Study of the Interface Microstructure of Sn-Ag-Cu Lead-Free Solders and the Effect of Solder Volume on Intermetallic Layer Formation.

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Abstract

Although the primary driver for the current interest in developing lead-free soldering is global market pressure for more environmentally friendly products, the main concern continues to be lead contamination from end-of-life electronic products in landfill sites. In response to existing and impending legislation in Europe and Japan for the elimination of lead from electronic products, the industry has embarked on a number of studies in search of suitable lead-free alternatives. Several reports [1,2] have been published, but there are as yet no drop-in solutions with respect to reflow temperature, joint reliability and assembly costs. Our survey show that the Sn-Ag-Cu alloy is one of the promising lead-free alloys currently being evaluated by industry. There are however a number of issues regarding the use of Sn-Ag-Cu alloys, including the solderability and long-term reliability of the solder joints, which require further study. The lower solderability of Sn-Ag-Cu solder can alter the interface and microstructure of the solder joint formed because of the differing reaction rates between the molten solder and substrate surface. This also has an impact on the nature and extent of the intermetallic compounds formed at the interface, as the intermetallic is generally more brittle than the base metal. This can negatively impact the solder joint reliability.

In this paper we report a study on the effect of solder volume on intermetallic layer formation and thickness. For lead-free soldering this could prove to be very important, as a wide range of devices and components of varying joint size, e.g. plastic quad flat pack (PQFP), ball grid array (BGA), chip-scale packaging (CSP), and flip chip, may need to be assembled on a typical board. This means that the nature and thickness of the intermetallic layer formed for each joint size will be different. In the study, solder joints of different sizes representing different devices were used for evaluating the effect of solder volume on intermetallic compound formation. The layer thickness and microstructure were analyzed using scanning electron microscopy (SEM). SEM analysis was also carried out on joint micro-sections, which has undergone temperature cycling to evaluate the effect of intermetallic layer the joint reliability. Our results show that increasing the solder volume (and solder joint size) does not significantly affect the growth of the intermetallic layer thickness. Therefore the intermetallic layer thickness provides the lower limit for solder joint design for ultra-fine pitch flip-chip applications.

Key words: Lead-free soldering, tin-silver-copper alloys, intermetallic compound formation, and solder joint reliability.

2. Introduction

Tin/lead solders are the primary materials used for interconnecting electronic components. However, the safe use and disposal of lead-containing electronic products is an issue that is attracting considerable interest from both environmental pressure group and increasingly, from legislative bodies. It is widely anticipaded that the use of lead containing solders by the electronic industry will be seriously constrained by a legislative ban on lead use in solders. An example of the legislation is the environmentally conscious engineering in electronics committee in Japan, who have scheduled that lead-free solders should become standard by 2003. Furthermore, European legislation under the Waste from Electrical and Electronic Equipment (WEE) is scheduled to eliminate the lead from electronic products by the year 2008. Besides the legislation, some European countries have considered imposing a new regulation requiring the manufacturers to take full responsibility for the recycling of their products [3]. In addition, switching to lead-free soldering can bring some advantages, in particular by improving the reputation of companies who are environmentally conscious. There are also potential technical benefits as well as cost savings in assembly and manufacture.

The industry has embarked on a number of studies in search of suitable lead-free alternatives but there are as yet no drop-in solutions with respect to reflow temperature, joint reliability and assembly costs [1,2]. Our survey show that the Sn-Ag-Cu alloy is one of the promising lead-free alloys currently being evaluated by industry. The optimal composition in this alloy is 95.4Sn/3.1Ag/1.5Cu [4], which has good strength, fatigue resistance and plasticity. The additional benefits of this alloy are the availability. There are however a number of issues regarding the use of Sn-Ag-Cu alloy, including its solderability and long-term reliability of the solder joints, which require further study.

The lower solderability can alter the interface and microstructure of the solder joint formed because of the differing reaction rates between the molten solder and substrate surface. This has an impact on the nature and extent of the intermetallic compounds formed at the interface. The Intermetallic Compound (IMC) is the actual bond formed in soldering from the interdiffusion of two or more metals [5]. Besides its advantage for bonding the solder and the substrate, its disadvantage is that it is generally the most brittle part of the solder joint. This can negatively impact the solder joint reliability. In addition, electronic components vary in their size, starting from plastic quad flat pack (PQFP), ball grid array (BGA), chip-scale packaging (CSP), and flip-chip and each size of the joints will have different interface microstructure behaviours. Therefore, The objective of this paper is to investigate the intermetallic compound thickness of Sn-Ag-Cu solder on different solder joint size.

