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Nickel (Ni) Microalloying Additions in Sn-Cu Lead-free Solder. Short Review

M A A Mohd Salleh[1], I G Sandu[1,2], M M A Abdullah[1,3], I Sandu[1,4] and N A Saleh[1]
[1]Centre of Excellence Geopolymer and Green Technology, School of Materials Engineering, Universiti Malaysia Perlis (UniMAP), Perlis, Malaysia
[2]Faculty of Materials Science and Engineering, Gheorghe Asachi Technical University of Iasi, Romania
[3]Faculty of Engineering Technology, Universiti Malaysia Perlis (UniMAP), Perlis, Malaysia
[4]Laboratory of Scientific Investigation, Arheoinvest Platform, Alexandru Ioan Cuza University of Iasi, Romania

E-mail: arifanuar@unimap.edu.my

Abstract. In this digital-age era, solder plays important role in electronic packaging industries. As interconnects material, solder provide an electrical and mechanical support to the electronics devices. Solder usually consist of two or more addition of microalloying. By microalloying addition, the solidification structure can be modified. This paper reviews the addition of Ni as microalloying in Sn-Cu lead free solder. Small additions of Ni resulted with an improvement of solder in microstructure and in intermetallic compounds. The stabilization of hexagonal structure of Cu_6Sn_5 in lead-free solder alloys occurred due to present of Ni.

1. Introduction

In decades, soldering act as main process of electronic packaging industry. It is a process of metallurgical joining between two metals which are used solder as a filler under its melting point [1]. Usually, the metallurgical joining process temperature used is below 400°C [2]. The physical interaction between the metals make electronic packaging industry growth rapidly and more advances in electrical connection and give good mechanical support [3]. The good performance and quality of solder create a multi-function of electronic devices that have been used in this century such as cellular phones and digital cameras [2].

Tin-lead solders have been used widely for several years ago in electronic technology to make an improvement in the performance. The presence of lead in the electronics device can cause problems to human and the environment because it has higher toxicity. Due to environmental and health concern, the European Union makes a general instruction remove the used of lead in electronic packaging industry that has been issued by Waste of Electrical and Electronic Equipment (WEEE) and the Directive of the restriction of the Use of Certain Hazardous Substances (RoHS) after July 2006 [3].

Nowadays, lead-free solders alloy take a led towards the green technologies to replace the conventional tin-lead solder alloy [4–6]. Kang [1] summarized that there a few requirements needed by lead-free solders alloy exchange in terms of wettability, melting temperature, thermal fatigue resistance and cost. Currently, Sn-Ag-Cu alloy is one of the most excellent solder composition to select as replacement due to their performance [1]. However, the increasing cost of silver makes Sn-

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Cu-Ni alloy is targeted in electronic packaging industry [7]. Sn-Cu-Ni alloy has been discovered due to limitation of Sn-Cu in terms of poor wettability, low resistance to thermal fatigue and high melting temperature.

The additions of nickel are proven to improve the flow characteristic and increase the amount of eutectic microstructure of the solder alloys [8]. Recently, Sn-Cu-Ni or known as SN100C is patented by Nihon Superior have been chosen as matrix based alloy in electronic packaging industries [9]. The additional of third or fourth elements in solder alloys has been known to improve the mechanical, physical and thermal properties of the solders. Usually the additional of microalloying element such as indium, titanium, zinc, bismuth, nickel and aluminum are used by the researcher because of their excellent properties [10]. With the addition of microalloying, the better solder alloys have been introduced and used in application of electronics device.

According to Reichencker [11], the growth of intermetallic compounds (IMCs) between two metals reduces the strength of solder joint due to brittle nature of these compound [11]. The crack growth in the intermetallic compounds (IMCs) also give limitation of the compound [12]. To increase the performance of the solder, the addition of third or fourth elements are needed in the solder such as zinc, bismuth and phosphorus [13].

2. Fabrication Method

There are several of fabrication technique in lead-free development. This technique usually is divided into two groups which are casting and powder metallurgy method [14]. Both of the method is commonly used in electronic industry by giving different properties of soldering alloy. Figure 1 shows the densification process for both method in bulk solder by showing that the casting method is depending on the cooling rate of molten metal while for powder metallurgy, heating rate during sintering cause the particle growth in soldering alloy [14].

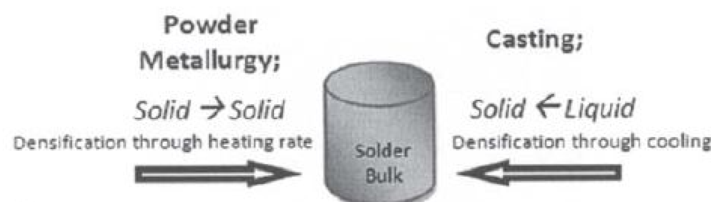

Figure 1. Densification process for casting and powder metallurgy method in bulk solder [14].

