Effect of rare-element (Ga) addition on the microstructure and mechanical properties of Sn-0.7Cu and Sn-0.7Cu-0.05Ni lead-free solder alloys

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Abstract. The effects of rare element Ga on wettability, microstructure, and mechanical properties of Sn-0.7Cu (SC) and Sn-0.7Cu-0.05Ni (SCN) lead-free solder alloys were investigated. The experimental results show that Ga plays a positive role in improving the wettability and the microstructure of the solder. When the content of Ga is at 0.05 wt%, the grain size of the solder is smaller and the hardness is enhanced greatly. It is also found that the thickness of the IMCs at the solder/Cu interface is reduced with proper addition of Ga. The increase of mechanical properties may be related to the refining of IMCs of the solder due to Ga addition.

1 Research Background

Conventional Sn-Pb solders in microelectronic devices have been generally used since decades ago. The lead-free solder has been fully realized into electronic products due to environmental and toxicological issues [1-6]. Sn-0.7Cu-0.05Ni solder alloys free of lead are regarded to be one of Sn-Pb's most successful substitute candidates. [7, 8] In developing the electronics industry there were greater demands for lead-free electronic assembly. Because of reliability and property issues, the current Sn-0.7Cu solder does not fulfill the recent trends in electronic packaging. Therefore, the Sn-0.7Cu-0.05Ni solder idea for the next generation solder alloy was suggested [9-15], its prominent feature is the reduction of β-tin, which directly improves the mechanical reliability of the solder alloy. In the meantime, good soldering performance and mechanical properties of the solder can be achieved. Ga has a low melting point of 29.78 °C and a 3.4% increase in volume during solidification [16]. Moreover, it can be a very appealing property for microelectronic systems to weigh the majority of metals and oxides with no flux [17]. Previously, Ga was chosen by many researchers as a lead-free solder modifier. [18-20].

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Ga played a key role in enhancing the solders’ microstructure, melting performance and other characteristics. The objectives of this work are to investigate the effect of the Ga addition on the microstructure of Sn-0.7Cu and Sn-0.7Cu-0.05Ni solder alloys and to compare it directly with the based solder alloy. Furthermore, to explore the wettability and wetting reactions between the solder and the Cu substrate, and to prepare a new solder alloy with a fine microstructure and decent stability of properties.

2 Experimental

2.1 Solders design and preparation

The SC-xGa and SCN-xGa alloys were prepared from Sn-0.7Cu and Sn-0.7Cu-0.05Ni solder alloys supplied by Nihon Superior (M) Sdn. Bhd. (NSM) and 99.9 % Ga. The solders have been introduced to the proper amount of pure Ga (0 and 0.05wt%). The solder was kept for approximately 5 minutes, while every 1 minute the mechanical stirring was done carefully. For Ga addition samples, Ga was added to the melted alloys after the oxide layer formed on the top was removed and thoroughly mixed to ensure homogenous mixture occurred. The reflowed samples were cross-sectioned and mounted in resin. The polished bulk morphology of the solder joint has been observed using an optical microscope. The cast metals were then further processed for a microstructural study. The casting was carried out to allow the solder mixture liquid to attained the desired shape, and then let it solidify.

Table 1. List of Sn-based Solder Alloys Samples

| Base materials | Solidus Temperature (℃) | Weight of base alloy (g) | wt.% of Ga | Materials Designation |
|----------------|-------------------------|--------------------------|------------|-----------------------|
| Sn-0.7Cu       | 227                     | 150g                     | 0 Ga       | SC                    |
|                |                         |                          | 0.05 Ga    | SCN-0.05Ga            |
| Sn-0.7Cu-0.05Ni| 227                     | 150g                     | 0 Ga       | SCN                   |
|                |                         |                          | 0.05 Ga    | SCN-0.05Ga            |

2.2 Wettability test

The wetting balance method was adopted to test the solderability of the solder with a must 3 Wettability Tester Machine (GEN3 System) according to Japan’s Industry Standard JIS Z3198-4 for lead-free solders. The Cu strips (30 mm x 10 mm) were ultrasonic cleaned in acetone for 3 min, then cleaned in ethanol and dried before testing. Wetting force and wetting time were tested at 250 ℃ temperature to assess the wetting characteristics of the solder. Besides, the water-soluble flux was used to enhance wettability during the experiment and the temperature, velocity and moment of immersion were 2 mm, 4 mm / s and 10 s respectively. The tested result here was a mean value of five tests.
2.3 Microstructure analysis

The samples of solders were prepared by polishing with 0.3 μm of Al₂O₃ dust according to the United States Department of Defence MILSTD-883 [21]. Optical camera and imaging microscopy (SEM) have been used for observing the microstructure. The samples were perpendicular to the solder / Cu interaction on the solder joints in the first interaction study. SEM was used to test the morphologies of the surfaces, and power dispersive X-ray (EDX) was used to determine the chemical characteristics.