The thickness of the intermetallic compound layer depends on a number of factors, such as temperature/time, volume of solder, property of the solder alloy and morphology of the deposit [6]. The IMC growth rate in terms of temperature dependent can be described in the following equation:

$$z_o = \sqrt{Dt}$$

Where:

z_o = the intermetallic layer thickness [m]

D = overall diffusivity for growth of the intermetallic layer [m^2s^{-1}]

t = time [s]

The overall diffusion (D) varies with temperature and is given by the Arrhenius equation:

$$D = D_o \exp^{\left(-\frac{Q}{RT}\right)}$$

Where:

D_o = the diffusion coefficient [m^2s^{-1}]

Q = the activation energy for intermetallic growth [$J.mol^{-1}$]

R = Boltzmann constant = 8.314 [$J.mol^{-1}.K^{-1}$]

T = temperature [K]

Results on the study of the IMC growth under various temperatures [5,6,7,8,9] are in agreement with the above equation. A power law equation has also been used to model the isothermal growth kinetics of the intermetallic layer thickness [11].

A number of studies have been reported [6,8,10], aimed at understanding the properties of the intermetallic layer of solder joints. These studies have been mainly directed to the modelling of the growth of the intermetallic layer in the solid state condition. For instance, the growth kinetics and mechanical behaviour of intermetallic in the eutectic Sn-Ag and Sn-3.5Ag-Zn alloy have been reported [8]. This study found that the Cu_6Sn_5 and Cu_3Sn intermetallic layers are formed in the interface between the eutectic Sn-Ag alloys and Cu substrate, but in the Sn-3.5Ag-Zn joint only the Cu_6Sn_5 intermetallic layer is formed. In addition, the diffusion coefficient of Cu_3Sn is smaller than that of the Su_6Sn_5. In another study, experiments for investigating the intermetallic growth between 62Sn-36Pb-2Ag solder alloy and Pd-Ag metallisation has been reported [10]. This study concluded that the intermetallic compound layer formation, and in particular the tin diffusion led to the degradation of fatigue life, the strength and the electrical contact quality of the solder joint. A further study, which investigated the formation of intermetallic layers in lead-free solder alloys have been reported [6]. They investigated the effect of solder volume on the IMC thickness by experimenting with two different soldering techniques (wave and reflow soldering). For wave soldering, joints are formed by using a massive solder volume, whilst reflowed solder joints are formed with a much smaller solder volume. Their results show that the quantity of IMC formed during joint formation is a function of the temperature, the time, the volume and the composition of the joint. Unfortunately, the study did not include experiments on the effect of the solder volume on intermetallic growth, and in particular the effect of temperature. This is the main focus of this paper.

Other studies on intermetallic phase formation have been reported [5, 11]. In the first study [5], the main focus was on the description of the combine effects of intermetallic growth and intermetallic dissolution for solder-substrate systems. The second study was concerned with the investigation of how the process parameters (time and temperature) and joint design (substrate area and solder volume, A:V ratio) influence the intermetallic layer formation [11]. They concluded that the large A:V ratio joint would experience faster IMC growth and dissolution. Unfortunately, the study did not quantify this effect.

In another study [9] the interfacial morphology and concentration profile of IMC's in solder joints has been presented. The results shows that the Cu_3Sn intermetallic is formed on the copper side whilst the Cu_6Sn_5 intermetallic forms on the solder side. The study of the concentration profile can provide better understanding of the intermetallic layer formation process.

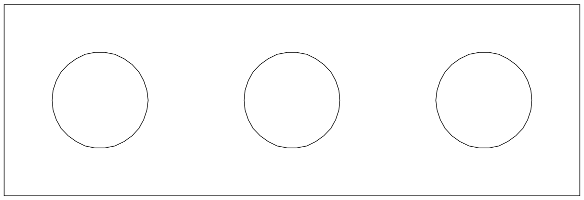
3. Research Methodology

To evaluate the effect of solder volume on intermetallic compound formation, different volumes of solder paste were reflowed on the specimen board, as seen in figure 1. Two types of the specimen board was used: type A which had three pads of the same dimension (figure 1a) and type B which had different pad size board (figure1b). The dimensions of the pads are as follows: 2.5mm for type A, and 2.0mm, 2.5mm and 3.6mm, for the type B.