Powder metallurgy is also recently popular in electronic packaging applications [14]. In this method, sintering play role important part to reveal the end properties [15]. For sintering method, the direction of heating is transfer from outside to inside of compacted powder and usually it gives poor microstructure characteristic to the solder. To recover the limitation faced, advance of microwave-assistance for rapid sintering is introduced and forms uniform heating. It is also lower in cost and energy efficient [15]. The microstructure of powder metallurgy technique for Sn-0.7Cu is shown in figure 2 by using optical microscope which contains pores [14].

Casting is one of technique used by melting the alloy above their melting point. The technique used by melting the alloys and poured into a mold that has desired shaped and then it through a solidification process. By using this method, solidification of molten solder is faster but the grain growth only focuses by heating.

The rapid of solidification can be done with the help of medium such water or air at low temperature.

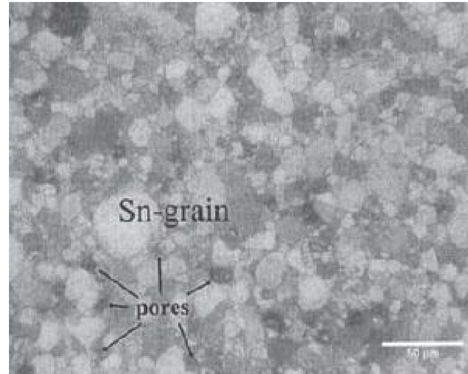

Figure 2. Microstructure image for powder metallurgy [14].

Figure 3 shows the microstructure image for casting method for Sn-0.7Cu by using optical microscope which consists of finer β-tin and eutectic region (Sn + Cu_6Sn_5) [14].

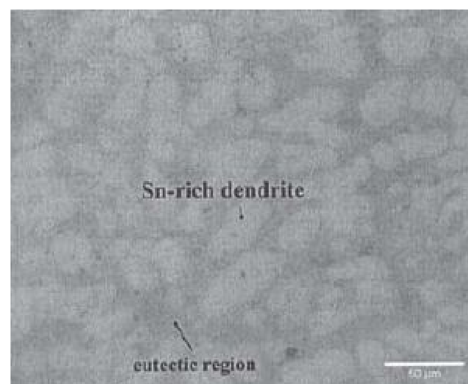

Figure 3. Microstructure image for casting method by using optical microscope [14].

3. Effects of Ni to microstructure in Sn-Cu solders

In a recent year, several researchers have been developed improvement of Sn-Cu solder alloy. Because of poor wettability, high melting temperature and low resistance to thermal fatigue, some of the alloying elements are added into Sn–Cu solder alloys such as Ni and rare earths [8]. The additional of Ni in Sn-0.7Cu solder was studied to improve flow characteristics and there several reasons are reported which is (i) it includes the composition of the commercial solder SN100C, (ii) it is important to start with a hypoeutectic alloy but it must close to the binary eutectic composition and (iii) it can make comparisons with the binary system Sn-Cu [8,16].

The addition of Ni in Sn-0.7Cu also can increase the amount of eutectic microstructure and it can be seen in Figure 4 [8]. Due to application in lead free solder, the melting temperature used for Sn-Cu-Ni solder alloy is around 240°C [7]. Figure 5 showed the system of Sn-Cu-Ni has been studied by Ghosh [7] especially in the sections from Ni_3Sn to Cu_3Sn and from Ni_3Sn_2 to Cu_6Sn_5 [7]. The increasing content of Ni in Sn-Cu-Ni makes Cu_6Sn_5 phases to become more rounded and lower the volume fraction for Sn-dendrites [8].

A.K. Dahle [16] investigated that the Ni addition in Sn-Cu are shifted from the hypoeutectic binary composition to ternary eutectic which is can improves the fluidity and reduce the freezing range.

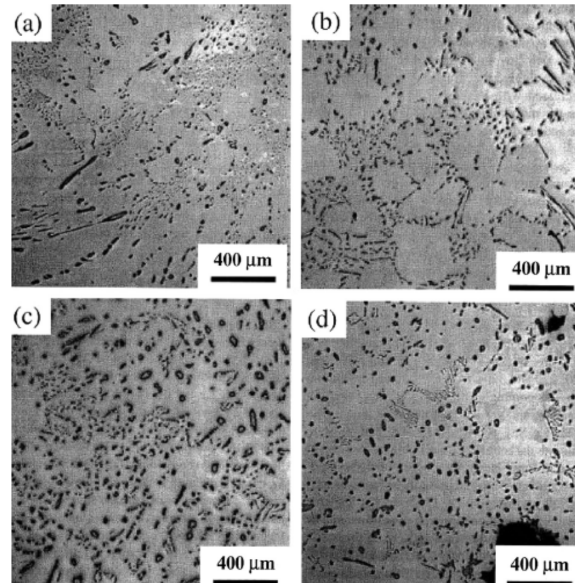

Figure 4. Example the additional of nickel in Sn–0.7Cu (a) Pure (b) 100 ppm Ni, (c) 600 ppm Ni and (d) 1000 ppm Ni [8].

