IMPACT OF LANTHANUM DOPING ON SAC305 LEAD FREE SOLDERS FOR HIGH TEMPERATURE APPLICATIONS

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ABSTRACT

The environmental concerns over the toxicity of lead- bearing electronics are forcing electronic industry to use lead-free solders. Among various lead-free candidate material, Sn-3.0Ag-0.5Cu (SAC305) appeared as a strong candidate. However, due to the coarse microstructure and formation of hard and brittle Inter-Metallic Compounds (IMCs), a number of reliability problems are hindering its use in high-temperature microelectronics. To improve the properties, a number of researchers used the Rare-Earth (RE) materials to refine the microstructure of lead-free solders due to their surface-active properties. The focus of this research is to investigate the effect of lanthanum-doping and thermal aging on the growth of the IMCs of SAC305 solder alloy in terms of size and dispersion. It was observed that addition of lanthanum refined the microstructure to a great extent by reducing the IMCs particle size.

KEYWORDS: *lead-free solders, SAC305, lanthanum doping, thermal aging*

INTRODUCTION

Soldering is a low-temperature bonding technique to join metals by introducing a pool of molten metal, the solder, between them[1]. Lead-based solders were traditionally used to join components in the circuit boards in many commonly used electronic devices including computers and mobile phones[2]. The lead-bearing solders offer numerous benefits such as low melting temperature, ductility and excellent wetting on copper and its alloys[3].

The increasing environmental concern over the toxic nature of lead (Pb) and the resulting environmental regulations in some countries to ban the use of lead has led to vigorous development of alternative lead-free solders[1, 4-6]. Since mid-1990s, a number of industrial and academic researchers have conducted substantial research in search of replacement materials. Though no reliable and cost-effective solution has yet been proposed for tin-lead solder. However, tin-based solders with elements such as silver, copper, antimony and bismuth are leading candidate materials[7]. Due to better thermo-mechanical properties, SAC alloys are considered as the most promising choice and therefore covers a big market place as compared to its other competitor alloys. A number of industrial consortiums have proposed the use numerious types of SAC alloys for use in electronic industry. For example, the Japan Electronic Industry Development Association (JEIDA) has recommended 96.5wt%Sn-3wt%Ag-0.5wt%Cu (SAC-305). The US consortium - National Electronics Manufacturing Initiative (NEMI) has recommended 95.5wt%Sn-3.9wt%Ag-0.6wt%Cu (SAC-396) for reflow soldering and 99.3Sn-0.7Cu for wave soldering. The European Consortium - the Industrial and Materials Technologies Program Brite-Euram - recommended 95.5wt%Sn-3.8wt%Ag-0.7wt%Cu (SAC-387)[8].

Although, SAC-305 alloy is commonly used as a lead- free solder alloy in many electronics industries, it has several problems to be solved. One of the core issues pertaining to SAC-305 is the formation and growth of large intermetallic compounds (IMCs)[9]. IMCs are produced as a result of chemical reaction between solder material with copper[10, 11]. Though, the presence of a thin layer of IMCs is desirable because it improves metallurgical bonding[11]. However, a thick IMCs layer significantly reduces the reliability of the solder joints due to the their brittle nature and tendency to generate structural defects[11-13].

Prolonged exposure to high thermal environment increases the growth of IMCs[14, 15]. For example electronic devices in oil and gas, aerospace and automotive industry are subjected to severe vibration and very high temperature as compared to consumer electronics[16, 17]. In such high temperature applications, the increased growth of IMCs increases the possibility of solder joint failures and thus are subjected to compromised stability and reliability[18, 19].

To address these issues, the Rare Earth (RE) elements

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have been used by many researcher[20, 21]. Addition of small amount of RE elements to metals can significantly refine the microstructure, and thus improves the mechanical properties. Due to this unique nature, RE elements are extensively used in the field of materials and metallurgy[22].

