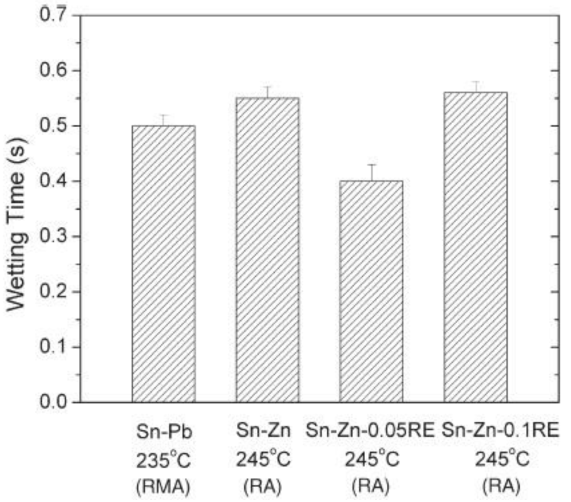


Fig.10. Variation of wetting time with amounts of RE elements at 245°C.

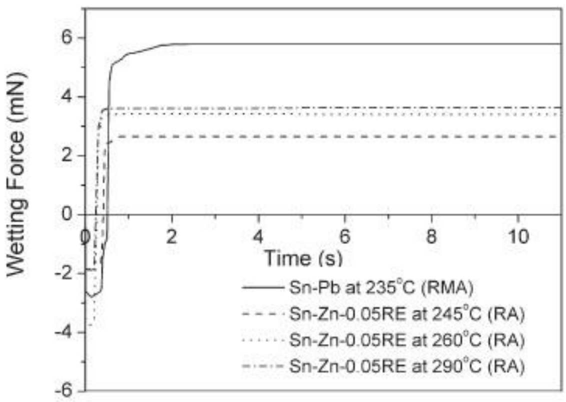


Fig.11. Wetting curves of Sn-Zn-RE solders compared with Sn-Pb.

Micro hardness increases by 13% on addition of 0.05% and 0.1% RE elements to the solders as shown in Fig 12 [18].

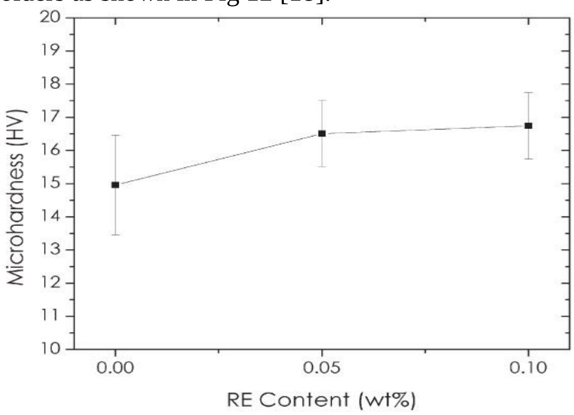


Fig.12. Variation of micro hardness with RE content.

Adding Re elements to the solders has very little influence on the melting temperature as shown in Fig 13 [18].