Due to present of Ni, the eutectic are weakly irregular in the binary system while strongly irregular in the ternary alloys [16].

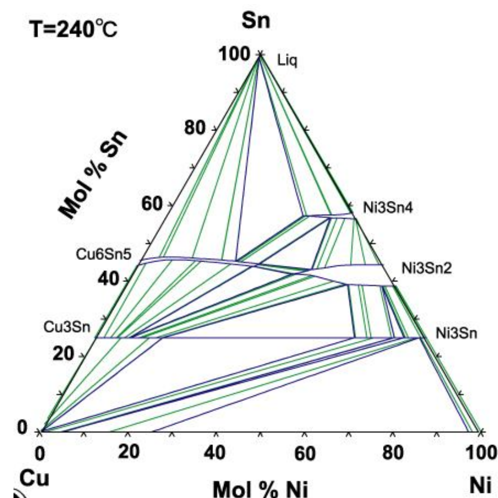

Figure 5. Sn-Cu-Ni phase diagram [7].

According to Stuart [17], the uniformity and stability of microstructure are identified for lead-free solder alloys in achieving of mechanical properties balance. The additions of microalloying can give refinement to Cu_6Sn_5 and give improvement the solder reliability [17]. By addition of Ni into Sn-0.7Cu solder, indirectly it gives improvement in solder revolution, and this formulation (Sn-Cu-Ni) was known as SN100C and patented by Nihon Superior Co. Ltd. Todays, Sn-Cu-Ni appears as new composite solder with a good compromise between cost and quality.

4. Effects of Ni to Intermetallic Compound of Sn-Cu solders

The important factors which developed by influencing the solder joint reliability are the intermetallic compounds (IMCs) layer [18]. Formation of intermetallic compounds (IMCs) is one of mechanisms to connect between the solder and substrate. Harris [12] who investigates the presence of the intermetallic Ag_3Sn and Cu_6Sn_5 in the tin solid solution of Sn-3.5Ag and Sn-0.7Cu state that it will improves hardness and resistance to fatigue [12]. The brittle nature of the intermetallic layer was confirmed by Reichencker [13] has excessive IMCs growth which decreases the strength of solder joint [13]. The addition of third or fourth elements is one of way to give excellent performance of the interfacial IMCs layers which help to increase the solder alloy properties.

Usually addition of another element in solder has effect between the solder and substrate reaction that can make the IMCs growth rate instable, it also can change the physical properties of the phase formed in solder and form additional layer reaction at the interface of IMCs. Nogita [19] claims that the high temperature hexagonal phase are stabilize with the present of Ni in the intermetallic. In intermetallic compound layer between the solder alloy and Cu substrate, it can be seen a visible crack which is known to be Cu_6Sn_5 and apparent significantly fewer cracks are present in the Cu_6Sn_5 layer when Ni are added into Sn-Cu solder. Figure 6 shows the cross sectioned ball grid alloy on Cu substrate by Sn-Cu solder with Ni and without Ni [19].

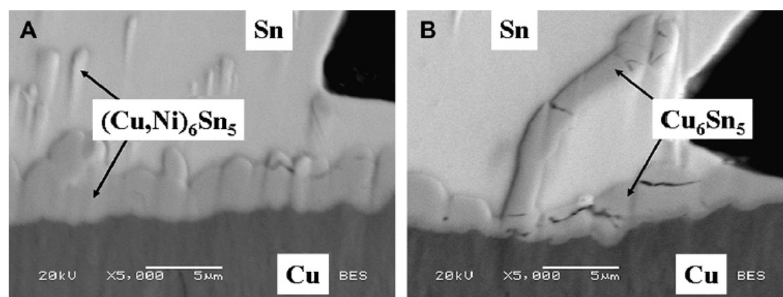

Figure 6. The cross sectioned ball grid alloy on Cu substrate (a) Sn-0.7Cu-0.05 Ni solder and (b) Sn-0.7Cu solder.

Cu_6Sn_5 is a relatively brittle phase after thermal cycling are stated by Stuart [17]. Due to volumetric changes experienced during polymorphic transformation between the hexagonal and monoclinic Cu_6Sn_5 crystallographic, the cracking are occurred at equilibrium condition [17]. However, the creep and mechanical properties of Cu_6Sn_5 by the present of Ni at the elevated temperature is still unknown [20].

5. Conclusions

This study is focused on the microstructure and intermetallic compounds of lead-free solder alloy due to the additions of the Ni as a microalloying element. The previous studied was show the effect of Ni in microstructure and intermetallic compounds that give improvement in the solder alloy. With the Ni addition in Sn-Cu, the microstructure is shifted from the hypoeutectic binary composition to ternary eutectic which is can improves the fluidity and reduce the freezing range. While the high temperature hexagonal phase are stabilize with the present of Ni in the intermetallic compounds.

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