2.4 Mechanical property test

Due to geometric effect as well as the formation and evolution of the brittle IMC at the interface, the solder/substrate interface is the weakest part of a solder joint. The nature of the force of the solder joints is usually the interfacial shear stress caused by the expansion failure. To assess the reliability of the solder joints, the Vickers hardness test was carried out. The machine operated according to the ASTM B933-09 standard test method. Before been test, the sample will be grinded using Si-C sandpapers (200, 320, 400, 600, 800 and 1200) grit size and indentation load of 1kg for a 10s dwell time. The precision of the median outcomes is calculated using 10 indention marks for each sample. Without checking the hardness values of Vicker’s output resistance and the final tensile strength can be measured. Using formulas, yield strength (YS) and ultimate tensile strength (UTS) can be calculated.

3 Results and Discussion

3.1 Wettability of solder alloys

To get a magnificent solder joint, decent wetting properties are a prerequisite. The Wettability and wetting reactions between the solder and Cu substrate have been investigated in this research work. Figure 1 shows the wetting time and wetting forces of SC-xGa and SCN-xGa solders at 250 °C temperature. At this temperature, it can be seen that the wetting time significantly increase at Ga addition of 0.05 %, and then gradually increases. The most significant increase is when added to the SCN solder alloy the wetting force exhibits the same trend. Klein et al. [22] pointed out that the short wetting time and high wetting force are considered to be excellent. Consequently, the wetting properties of SC and SCN solder alloys can be enhanced momentously with the addition of Ga and the best wetting properties can be attained with a Ga addition of 0.05wt%. The liquid solder takes capillary caulking during the soldering process and it diffuses mutually with the base metal at the same time, liquid solder must penetrate the surface of the base metal to fill the solder joints. The droplet placed on a solid surface, if the change in the droplet and the solid interface lowers the liquid-solid system free energy, the droplet will flow automatically along the solid surface. This is based on the basic principles of physical chemistry.

Any element that can improve the interfacial pressure of solid gases or decrease the interfacial pressure of liquid gases or liquid gases can enhance solder's wetting characteristics. Besides, Ga can easily accumulate at the solder interface in the molten state because of its surface-active element characteristic. Therefore, the surface tension of the liquid solder is reduced, enhances flexibility, which results in better solderability [23]. Moreover, Ga segregated seems to react with Sn, decrease the function of Sn and suppressing the excessive reaction of the interface. In the meantime, the wettability is enhanced caused by the diffusion between the solder and Cu substrate becomes effortless.
Additionally, the diffusion movement between the liquid solder atoms and the surface atoms at high-temperature increases, i.e. the velocity of diffusion is increasing and the solderability improves.

![Figure 1](image)

**Fig. 1.** Wetting properties of Sn-0.7Cu and Sn-0.7Cu-0.05Ni solder alloys with the addition of Ga at 0.05wt%

| Solder Alloy Designation | Wetting Force, Fmax (mN) | Wetting Time, 2/3 Fmax (s) |
|-------------------------|--------------------------|---------------------------|
| SC                      | 2.14                     | 4.00                      |
| SC-0.05Ga               | 2.87                     | 3.64                      |
| SCN                     | 2.81                     | 3.66                      |
| SCN-0.05Ga              | 4.69                     | 3.44                      |