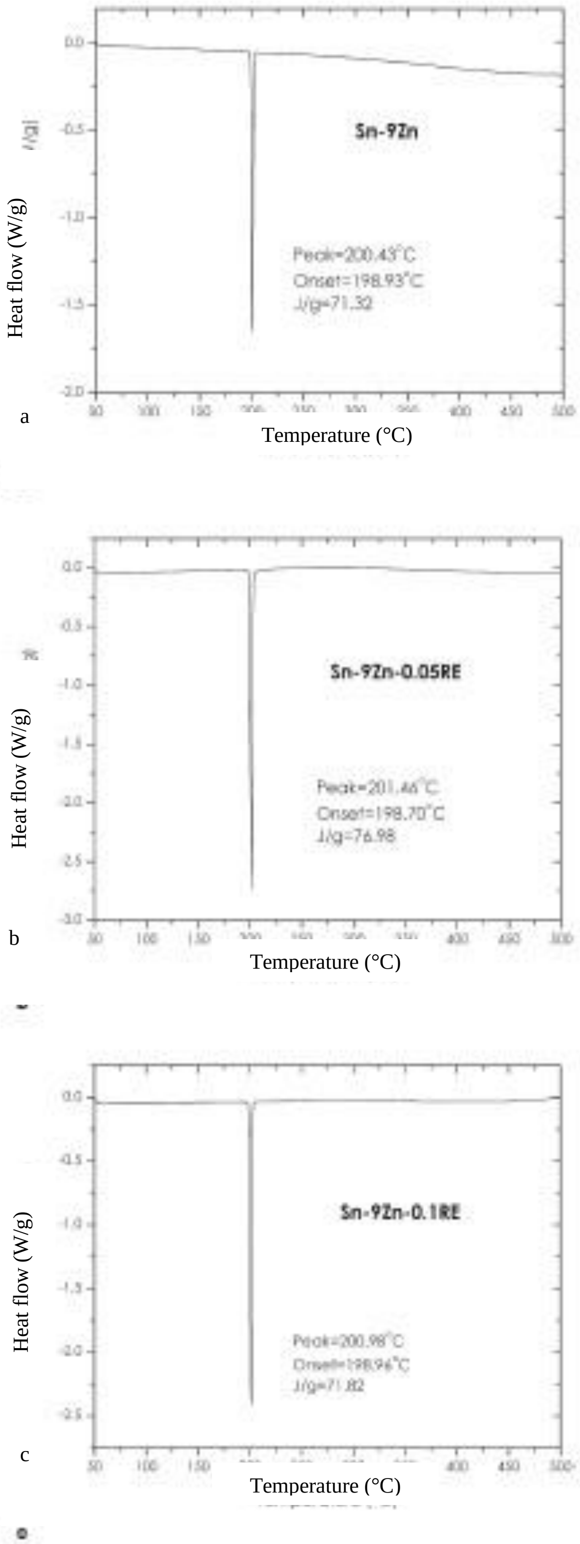


Fig.13 The DSC curves (a) Sn-9Zn, (b) Sn-9Zn-0.05RE, and (c) Sn-9Zn-0.1RE.

2.3 Effect of RE on Sn-Cu lead free solder alloys

On addition of RE elements, about one-third to half of the β-Sn grains have been transformed into smaller grains and the grains are refined as shown in Fig 14 [19].

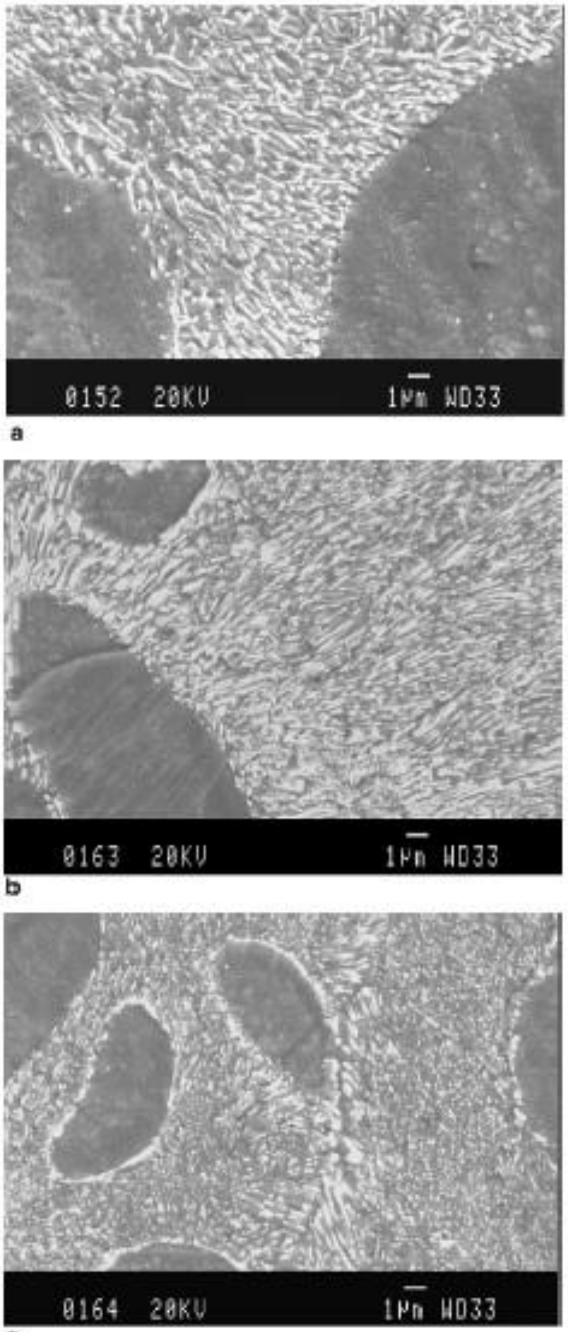


Fig. 14 SEM micrographs for (a) Sn-0.7%Cu, (b) Sn-0.7%Cu-0.25%RE, and (c) Sn-0.7%Cu-0.5%RE.

In the eutectic band Cu-Sn intermetallic were found in the β-Sn matrix. Addition of RE elements decreases the flake size of Cu_6Sn_5 intermetallic and become finely dispersed in the eutectic networks [19].

To study the stability of microstructure the Sn-Cu-RE alloys were aged at 150°C for 20 hrs and it was found that after aging of Sn-Cu, the intermetallic Cu_6Sn_5 particle become coarse and there dispersion was not uniform and also the eutectic colonies were no longer noticeable. The microstructure of Sn-Cu-RE alloys after aging was uniform and the precipitates were fine uniformly dispersed as shown in Fig 15 [19].

