Effect of Lanthanum Doping on the Microstructure Evolution and Intermetallic Compound (IMC) Growth during Thermal Aging of SAC305 Solder Alloy

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Abstract
Sn96.5Ag3Cu0.5 (SAC305) is widely used as lead-free solder for surface mount technology (SMT) card assembly and for ball-grid-array (BGA) interconnection in the microelectronic packaging industry as solder balls and pastes. In this study the effects of Lanthanum (La) doping on SAC305 under thermal aging was investigated as a function of intermetallic compounds (IMCs) growth and grain size evolution. The morphology of the microstructure was analyzed under Scanning Electron Microscope (SEM) and optical microscope, the elemental distribution was confirmed by Energy Dispersive Spectroscopy (EDS) and phase identification of the crystalline structure was performed by x-ray diffraction (XRD). It was found that the microstructure of SAC305 solder alloy changes significantly with addition of La. Quantitative analysis of grain size and intermetallic particle size was performed both for undoped and La-doped SAC305 alloys.

Keywords: IMCs; Thermal aging; Grain size; Particle; Solder; SAC305

Introduction
The increasing environmental concern over the toxicity of lead (Pb) combined with strict environmental regulations around the world have been targeted to eliminate the usage of Pb-bearing solders in electronic assemblies and to adopt lead-free solder alloys [1-5]. The European Union Waste Electrical and Electronic Equipment (WEEE) Directive, published in 2002 and Restriction of Hazardous Substances (RoHS) Directive of European Community, published in 2003 restricted the usage of certain toxic materials including Lead (Pb) in production of electronic devices used in European Union effective on 1 July 2006 [6].

Owing to the enforcement of these directives, all electrical or electronic equipment and devices produced in or imported to EU member countries must meet the lead-free standards except those items that are exempted from the bans. Furthermore, several Japanese electronics manufacturers have successfully created a market differentiation and increased market share based on “green” products that use Pb-free solders and many Japanese companies have brought their lead-free products into the market much earlier than the EU directives’ effective dates, including Panasonic in 2001, Sony in 2001: Toshiba in 2000, NEC in 2002, and Hitachi in 2001. In the United States, there are no specific government regulations regarding usage of Pb solder in electronic consumer products. However, the U.S. Environmental Protection Agency (EPA) has listed lead among the top 17 chemicals that conduce to threat for human health. The IPC (formerly known as the Institute of Interconnecting and Packaging Electrical Circuits) has also developed a roadmap for the lead-free movement in the U.S. [7].

Moreover many U.S. companies, including Motorola, Cisco, and Intel, have also been actively pursuing lead-free products in order to protect their world-wide market shares. Many universities have also been actively funding lead-free related research. Other countries, such as China and South Korea, which are emerging electronic manufacturing bases, have also adopted or are in the process of adopting directives similar to those of the European Union.

This multinational decision has led to vigorous development of alternative solder alloys and the most promising of these falls into the general alloy families of tin-silver (Sn–Ag) and tin–silver–copper (Sn–Cu–Cu). They were first developed in 1996 by a joint research group at Ames Laboratory in USA [8]. Various type of Sn–Ag–Cu or SAC alloys have been the proposed by industrial consortiums e.g. In Japan, the Japan Electronic Industry Development Association (JEIDA) has recommended 96.5wt%Sn–3wt%Ag–0.5wt%Cu (SAC-305), in the EU, the European Consortium - the Industrial and Materials Technologies Program Brite-Euram, recommended 95.5wt%Sn–3.8wt%Ag–0.7wt%Cu (SAC-387), and in US, 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 [9].

Among the various lead-free solders SAC-305 alloy has emerged as the most widely accepted to replace Sn-Pb solders. It is widely used as lead-free solder for surface mount technology (SMT) card assembly and for ball-grid-array (BGA) interconnection in the microelectronic packaging industry as solder balls and pastes. More than 70% market for reflowing lead-free solders are in the SAC series. Due to having good mechanical properties, acceptable wetting properties, and suitable melting points, the International Printed Circuit Association has suggested that SAC-305 and SAC-396 will be the most widely used alloys in the future [10-16].