Some studies reported that RE elements agglomerate at the grain boundaries and changes the growth velocities between the crystalline directions of the polycrystalline IMC, which restrain the growth of the IMC particles and distributes them uniformly[23]. Several studies have been conducted to find the effect of RE doping in solder alloys. These studies demonstrated that RE doping increases the wetting property of solder[20, 21, 24-28], enhances the mechanical strength and creep rupture life of solder alloys, promotes strong bonding at the soler-metal interface[29-32], reduces IMCs size and their growth[33]. Some researchers suggest that the smaller size of the RE elements atomic radius compared to Sn make them gather at defects[34, 35]. All these factors significantly contribute to increase the reliability of solder joint.

In the present study RE Lanthanum-La is selected for the investigation. The main objective of this paper is to study the effect of adding small amount of La on the microstructure and IMS formation of SAC-305 solder alloy with varying environmental conditions implemented during service. Lanthanum (La) is considered as the best doping element for SAC solder alloys due to their lower cost, wide availability and low melting point compared to the other RE elements.

EXPERIMENTAL PROCEDURE

In this research work, the effect of three major parameters on the microstructure and mechanical properties of lead-free solder alloys are studied. These parameters are: RE additions, thermal aging temperature and thermal aging time. The first parameter is to understand and explore the impact of lanthanum (La) doping on SAC alloys. Therefore, three different La compositions are selected for this study along with an undoped SAC alloy. The composition of the sample alloys is given in Table 1.

For thermal aging, the samples were kept for a set period of time in a high temperature oven. Two levels of temperature were used for the thermal aging: 90°C and 180°C. Similarly, two levels 60 hours and 120 hours were used as aging time factor. Including no thermal aging condition (as-cast), there were 5 combinations of thermal treatment on the specimens and considering the four alloy compositions used in this study, there were 20 (4x5) test conditions.

Table 1: Composition of selected solder alloys

Solder Alloy	Elemennt (wt%)			
	Sn	Ag	Cu	La
SAC305	96.500	3.000	0.500	0.00
SAC305-0.05La	96.452	2.999	0.499	0.05
SAC305-0.25La	96.259	2.993	0.499	0.25
SAC305-0.5La	96.018	2.985	0.498	0.50

The 96.5Sn3.5Ag0.5Cu solder was obtained from Nathan Trotter & Co., in the form of solder bar. Other La doped SAC305 alloys were obtained from Atlantic Metals & Alloys Inc., in the form of solder bar. All samples were cross-sectioned and were ground by different sized silicon carbide (SiC) emery papers in a sequence of 320, 600, 800, 1000 and 1200 and subsequently polished with diamond paste (6 µm, 3 µm and 1 µm) and 0.05-µm alumina suspensions. Pressurized water coolant was applied during the grinding process to prevent sample heating. Ultrasonic cleaning for 2 minutes was carried out after each step of diamond paste polishing to remove any diamond abrasive on the sample surface. Polishing with alumina suspension does not reveal the precipitates. To reveal the precipitates, the sample was again polished with alkaline 0.05µm silica suspension. The alkaline solution preferentially etches the Sn grains at a higher rate and therefore helps to clearly identify the Ag_3Sn precipitates[36].

Table 2: Etching time

SAC Alloy	Etching Time (sec.)
SAC305	9
SAC305-0.05La	18
SAC305-0.25La	28
SAC305-0.5La	58

After polishing, the samples were then etched. The etching time for each composition is shown in Table 2.

RESULTS AND DISCUSSION

The SEM micrographs of various SAC305 and SAC305-La solder alloy samples obtained for the analysis are shown in Figure 1. The microstructure is composed of a soft Sn matrix and hard IMCs of Ag and Cu with Sn. The dark grey areas is the matrix material that is mainly composed of Sn and the light grey area are the IMCs. The IMCs are hard and brittle in nature as compared to matrix. The size and distribution of the IMC particles greatly affect the mechanical properties of the solder[37, 38].

The experimental results and discussions are organised in the following three sub-sections:

Effect of La Doping on IMCs' Particle Size

To study the effect of the La-doping on the average IMCs particle size of SAC305 solder, SEM images of the samples were analysed using ImageJ software. For each sample, three images of different magnification were used. An example setup of particle size analysis using ImageJ is shown in Figure 2.

