

Experimental investigations on the effect of addition of Ag into ternary lead free solder alloy Sn-1Cu-1Ni

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Lead cannot be used in solder alloys due to its deep-rooted toxicity. In the view of this fact, much legislation came into existence to prohibit the usage of lead in solder joints. Many lead free solder alloys came to replace the conventional Sn-Pb solder alloy. This study investigates the effect of addition of Ag (0.25, 0.5, 0.75, 1 wt.%) on the melting behavior, wetting characteristics, hardness and microstructure properties of ternary lead free solder alloy — Sn-1Cu-1Ni. Melting temperature is found to be decreased slightly from 232.2°C to 228.7°C. The distance between the adjacent atoms and the root mean vibration amplitude determines the melting temperature property. Ag₃Sn formed in the matrix has changed the melting point characteristics which resulted in the slight decrease of the melting temperature. Contact angle get reduced from 36.75° to 22.87°. Hardness value is found to be increased from 16.1 to 19.2. Ag is found to be uniformly distributed in the microstructure analysis. As far as the data available show, the microstructure of this lead free solder alloy consists of coarse β-Sn grains. Ag₃Sn, Cu₆Sn₅ and tin in the alloys are found in the eutectic region. The refinement of β-Sn grains is happened in a good manner due to the addition of particle of Ag. The recommended amount of Ag addition in to the Sn-1Cu-1Ni is 1wt.%. This lead free alloy can be used in electronic packages exposed to relatively high temperatures.

Keywords: lead-free, solder alloy, melting temperature, hardness, microstructure.

УДК: 539.21

Экспериментальное исследование влияния добавки Ag в тройной бессвинцовый сплав для пайки Sn-1Cu-1Ni

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Свинец не может быть использован в сплавах для пайки из-за сильной токсичности. Ввиду этого, было принято много законодательных актов о запрете использования свинца в припоях. Взамен обычного сплава для пайки Sn-Pb было предложено множество бессвинцовых припоев. В данной работе исследуется влияние добавки Ag (в количестве 0.25, 0.5, 0.75, 1 вес.%) на температуру плавления, характеристики смачиваемости, твердость и микроструктурные свойства тройного бессвинцового сплава для пайки Sn-1Cu-1Ni. Обнаружено некоторое снижение температуры плавления от 232.2°C до 228.7°C. Температура плавления определяется расстоянием между соседними атомами и среднеквадратичным отклонением амплитуд их колебаний. Соединение Ag₃Sn, образующееся в матрице, изменяет поведение вблизи точки плавления, что приводит к снижению температуры плавления. Контактный угол уменьшается с 36.75° до 22.87°. Твердость повышается с 16.1 до 19.2. Микроструктурный анализ показывает, что серебро распределено в материале однородно. Как показывают имеющиеся данные, микроструктура этого бессвинцового сплава состоит из крупных зерен β-Sn. В эвтектической области сплавов обнаруживаются Ag₃Sn, Cu₆Sn₅ и олово. Благодаря добавке Ag происходит измельчение зерен β-Sn. Рекомендуемое количество добавок Ag в сплав Sn-1Cu-1Ni составляет 1 вес.%. Этот бессвинцовый сплав для пайки может быть использован в электронных блоках, эксплуатируемых при достаточно высоких температурах.

Ключевые слова: бессвинцовый, сплав для пайки, температура плавления, твердость, микроструктура.