Although SAC-305 alloy is widely used in electronics industry, 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) in this alloy [17]. IMC are produced as result of the reaction of a molten solder with a conductive metal i.e. Cu. [18,19]. Although the presence of thin layer of IMCs between solders and conductor metals is desirable because it results in good metallurgical bonding [19]. However, a thick IMCs layer at the solder/conductor metal interface significantly reduces the reliability of the solder joints because of their inherent brittle nature and their tendency to generate structural defects because physical properties (such as elastic modulus and coefficient of thermal expansion) of IMCs are not compatible with parent metal i.e. SAC alloy [1,10,19-26]. IMC have much higher strength than the bulk solder material [27,28]. "They are stoichiometric combinations of two or more metal atoms where the atomic fractions of the metals are generally fixed (for example Cu3Sn). This can be contrasted with solid solutions where the atomic fractions can sometimes vary as widely as 0 - 100%. Metals and alloys exhibit metallic bonding between the atoms, whereas IMCs exhibit a more covalent character. This is why IMCs tend to be much harder and have much higher elastic moduli than either of their respective metallic elements i.e. Sn, Ag & Cu" [29].

Prolonged exposure to high thermal environment causes these IMCs to grow [30,31]. Figure 1 shows how thermal aging leads to growth of the IMC layer between SAC305 solder and copper. The operating temperature of many new electronic systems could be as high as 200°C, for example electronics in oil and gas exploration, operating temperature of many new electronic systems could be as high as 200°C, for example electronics in oil and gas exploration, avionics, automotive industry, and defense applications typically have more demanding thermal life cycle environments than consumer electronics [32,33]. In oil and gas well drilling nearly 15% of the wells have bottom hole temperature in the range of 150°C-175°C and 2 to 3% have temperature up to 200°C or higher [34]. A typical application of high thermal environmental conditions experienced by electronic system during oil and gas well drilling is running of wireline logging & gas well encountered to a temperature range of 150°C-175°C with Ar+ ions. Therefore, Kirkendall voids may be more common than reported [37]. Ag3Sn is the other IMC that can form in the matrix of the SAC solders as needle like structure. Large Ag3Sn plates is the least desirable phase since it extensively affect the mechanical properties of solder joints [49,50] by producing local plastic deformation [51] and conduc to stress concentration at the interface between the hard Ag3Sn particles and soft Sn [52] that results in catastrophic failures of electronic components. They are generally believed to be detrimental in both crack initiation and propagation, and numerous studies have attributed the failure of SAC305 solders as plate-like Ag3Sn IMCs under impact and thermal cycling stimuli [10,17,53]. In addition, the formation of large plate like Ag3Sn IMCs causes solid dissolution and precipitation hardening, which in turn decreases the matrix strength [54,55]. The overall reliability of the solder joint can be greatly affected by the amount and size of Ag3Sn IMCs in the microstructure [56]. Since the Cu content in the SAC-305 alloy is very small, the majority of the IMCs formed in SAC305 are Ag3Sn particles.

To cater these problems, the rare earth (RE) elements have been added into the Sn-Ag-Cu based solder. The RE elements has some unique properties that make it have extensive applications in material and metallurgy field. Rare earth elements (RE) have been successfully used in the steel industry [57]. RE are the surface-active agents which greatly affect the metallurgy of materials e.g. refinement of microstructure, purification of materials and metamorphism of inclusions [58]. They have been regarded as the vitamin of metals, whereby addition of a small quantity of rare earth elements may dramatically change the performance of metals e.g. refining the microstructure [57-80]. They can more easily agglomerate at the grain/dendrite boundary and lower the grain/dendrite boundary energy to stabilize the boundaries and restrain the moving or sliding of the boundaries [25]. Some studies consider that RE elements are adsorbed at the grain/dendrite boundaries of the IMC and alter the relative correlation of the growth velocities between the crystalline directions of the polycrystalline IMC, which decrease the size of the IMC particles and distributes the IMCs more uniformly [81-87]. Several studies [57-80] have been conducted to find the effect of RE doping in solder alloys, the RE used generally are La, Ce, Y and Er. These studies demonstrate...
that RE doping can significantly increase the wetting property of solder [14,57-58,64,75-76,81], it can reduce IMCs particle size and their growth on solder/pad interfaces, and thus greatly increase the solder joint reliability [73]. Some researchers have found that the difference in atomic radius between Sn and RE atoms makes it difficult for them to form replacement atom-type solid solutions, so the RE atoms gather at defects, such as dendrite boundaries. Since the mechanical behavior of solder alloys depends on the microstructure, it is critically needed to conduct a systematic quantitative microstructure study at all relevant length scales [57]. RE element enhances the mechanical strength and creep rupture life of solder alloys like Sn-Ag, Sn-Cu and SAC lead free solder alloy because RE elements can promote chemical reactions at the interface and provide very strong bonding during soldering [14,58,75-76,80,82-85].