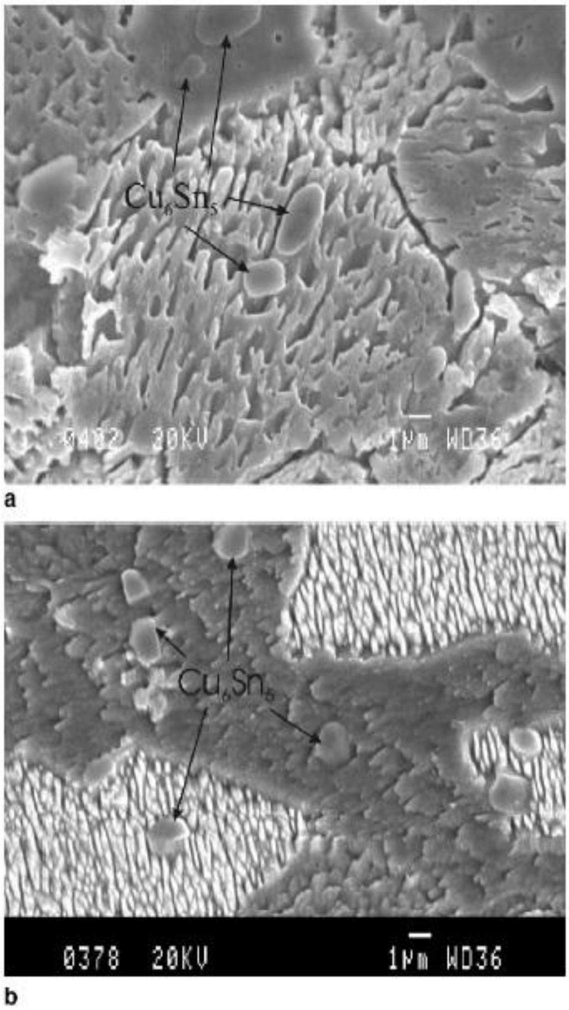


Fig.15 SEM microstructure after aging at 150°C for 20 h: (a) Sn-0.7%Cu and (b) Sn-0.7%Cu-0.5RE.

On addition of 0.25% and 0.5% Re elements increases ultimate tensile strength by 20% and 27 % but there is decrease in elongation as shown in Fig 16 [19].

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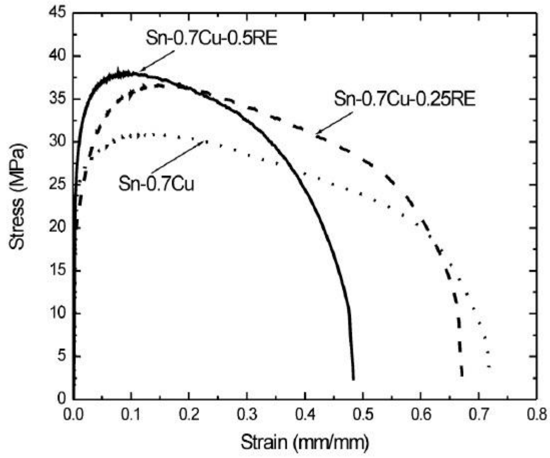

Fig.16. Comparative tensile stress-strain curves for Sn-0.7%Cu, Sn-0.7%Cu-0.25%RE, and Sn-0.7%Cu-0.5%RE solder alloys.

Adding RE elements to the solder increase the hardness for both 10g and 50g load tests as shown in Fig 17 [19].

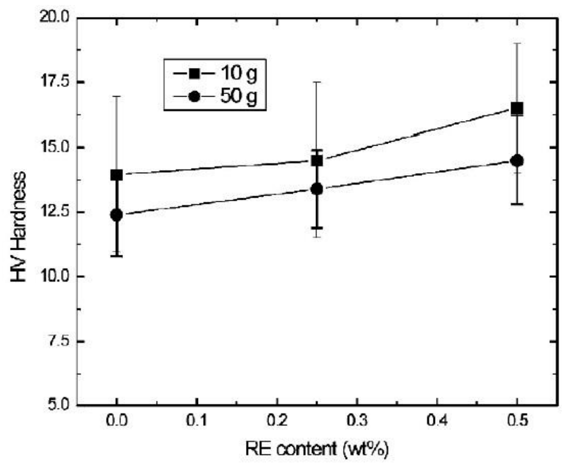

Fig.17. Micro hardness data for Sn-0.7%Cu, Sn-0.7%Cu-0.25%RE, and Sn-0.7%Cu-0.5%RE using 10 g and 50 g loads.

III. CONCLUSION

Addition of trace amounts of rare earth (RE) elements enhances the properties and reliability of lead free solder alloys making the resulting alloys a better alternative for Sn-Pb solder replacement.

The micro structure, tensile strength and hardness of the Pb solder containing RE elements is significantly improved without too much loss in ductility and also the thickness of inter metallic layer is decreased.

Wettability of the solder contain RE elements has been greatly improved because RE have surface active properties which decreases the interfacial surface tension between the solder and the substrate, thus accelerating wetting of the solder alloys.

Addition of RE elements to Pb free solder alloys should be up to a certain range otherwise it would deteriorate the microstructure and other properties.

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