1. Introduction

For the last two decades solder alloys are having revolutionary changes because of the ban on lead in the alloy citing its inherent toxicity and environment issues. Strict government regulations and the demand from customers forced the advanced electronic package industries to progressively increase the usage of lead free solder alloys. [1,2,12]. The commonly used Sn-Pb alloy is therefore replaced by a large number of lead free alloy groups. As a replacement for the Sn-Pb alloy, following alloys are mainly used: Sn-Zn, Sn-Cu, Sn-Bi, Sn-Bi-Ag, Sn-Ag-Cu, Sn-Zn-Bi etc. [3–11]. Melting point, hardness, wetting property and the microhardness are the important properties that should be considered while selecting an alternate for the Sn-Pb alloy [13–16]. Sn-Cu received much attention as a lead free solder alloy choice when cost is considered as a variable. But Sn-Cu alloy is having inferior wetting characteristics and mechanical properties. [16–19]. The microstructural and mechanical properties of the lead free solder alloys can be improved substantially by the addition of foreign materials. The addition of Ni into the Sn-Cu enhances the properties of the solder alloy [20,21]. In this study, analysis is done on the perspective of the addition of Ag in to the ternary Sn-1Cu-1Ni alloy. The Ag is added in 0.25, 0.5, 0.75 and 1 wt.% into the solder alloy matrix of Sn-1Cu-1Ni. Hardness, melting temperature, contact angle and the microstructure of these five alloys (one sample of Sn-Cu-Ni and four samples of Sn-Cu-Ni-xAg) were analyzed. The amount of silver should be very carefully determined because of the fact that the silver will increase the cost of the solder alloy drastically.

2. Experimental procedure

2.1. Sample preparation

The most commonly followed method for the preparation of the solder alloys is powder metallurgy. The elements in the composition will be in the form of powder. This powder will be compacted as a green body. This is then sintered into the required shape at enhanced temperatures. Sn, Cu, Ni and Ag were made available in the form of powder and are allowed to melt at enhanced temperature of about 900°C for 45 minutes. This molten material is then transferred into specially designed cylindrical molds. All these five alloys with variation in the composition of Ag is allowed to quench and were kept in the room temperature for 2 days. Visual analysis of these alloys was conducted for the initial acceptance. These alloys were undergone chemical composition analysis.

2.2. Melting temperature analysis

Higher melting temperature of the solder alloy is considered as a bad property citing the fact that the electronic package will fail at higher temperatures. Melting temperature analysis of all the five samples were conducted using Thermo Gravimetric and Differential Thermal analysis (TG-DTA). Thermo Gravimetric analysis (TGA) measured the weight loss or gain as a function of temperature, the TGA trace appear as steps, it can be deal with the derivative of TGA

with respect to time or temperature. Differential thermal analysis (DTA) is a technique for recording the difference in temperature between a substance and a reference material as a function of time or temperature as the two specimens are subjected to identical temperature regimes in an environment heated or cooled at a controlled rate.

2.3. Microhardness measurement and wetting analysis

Abrasion and wear characteristics of a material can be assessed using hardness analysis. Hardness tests were performed using hardness testing machine. Each HV value was the average of fifteen different readings which were noted down at random points on the surface of the sample. Sample preparation was done using grinding by taking different grades of SiC papers. Then the samples were polished. The surfaces of the alloys were analyzed in Axio Vertical A1 metallurgical microscope before and after the microhardness test.

Wetting can defined as the ability of the molten solder alloy to react with the bottom substrate. Intermetallic compounds (IMC) will be formed which acts as the adhesion layer to join the solder and the substrate. The molten sample of the five alloys was spread over the Cu substrate. Then the contact angle is measured. Generally if the wetting or contact angle lies between 0° and 90° the system is said to be wet. If the wetting or contact angle is between 90° and 180° the system is considered to be non-wetting.

2.4. Microstructure analysis

Four grades of SiC papers were used for grinding the five alloy samples which is followed by the mechanical polishing with a diamond suspension. 95% ethanol solution/5% HCl is used for chemical etching. The surface details of the samples were analyzed by field-emission scanning electron microscopy (FE-SEM, Carl Zeiss Sigma). All the images were taken at a magnification of 5.00 KX, scale=1 μm, Electron High Tension (EHT)=5.00 Kv, Working Distance (WD)=3.2 mm

3. Result and Discussion

3.1. Chemical Composition

Five alloy samples were made with different composition. Chemical compositions of the alloys were analyzed using ICP-OES. The results of the analysis are shown in the Table 1.