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 IMMS formation of SAC-305 solder alloy with varying environmental conditions implemented during service. Lanthanum (La) is considered as the best element for SAC solder alloys due to their lower cost, wide availability and low melting point as compared to the other RE elements [88,89]. In steel industry Lanthanum is added to steel to improve its malleability, resistance to impact and ductility. Being surface active agents, even minor quantity of La significantly enhance the reliability of solder [90]. In addition the diameter of a La atom is 0.181 nm, while that of Sn is 0.141 nm which is 28% smaller than that of La. Owning to this it is difficult for La atoms to substitute Sn atoms in the matrix. Consequently it is easy for La atoms to agglomerate at dendrite boundaries, and refine dendrite of the grains [67]. This may enhance the resistance to grain growth which may results in the refinement of the microstructure.

Experimental Procedure

The base material used in this study is SAC305 lead free solder alloy and the RE used is Lanthanum-La. Three levels of RE doping were used and the final alloy compositions in weight percent are shown in Table 1 below:

<table>
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<tr>
<th>Solder Alloy</th>
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<tr>
<td></td>
<td>Sn</td>
</tr>
<tr>
<td>SAC305</td>
<td>96.5</td>
</tr>
<tr>
<td>SAC305-0.05La</td>
<td>96.45</td>
</tr>
<tr>
<td>SAC305-0.25La</td>
<td>96.26</td>
</tr>
<tr>
<td>SAC305-0.5La</td>
<td>96.02</td>
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After thermal aging, microstructure of the polished samples was performed using optical microscope (Olympus GX51, Olympus Co. Japan) and Scanning Electron Microscope - SEM (S5-5910, JEOL Japan) coupled to an Energy Dispersive X-ray Spectroscopy - EDS (Oxfordinca Inca-200). In order to hinder the charging of the epoxy mount, gold sputter coating was performed on the SEM sample with SPI Sputter coater JEE-420. Dispersion of different solder elements and the elemental analysis of IMC phases were performed using a JEOL JXA-733 superprobe electron probe microanalyzer equipped with Bruker AXS 4010 XFlash silicon drift energy dispersive X-ray (EDX) detector and QUANTX software. X-ray diffraction (XRD) measurements were carried out in order to determine the constitution of the phases forming the samples microstructure. XRD patterns were obtained utilizing a JDX-3532 (JEOL Japan) with a 2-theta range from 5° to 80°, Cu-Kα radiation with a wavelength, λ, of 0.15406 nm.

Results and Discussion

XRD analysis

XRD analysis was conducted to identify the type of IMC phases. Figure 2 exhibits the resulting XRD patterns for as-cost SAC305 with no La doping and that SAC305 with 0.5wt% La after thermal aging of 120 hours at 180°C of each sample. It was observed that the microstructure of un-doped SAC305 alloy contained two IMCs phases, i.e. Ag3Sn and Cu6Sn5 while that of lanthanum doped SAC305 alloy contained three IMC phases i.e. Ag3Sn, Cu5Sn3 and La5Sn3. Previous studies [25,57,61,86] found that Lanthanum doped SAC alloy will cause La5Sn3 IMCs while our results shows the presence of La5Sn3 instead of LaSn3.

Grain size

To study the grain size of the solder material, optical microscopy with cross polarized light was used. With the help of cross polarized light, grains with different shade can be viewed under the microscope. Figure 3 shows the typical images of 96.5Sn3Ag0.5Cu and 96.5Sn3Ag0.5Cu-0.5La after thermal aging of 120 hours at 180°C of each sample [92,93]. These Figures shows a significant decrease in grain size, due to the addition of lanthanum.

The grain size as a function of different La composition and aging temperature is plotted in Figures 4 and 5 respectively. The Figures illustrate that the grain size of lanthanum alloy is much smaller than un-doped SAC305 alloy. Also grain size decreases significantly up to 0.05% of La doping and then increase slightly with increasing amount of La doping. This is consistent with the previous studies conducted by Min et al. [25] and Sadiq et al. [94] for Sn-3Ag and SAC305 alloy respectively with similar La doping. Also a slight change in the grain size for La-doped alloy has been observed with thermal aging. This demonstrates that La-doping refines the grains which comply to
The work of Min et al. [25] and Sadiq et al. [94]. The philosophy of this refinement is because of the particular effect of La adsorption at different planes in the Sn-Ag-Cu alloys.