The result of the IMCs average particle size analysis is plotted in Figure 3. The graph shows the change in the particle size as a function of lanthanum-doping level. From the graph, it can be seen that increasing La content reduces the size of IMCs particles. The small particle size of the IMCs refines the microstructure and as a result increases the strength of solder. The increased strength of the solder can potentially result in increased reliability of the solder joint.

Effect of Thermal Aging IMCs Particle Size on SAC305 and SAC305-La Alloys

To study the effect of thermal aging on the microstructure of on the SAC305 and SAC305-lanthanum solder alloys in terms of IMCs particle size, the SEM images were taken and analysed. Vast changes in the microstructure due to the thermal aging were observed.

The change in the average IMCs particle size were recorded as a function of aging time, temperature, and amount of La doping. ImageJ software was used to measure the average particle size of IMCs for each sample. The results for aging temperature of 90°C are plotted in Figure 4 as a function of aging time.

As seen from the Figure 4, the thermal aging resulted in the coarsening of the IMCs. From the graph it can be recognised that the amount of coarsening increases with the aging time. By comparing graphs, it can be seen that the coarsening rate for lanthanum-doped alloy is much slower than that for the un-doped alloy. Thus, it can be concluded that the coarsening rate of IMCs due to thermal aging can be controlled with the help of lanthanum dopping.

To study the effect of the aging temperature, samples were thermally aged at 180°C for 60 hours and 120 hours. The average IMCs paricle size are then calculated and compared to the average IMCs size of thermally aged samples at 90°C. The comparison of the average IMCs size is shown in Figure 5. From Figure 5, it is can be seen that by increasing the aging temperature the IMCs particle size further increases. Thus, it can be concluded that the IMC particle size is a function of La doping level and as well as thermal aging period and operating temperature.

Effect of La Doping on IMCs' Interparticle Spacing

Han et al.[39] reported that the interparticle spacing can play a major role in the back stress in lead-free solder alloys. There has been several stoichiometric studies that show that the volume fraction of IMCs in the eutectic Sn3.5Ag alloy composition is 0.07[40]. In this study, the Ag and Cu amounts are kept constant for all compositions and also the La is limited to a maximum of 0.5 (wt%), it is logical to assume that the IMCs volume fraction would be constant[41]. Thus if the IMCs are considered to be spherical and also uniformly distributed in the matrix then the average interparticle spacing can be easily calculated from the volume fraction at the eutectic region.

The average interparticle spacing of SAC305, SAC305-0.05La, SAC305-0.25La and SAC305-0.5La samples is calculated in this research. The resulting