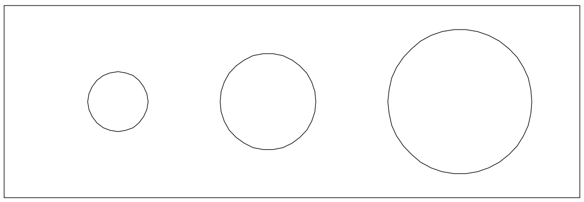
The stencil used for printing the solder paste was 0.7mm thick and had three round apertures of 2.4mm, 3.0mm and 4mm diameter size respectively. Printing tests were performed and the evaluation was conducted by measuring the weight of the solder bumps. The results show good yield with deviations of approximation one milligram.

The weight of the solder bumps created with this stencil are as follows: 10mg, 15mg and 28mg for 95.5Sn/4.0Ag/0.5Cu alloy and 4mg, 6mg and 15mg for 63Sn/37Pb alloy.

The solder pastes were 95.5Sn/4.0Ag/0.5Cu and 63Sn/37Pb alloys. Figure 2 and 3 show the reflow profile of 95.5Sn/4.0Ag/0.5Cu and 63Sn/37Pb alloys respectively. The solders were reflowed using a convection reflow oven.



a. Specimen Board Type A having the same pad sizes



b. Specimen Board Type B with different pad sizes

Figure 1. The Specimen

After different volumes of solder bump samples were formed, they were stored in a constant temperature chamber at 120°C for 100, 200 and 300 hours. The purpose was to investigate the microstructure changes at the higher temperature. The climatic chamber was Heraeus - HC4020. Finally, each of the samples was cross-sectioned and viewed with an optic microscope and SEM for intermetallic compound layer growth and the microstructure investigations.

4. Result and Discussion

Figure 4a to 4d present the microstructures of the 95.5Sn/4.0Ag/0.5Cu alloy. Before isotherm ageing, some column microstructures (figure 4b) were observed in the medium and the large size bumps of the specimen B and no column microstructures were present in the small bumps. These microstructures were also formed near the interface of specimen A's solder bumps.

For 100 hours ageing, the column microstructures became smaller and white colonies of equiaxed grain were present (figure 4a). For 200 hours ageing, the column microstructures continuously became smaller (figure 4c). For 300 hours ageing, the white colonies moved apart (figure 4d) and no column microstructures were observed.

The presence of the column microstructure maybe because the bigger size bumps experience a slower cooling rate, even though the same reflow profile was applied to all solder bumps. It is known that at sufficiently fast cooling rates, the microstructure grain becomes finer [13]. Furthermore, it means that this type of experiment can be used to investigate the effects of the cooling rate to the microstructure of the Sn/Ag/Cu alloy.

Figure 4e and 4f respectively show the initial morphology and the morphology after ageing above 100 hours of intermetallic compound layer for 95.5Sn/4.0Ag/0.5Cu alloys. The thickness of the intermetallic layer is not uniform in any case and this is owing to the combined effects of the morphology of the layer immediately after freezing together with the effect of crystallographic orientation on diffusion rate. Figure 4f displays the unusual spiked structures in the intermetallic layer, which grows longer with increasing ageing time.