### Table 2. List of the SC and SCN solder alloys that involved in the wetting balance test

3.2 Microstructure analysis of the solder alloys

The microstructure morphology from the optical microscope of SC-xGa and SCN-xGa is shown in **Fig. 2.** In **Fig. 2.,** the microstructure of SC-xGa and SCN-xGa base solder consists of β-Sn matrix phase, bulk intermetallic and eutectic structures [7]. Compared with the microstructures of based Sn-0.7Cu and Sn-0.7Cu-0.05Ga solder alloy, the solder alloys with the Ga addition shows the smaller dendritic formation of crystal β-Sn phase. This is mainly because the nearly eutectic composition is at Sn-0.7Cu-0.05Ni [24], of which the content of Ga is in quite a great difference from Sn-0.7Cu. Large IMCs formation may well affect the mechanical reliability of the solder because of their high hardness [25]. Not only that, the matrix structure is refined—the coarse IMCs become smaller and distribute more uniformly with the addition of Ga. Although, this paper only shows 0.05wt% addition of Ga, a range of a proper amount of Ga addition will be a later study to get the optimum addition percentage. But, for now at least the Ga show a positive effect to especially to the microstructural formation. When the content of Ga reaches 0.05wt%, the most uniform structure is obtained and the grain achieves the highest degree of refinement. There are two main primary explanations, according to the adsorption theory. First and foremost, the adsorbed Ga reduces the surface energy difference of the crystal surfaces. Secondly, due to the pinning effect, the growth rate of the crystal surface adsorbing Ga is reduced, thus the formation of the grains get smaller and distribute homogeneously. The IMC particles are small and uniformly dispersed instead of large and coarse, and therefore the mechanical properties of the solder can achieve the best in this component as well. However, the optimum value of the Ga addition still will be carried out. As depicted in **Fig. 3.,** the result
of the SEM-EDX analysis for the Sn-0.7Cu-0.05Ga solder alloys is shown. The EDX analysis shows that the black phases consist primarily of Sn, Cu, and Ga, the existence of which may also affect the mechanical properties of SC and SCN solder joints. Based on the result, Ga mostly distributed at the primary IMC at 0.30 atomic percentage, wt% while at the bulk solder interface the reading recorded 0.02 atomic percentage wt%. **Fig. 4.** shows the elemental mapping of SC and SCN solder alloys.

**Fig. 2.** Optical micrographs show the microstructure of designated lead-free solder alloys: a) SC, b) SCN, c) SC-0.05Ga, and d) SCN-0.05Ga solder alloys

**Fig. 3.** SEM-EDX analysis of the Sn-0.7Cu-0.05Ga solder alloys
3.3 Mechanical properties of the solder alloys

In this research, as shown in Fig. 5, the maximum hardness impact of the solder alloys evaluated. The hardness can be improved significantly with the addition of Ga. When the addition of Ga was 0.05 %, the shear strength increased linearly. The reason for this is primarily the refinement of the bulk solder microstructure and soldering interface by Ga. In the meantime, when the Ga addition is at 0.05wt %, the maximum shear strength is obtained. Although this is only one range of the parameter, the best addition of Ga incorporated at SCN solder alloy. Not only that, the modified solder matrix is good for the mechanical properties of the solder alloy based on the fine-grain strengthening theory [26]. On the basis of the Ga-Sn phase diagram, Sn exhibits a maximum solubility of 6.4 % of Ga, so Ga may form a solid solution strengthening with Sn in this study. The dissolution of Ga in Sn contributed by the mechanical strengthening effect. Though, the produced Ga-rich phases of Sn, Ga and Cu may have an adverse effect on mechanical properties as the addition of Ga continue to raise. For now, it cant be concluded how much the appropriate amount of Ga content in SC and SCN solder alloys. But further research work and parameters will tackle this issue soon.
Fig. 5. Average microhardness for Sn-0.7Cu and Sn-0.7Cu-0.05Ni solder alloys with addition of 0.05 Ga %

4 Conclusion

From this preliminary study, this research work investigated the effect of Ga addition on the microstructure morphology and mechanical properties of Sn-0.7Cu and Sn-0.7Cu-0.05Ni lead-free solder alloys. Below are the early subsequent conclusions can be obtained:

1. The solderability of Sn-0.7Cu and Sn-0.7Cu-0.05Ni lead-free solder alloys was significantly improved by adding Ga and the solder achieves the peak values at the addition of 0.05 %. Besides, when applying the suitable temperature, the wetting performance can be enhanced greatly as well.

2. For this early result, the correct amount of Ga addition still is research. But the addition of 0.05 Ga can effectively improve the mechanical properties of the solder joints as a result of the smaller dendritic formation of crystal β-Sn.

With all due respect, this research project was mainly under the collaboration between Universiti Malaysia Perlis (UniMAP) and Nihon Superior (M) Sdn. Bhd. under CREST’s grant. The authors wish to deliver their gratitude to Higher Education Malaysia, Universiti Malaysia to Higher Education Malaysia, Universiti Malaysia Perlis (UniMAP), Nihon Superior (M) Sdn. Bhd. and CREST Grant Scheme no. P14C1-17/001 for financial supports, equipment-wise, and experiment setup.

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