Microstructure analysis

The microstructure of the doped and un-doped SAC305 solder alloy was investigated in SEM and ordinary secondary electron microscopy images have been produced for each alloy composition. In the as-cast condition, the microstructure of SAC305 alloy comprises of dendritic β-Sn phase and Sn-Ag-Cu ternary eutectic network where intermetallic particles were finely distributed in the Sn matrix as shown in Figure 6. From the EDS and XRD analysis, the IMC found were mainly Ag₃Sn and Cu₆Sn₅. There is very a clear boundary between dendritic β-Sn phase and Sn-Ag-Cu ternary eutectic regions. After thermal aging, the size of Ag₃Sn and Cu₆Sn₅ particles in Sn-Ag-Cu eutectic region increased and more uniformly dispersed. The reason for increase in the particle size of Cu₆Sn₅ with thermal aging is the increase in the diffusion rate of Cu into Sn [92].

The “as cast” and “thermally aged” SEM micrographs for un-doped SAC-305 and SAC305 with 0.5wt% La doped alloy are shown in Figure 7. After thermal aging coarsening of IMCs particles take place. It could be observed from the images that the microstructure of La-doped sample is more refine the un-doped sample. After thermal aging at 180°C the size of Ag₃Sn and Cu₆Sn₅ particles in SnAgCu eutectic region increased and more uniformly dispersed. Owing to this dispersion it is difficult to identify the boundaries of β-Sn dendrite and eutectic region clearly.

![Figure 2: XRD profile of (a) SAC305 (b) SAC305 with 0.5La after thermal aging at 180°C for 120 hr.](image)

![Figure 3: Optical microscopy (a) SAC305 (b) SAC305 with 0.5La after thermal aging at 180°C for 120 hr.](image)

![Figure 4: Grain size as a function of La percentage.](image)

![Figure 5: Grain size as a function of Aging Time.](image)

### Table 2: Etching time.

<table>
<thead>
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<th>SAC Alloy</th>
<th>Etching Time (sec.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SAC305</td>
<td>10</td>
</tr>
<tr>
<td>SAC305-0.05La</td>
<td>20</td>
</tr>
<tr>
<td>SAC305-0.25La</td>
<td>40</td>
</tr>
<tr>
<td>SAC305-0.5La</td>
<td>80</td>
</tr>
</tbody>
</table>
The La-Sn IMC has complex branch structure [89], which is usually look like clusters of snowflakes [57] in SEM images. With the help of EDX analysis very high amount of La concentration of observed in these snowflakes. Moreover it was also observed that quantity La5Sn3 IMC depend upon the concentration La doping i.e. with high 0.5wt% of lanthanum bigger snowflakes has been observed as shown in Figure 8 while small isolated snow can be seen with less La doping which is consistent with the results of Min et al [25].

La doping greatly reduces the Ag3Sn and Cu6Sn5 particle size particle during thermal aging. Surface area averaged particle size of Cu6Sn5 particles was obtained as per ASM handbook [95]. The particle sizes for the full data set are plotted in Figure 9 as function of La doping level. It can be seen that La doping effectively suppresses the growth of Ag3Sn and Cu6Sn5 intermetallic particle.

The distribution of Sn, Ag, Cu and La was observed by using electron micro probe analysis (EPMA) coupled with X-ray spectroscopy (EDX). The elemental analyses map in Figure 10 demonstrates that elemental La is uniformly dispersed on the whole solder area which is consistent with Min et al. [25].

Under thermal aging conditions, evolution of IMC particles i.e. AgSn, and Cu6Sn5 was observed. Owing to this Cu6Sn5 particle can be easily distinguished from AgSn, particles as shown in Figure 11.

**Concluding Remarks**

Keeping in view the result and observations of this study several conclusions can be made.

1. In the as-cast condition, the microstructure of SAC305 alloy comprises of dendritic β-Sn phase and Sn-Ag-Cu ternary eutectic network where intermetallic particles were finely distributed in the Sn matrix.
2. Addition of lanthanum to Sac305 solder alloy significantly reduced the IMC particle size.
3. La doping effectively suppresses the growth of Ag3Sn and Cu6Sn5 intermetallic particle during thermal aging.
4. La doping significantly reduce the grain size and keep the grain size stable during thermal aging.
5. Addition of lanthanum with 0.5 wt% conduces to a new type of IMC, observed as $La_5Sn_3$.

References


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