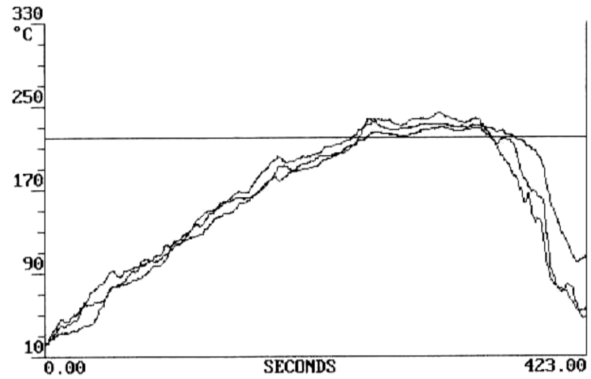


Figure 2. The Reflow Profile of Sn/Ag/Cu Solder Alloy

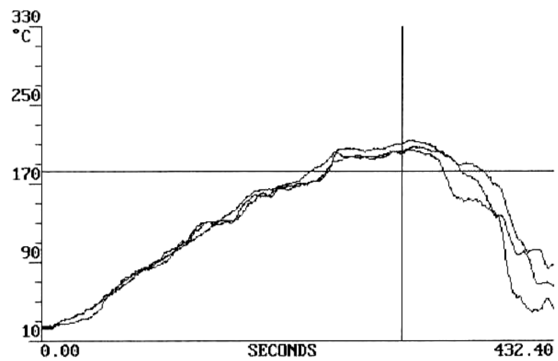
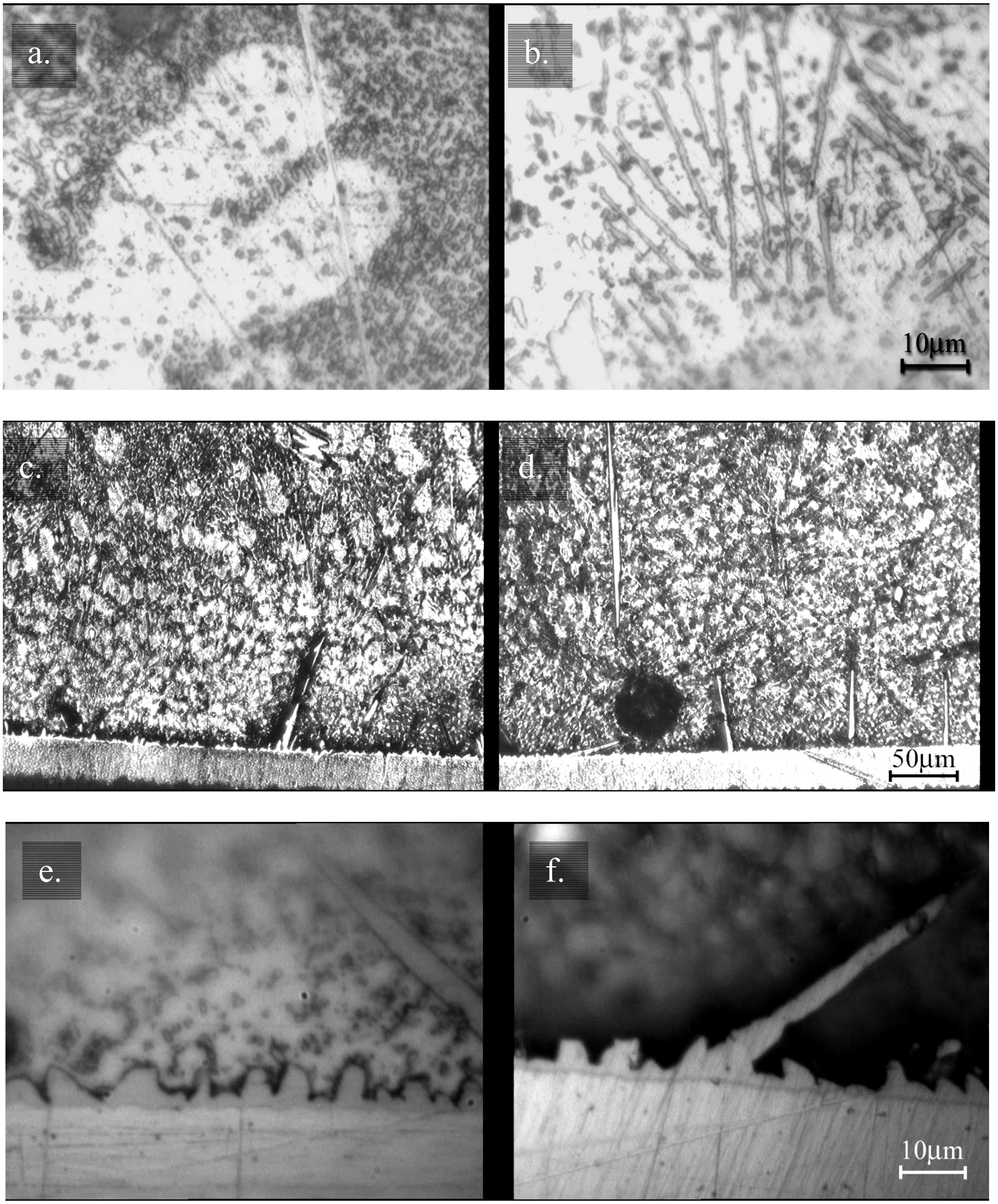