3.2. Melting Temperature

The melting points of all the five samples were tested using TGA analysis. The results were noted down and a comparison is shown in the Fig. 1. It can be seen that the melting temperature of Sn-Cu-Ni alloy is 232.2°C. The melting temperature of Sn-Cu-Ni-xAg (x=0.25, 0.5, 0.75, 1 wt.%) are 231.2, 230.1, 229.4, 228.7 respectively. So it can be concluded that with the addition of Ag into Sn-Cu-Ni, the melting temperature is decreasing slightly. The distance between the adjacent atoms and the root mean vibration amplitude determines the melting temperature property.

Table 1. Chemical composition required (%) and the composition results (%).

Solder Alloy	Composition required (wt.%)				Chemical Composition results (wt.%)			
	Sn	Cu	Ni	Ag	Sn	Cu	Ni	Ag
Sn-0.5Cu-1Ni	98.5	1	1	0	98.4833	1.0180	0.9987	0
Sn-0.5Cu-1Ni-0.25Ag	98.25	1	1	0.25	98.2234	0.9987	1.0456	0.2321
Sn-0.5Cu-1Ni-0.5Ag	98	1	1	0.5	98.0734	1.0534	0.9875	0.4857
Sn-0.5Cu-1Ni-0.75Ag	97.75	1	1	0.75	97.7545	1.0134	0.9523	0.7798
Sn-0.5Cu-1Ni-1Ag	97.5	1	1	1	97.4845	0.9895	0.9675	1.0580

Ag_3Sn formed in the matrix has changed the melting point characteristics which resulted in the slight decrease of the melting temperature. The undercooling of Sn-Cu-Ni solder material is found to be decreasing slightly with the addition of Ag.

3.3. Hardness and Wetting

Contact angle as a function of Ag addition to the Sn-Cu-Ni solder is shown in the Fig. 1. It can be seen that the contact angle of Sn-Cu-Ni alloy is 36.75° . The contact angle of Sn-Cu-Ni- xAg ($x=0.25, 0.5, 0.75, 1$ wt.%) are $27.54^\circ, 26.44^\circ, 24.12^\circ$ and 22.87° respectively. Therefore, the contact angle is getting reduced as the Ag is added.

It can be found that the hardness value increases as the amount of Ag is increased in the Sn-Cu-Ni alloy. The hardness value of Sn-Cu-Ni alloy is found to be 16.1 HV, and when 1% of Ag is added to this alloy, hardness value is found to be increased to 19.2 HV. A comparison of microhardness value of these five alloys with SAC305 and SAC405 were also conducted. The microhardness property values of SAC305 and SAC 405 were taken as 13.47 HV and 13.98 HV.

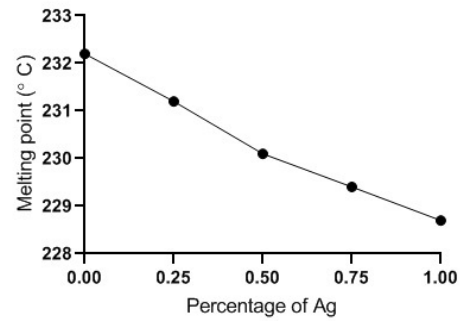
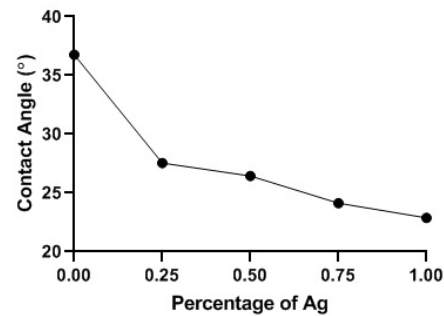
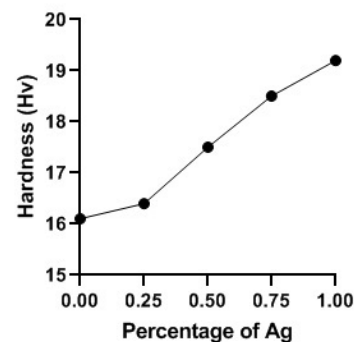
Comparison of variation of melting temperature, contact angle and hardness of the alloy with percentage of Ag addition are shown in Figs. 1, 2 and 3.