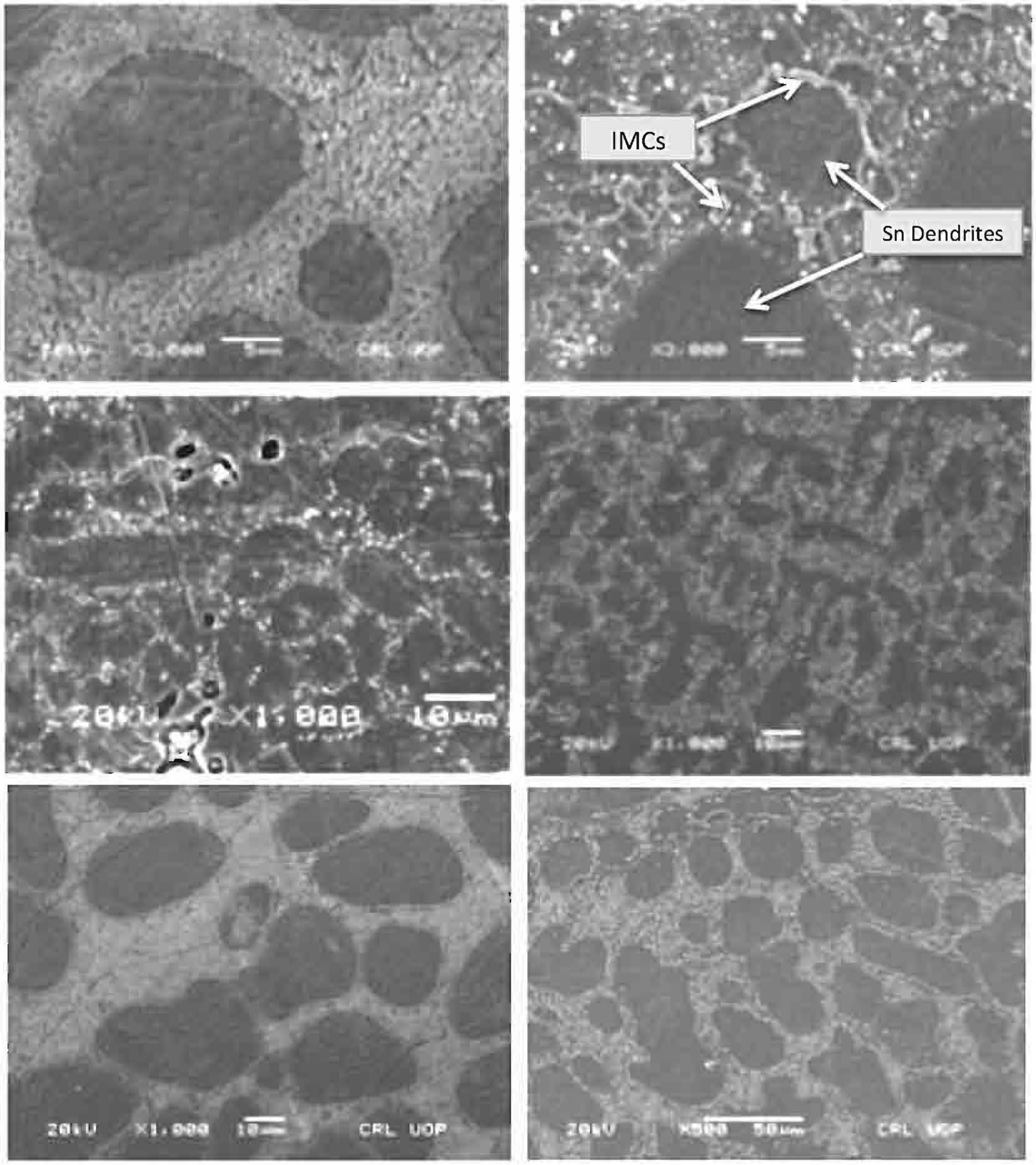

Figure 1: SEM micrographs of various SAC305 and SAC305-La alloys

Figure 2: Particle size analysis using ImageJ

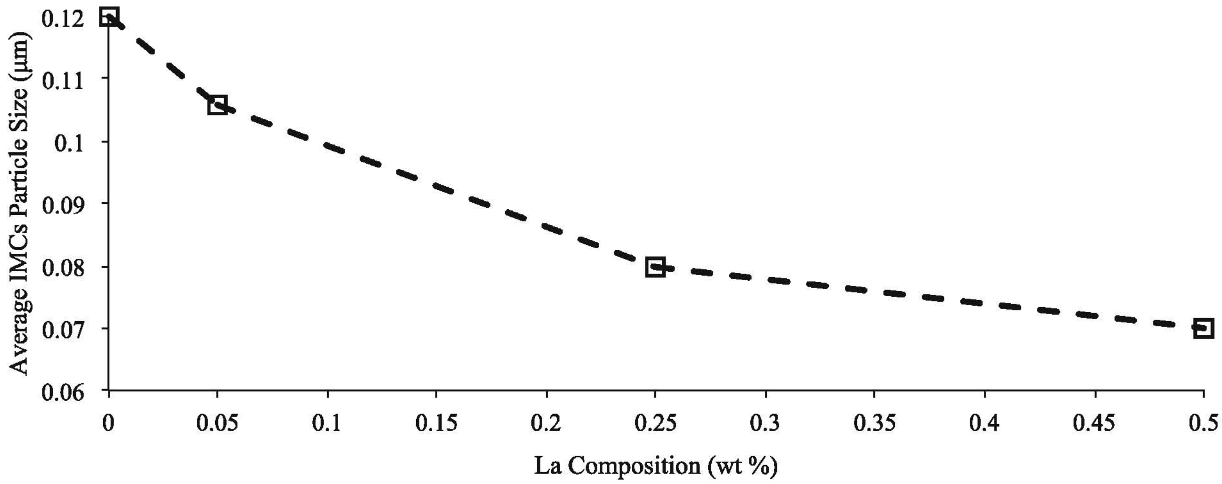

Figure 3: Change in the IMCs particle size due to La-doping

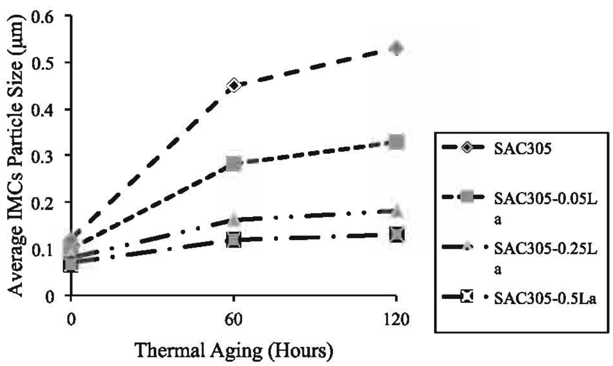

Figure 4: Evolution of the particle size of IMCs due to thermal aging at 90°C of SAC305, SAC305-0.05La, SAC305-0.25La and SAC305-0.5La

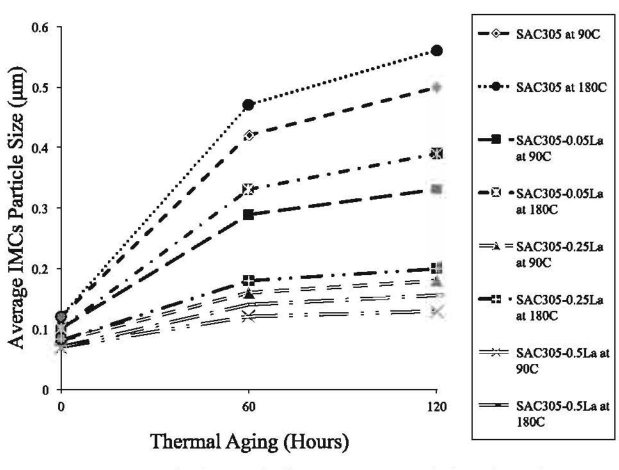

Figure 5: Evolution of the IMCs particle size due to thermal aging at 180°C of SAC305, SAC305-0.05La, SAC305-0.25La and SAC305-0.5La

values are listed in Table 3. It can be seen from the resuts that the interparticle spacing is not changing with La composition. This is noteworthy as it was conculded above that the La doping drastically reduces the IMCs size both for as-cast and thermally aged specimens. This could be described as; the high La doping causes reduction in size which increases the number of particles and keeping constant volume fraction provides almost constant interparticle spacing. This also leads to the fact that the high La doping would lead to higher volume fractions in the eutectic region[41].

Table 3: Interparticle Spacing

Solder Alloy	Interparticle Spacing (µm)
SAC305	0.05
SAC305-0.05La	0.06
SAC305-0.25La	0.05
SAC305-0.5La	0.05

CONCLUSION

To study the effect of La-doping and high-temperature thermal aging on the properties of SAC 305 lead-free solder, the microstructure of doped and undoped SAC alloys have been studied. For microstructure examination SEM images of the samples were obtained and then analysed using ImageJ software. A number of changes in the microstructure were observed. The addition of lanthanum refined the microstructure by reducing the IMCs particle size. The thermal aging resulted in enormous increase in the size of the IMCs particles. The increase in the IMCs size was function of both aging time and temperature. It was also observed that the La doping was able to control the growth of the IMC particles due to thermal ageing to a great extent during thermal aging. From the study, it can be concluded that lanthanum doping refines the microstructure and hence can result in potential improvements in the mechanical properties of SAC305 solders.

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