Figure 3. The Reflow Profile of 63Sn/37Pb Solder Alloy

Figure 5b shows the microstructures of the 63Sn/37Pb alloys before stored in a constant temperature chamber. After ageing, the microstructure sizes were increasing (coarsening), which this is in line with the earlier discussed literature [11].

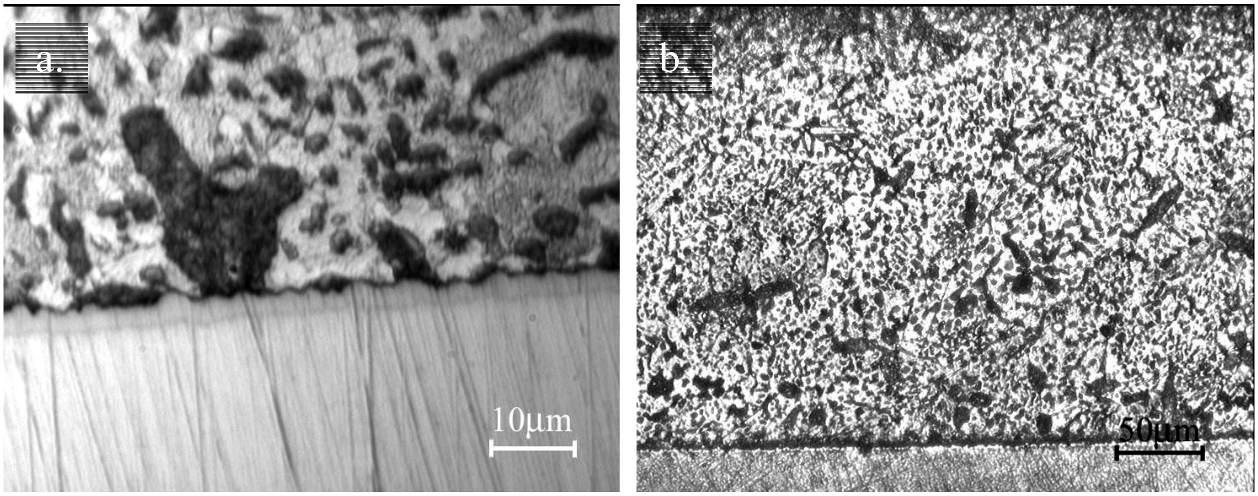
Figure 5a shows the intermetallic layer of the 63Sn/37Pb alloy after ageing 300h in a constant temperature chamber. The initial intermetallic morphology of the the 63Sn/37Pb alloys looked like figure 5a and the thickness of the intermetallic layer was quite uniform.

Figure 6 & 7 show the rate of growth of intermetallic compound on copper substrate with 95.5Sn/4.0Ag/0.5Cu and the 63Sn/37Pb alloys at 120°C. The area of pad to solder volume ratio (A:V) for specimen A (the similar pads) are 15.1, 9.8 and 5.3 and 9.6, 9.8 and 10.9 for specimen B (the different dimension pads). The A:V ratio of specimen B appears to be relatively similar. With large A:V ratio, the Cu saturation will occur rapidly and only after the Cu saturated in the joint, the intermetallic layer can start to grow [11]. The initial intermetallic thickness of Sn/Ag/Cu alloy in figure 6 for



a. Round Colonies in The Microstructure of 95.5Sn/4.0Ag/0.5Cu Solder
b. The Column Shape Microstructure of 95.5Sn/4.0Ag/0.5Cu Solder
c. The Shrinking Column Microstructure after Ageing above 200 hours.
d. The Round Colonies after Ageing above 300 hours
e. The Intermetallic Compound Layer of 95.5Sn/4.0Ag/0.5Cu before Ageing.
f. The Spiked Intermetallic Compound Layer of 95.5Sn/4.0Ag/0.5Cu after Ageing above 100 hours.