3.4. Microstructure analysis

As far as the data available show, the microstructure of this lead free solder alloy consists of coarse β -Sn grains. Ag_3Sn , Cu_6Sn_5 and tin in the alloys are found in the eutectic region. The refinement of β -Sn grains is happened in a good manner due to the addition of particle of Ag. Ag is found to be uniformly distributed on the solder matrix which can be observed from the microstructure analysis. Eutectic bands are found to be becoming narrow. The refined grain boundary is the reason for the slipping of the dislocation prevention. Another reason is the Cu_6Sn_5 dispersion at the grain boundary of β -Sn dendrites in a uniform fashion. Evaluation also revealed the α -phase Cu and β -phase Ag. The FE-SEM image of Sn-Cu-Ni when 1 wt.% Ag added is shown in the Fig. 4.

4. Conclusion

The mechanical and microstructure analysis of the effect of addition of Ag particles into the lead free solder ternary alloy Sn-1Cu-1Ni has been done. The Ag addition resulted in the slight decrease in the melting temperature. Ag_3Sn formed in the matrix have resulted in the slight decrease in the melting temperature. The microhardness of the alloys were found to

**Fig. 1.** Variation of Melting temperature.**Fig. 2.** Variation of Contact angle.**Fig. 3.** Variation of Hardness.

be increasing with the addition of the Ag. The prevention of sliding and the holding of the grain boundaries due to the presence of Ag in the solder matrix strengthens the microhardness of the alloy. When commenting about the wetting characteristics, a significant improvement is observed in the contact angle. The microstructure observations revealed that the Ag was uniformly distributed on the surface of the solder matrix. The recommended content of the Ag to be added into the Sn-1Cu-1Ni solder alloy is 1 wt.%. It can be used in the electronic packages in the automobiles where the temperature is relatively high.

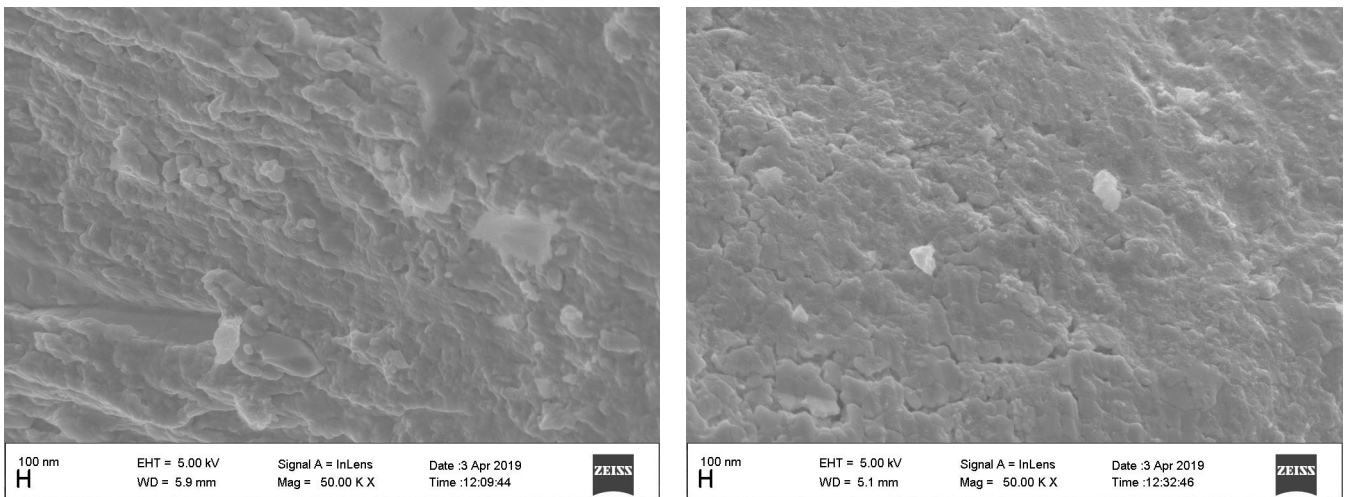


Fig. 4. Microstructures of the alloy at 50K X.

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