Figure4. The Microstructure and Intermetallic Compound Layer of 95.5Sn/4.0Ag/0.5Cu Alloy



a. The Intermetallic Compound Layer of 63Sn/37Pb Alloy after Ageing at 120^{o}C for 300h
b. The Microstructure of 63Sn/37Pb Alloy before ageing

Figure5. The Microstructure and Intermetallic Compound Layer of 63Sn/37Pb Alloy

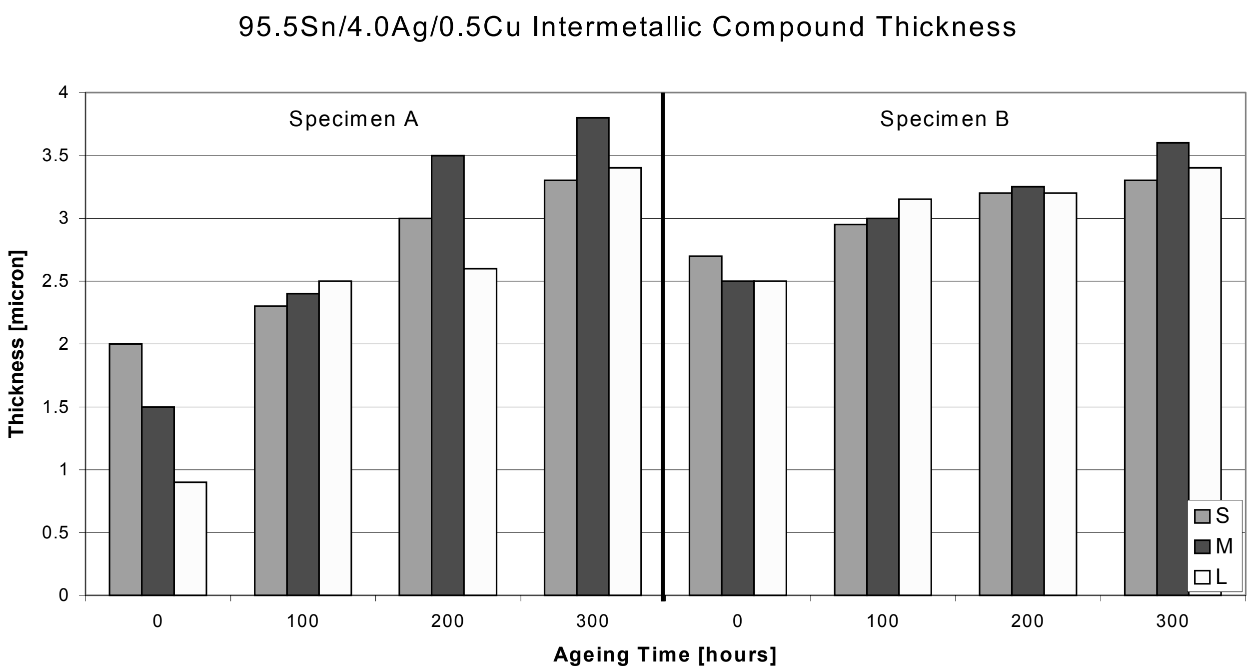


Figure 6. Intermetallic Compound Thickness of Sn/Ag/Cu Alloy at Room Temperature and Ageing at 120^{o}C for 100, 200 and 300 hours

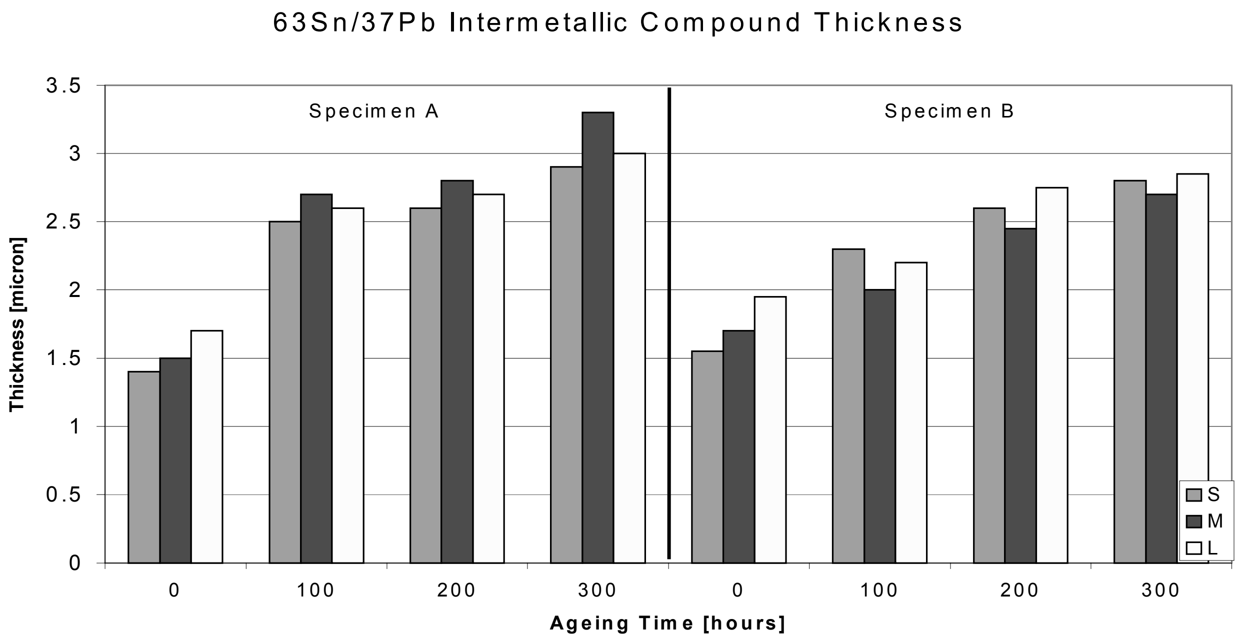


Figure 7. Intermetallic Compound Thickness of Sn/Pb Alloy at Room Temperature and Ageing at 120°C for 100, 200 and 300 hours

specimen A are thinner from small to big joint since the A:V ratios for specimen A are smaller from small to big joint so that Cu saturation of the small joint occurred faster than the other joints. Then this started the intermetallic of the smaller joint to grow first and became the thickest. However, this rule did not applied to Sn/Pb alloy, figure 7. It might be that in Sn/Ag/Cu alloy, the time required to approach Cu saturation is faster than the time of Sn/Pb alloy to approach Cu saturation, which the Sn-Ag-Cu alloy could reach Cu saturation during reflow.

From the results of the intermetallic thickness, no significant difference or trend of intermetallic compound thickness between different solder joint sizes was found either for 95.5Sn/4.0Ag/0.5Cu or for 63Sn/37Pb alloys. This fact implies that the size of the joint might be limited because as the joint gets smaller, the intermetallic layer thickness stays the same. For illustration, if solder joint height of future electronic component is around 50µm and the working temperature is 120°C. The joint would only last for 1000-1500 hours since the estimated intermetallic compound thickness, ageing at 120°C for 1000 hours, is around 15µm or thirty percentage of its solder joint height.

The growth rate of the intermetallic layer for 95.5Sn/4.0Ag/0.5Cu alloy was higher than that of the 63Sn/37Pb alloy, as seen in figures 6 and 7. However, The reliability of the Sn/Ag/Cu alloy might not be lower than that of 63Sn/37Pb alloy because the joint shear strength of Sn/Ag/Cu is 27 N/mm^2 which is higher than that of the Sn/Pb, 23 N/mm^2 [12].

Finally, the results of the intermetallic thickness measurement, as seen in figure 6 and 7, indicate that the microstructures formed in the different solder joint sizes do not influence significantly the growth of the intermetallic compound layer.

5. Conclusions

In this paper, results on the effect of solder volume on intermetallic layer formation and thickness has been presented. In the study, solder joints of different sizes representing different devices were used for evaluating the effect of solder volume on intermetallic compound formation. The layer thickness and microstructure were analyzed using scanning electron microscopy (SEM). SEM analysis was also carried out on joint micro-sections, which has undergone temperature cycling to evaluate the effect of intermetallic layer the joint reliability. Our results show that increasing the solder volume (and solder joint size) does not significantly affect the growth of the intermetallic layer thickness. Therefore the intermetallic layer thickness provides the lower limit for solder joint design for ultra-fine pitch flip-chip applications.

6. Acknowledgement

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