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Bakhtiar Ali
Department of Mechanical Engineering, University of Engineering and Technology, Peshawar, 25120, Pakistan

Salma Bilal
Electrochemistry Labs. National Centre of Excellence in Physical Chemistry, University of Peshawar, Peshawar, 25120, Pakistan

Correspondence:
Dr. Salma Bilal
Electrochemistry Labs. National Centre of Excellence in Physical Chemistry, University of Peshawar, Peshawar, 25120, Pakistan
E-mail: dresalmabilal@gmail.com

Impact of cooling rate on microstructure and mechanical properties of lanthanum-doped tin-silver-copper lead free solders

*Bakhtiar Ali, Salma Bilal**

Abstract

A detailed research study was carried out to suggest improvements in the properties of lanthanum-doped Tin-Silver-Copper (SAC) by eliminating the adverse effects caused by applying slow cooling rate during solidification. The effects of faster cooling rate during solidification on the microstructure and mechanical properties of lanthanum-doped SAC were studied. Scanning electron microscopic (SEM) images were studied and were further analyzed by ImageJ software to measure the average inter-metallic compounds (IMCs) size. These IMCs, present inside the bulk tin (Sn) matrix, are brittle in nature and have an adverse effect on the mechanical properties of the alloys. With faster cooling rate the IMCs formation was significantly controlled, both for the as cast and thermally aged samples and slow cooling rate led to undue IMCs growth. Optical microscopy with crossed polarized light was used to study the grains. The faster cooling rate resulted in much smaller grains and slow cooling rate caused an undue grain growth. MTS tensile machine was used to carry out quasistatic tensile tests to find out the mechanical properties. Yield stress and tensile strength were found to be greatly improved for the alloy with faster cooling rate. Finally, an optimum cooling rate was found to be 6°C/s.

Keywords: SAC alloys, Lanthanum, Intermetallic compounds, Grain size, Mechanical properties, Cooling rate.

Introduction

Good solder joints are desired to have good thermal and mechanical properties. These properties were well established for tin-lead (Sn-Pb) solder until certain restrictions were imposed by European Restriction of Hazardous Substances (RoHS) and Environmental Protection Agency (EPA), which identified Pb as toxic to both environment and health. Lead (Pb) and Pb-containing compounds, as cited by EPA, is one of the top 17 chemicals posing the greatest threat to human beings and the environment.[1] Moreover, the electronic industry has been pushed by strict government legislations and consumers demands towards lead-free solders. Different researchers have studied many lead-free solder alloys with a wide range of applications. Most of the newly defined lead-free solders are binary and tertiary alloys [2], out of which, Tin-Silver-Copper (SAC) tertiary alloys are considered as the best substitutes.[3] Like many other alloy systems, SAC alloys have certain limitations due to their coarse microstructure. To overcome these limitations, iron (Fe), cobalt (Co) and nickel (Ni) were used as potential additives.[4] In some studies, indium (In), bismuth (Bi), copper (Cu) and silver (Ag) were used as alloying elements.[2] Before classifying SAC as good substitute, extensive knowledge and understanding of the mechanical behavior of this emerging generation of lead-free solders is required to satisfy the demands of structural reliability. When subjected to severe conditions during service, electronic devices expose solder joints to elevated temperatures. This causes significant evolution of the microstructure of SAC alloys. SAC alloys consist of β-Sn, eutectic Sn phases and Ag-Sn and Cu-Sn Inter Metallic Compounds (IMCs). These IMCs are generally hard and brittle in nature and dictate the mechanical properties of the solder joints. Exposure to high temperature causes thermal coarsening due to which the size of these IMCs grow and further deteriorate the solder joints and hence alters the structural reliability of the whole assembly. Rare-earth (RE) elements, known as the vitamins of metals, were used in different studies to control this thermal coarsening with significant results.[5-7] These RE additives also refine the microstructure, which ultimately improve the mechanical properties of SAC lead-free solders.[6-10]

The best study considered among these property enhancement studies was by Sadiq *et al*.[11] in which lanthanum (La) was doped in SAC, using a cooling rate of 3°C/s, and it was reported that the thermal and mechanical properties of the La-doped SAC alloy were better than the other lead free solders. However, the cooling rate applied wasn't optimum and it is an established fact that cooling rate during solidification plays an important role in refining the microstructure, which ultimately leads to better mechanical properties.[12, 13] So the properties could have been improved greatly if an optimum cooling rate was applied during solidification. The cooling rate applied was slow for this alloy which led to an undue growth of grains as well as of IMCs. This slow cooling rate led to relatively low mechanical properties which could otherwise be far better, without a sacrifice in anything, if a suitable cooling rate was applied.

The purpose of this research study was to eliminate the adverse effects of the slow cooling rate application over the microstructure and mechanical properties of the La-doped SAC alloy. In this study cooling rate during solidification of La-doped SAC alloy was varied to investigate its effect on the microstructure as well as on the mechanical properties, and the other parameters were kept constant to have a better understanding of the effect of cooling rate. It was found that the alloy had a much refined microstructure and greatly improved set of mechanical properties at a faster cooling rate. These properties have not been previously achieved for any lead free solder, working at this temperature (150°C). Furthermore, an optimum cooling rate for solidification of La-doped SAC alloys was found for the first time.

Experimental Work

Synthesis of the test samples

Since sample preparation for any kind of experimental study is crucial, samples were prepared from pure metals in the form of 200g ingots with the composition (wt.%): Sn-3.0Ag-0.5Cu-0.3La. Three three-part casting dies, composed of two parts in aluminium and a central steel plate, were used to follow the "cast by melt" die casting to make some dog-bone shaped tensile specimens. The front part of the dies contained the path for the flow of molten alloy. The central plate contained cavities for sample casting which were designed in dog-bone shape. The backsides of the dies were used to tighten the plate to the front side and also to provide fins to expedite the cooling rate during solidification process. A temperature of 260°C was applied in the oven and the dies were heated for about 45 minutes before putting the molten metal into it. The 200g ingots were put in a crucible and then placed in the oven at 260°C for about 25 minutes. Water at a temperature of 15°C was used for quenching. The cooling rates of the specimens were measured with K-type thermocouples which were connected to computer to record the cooling rates. In order to impose three different cooling rates on the molten samples in the three dies, different portions of the dies were dipped in the water. Only a small portion of one die, twice as much portion of the second die and thrice as much portion of the third die was dipped in water to get cooling rates of about 3°C/s, 6°C/s and 9°C/s respectively. Thus, three samples with different average cooling rates were prepared.

Sample characterization

For Microscopy, the samples were mechanically polished with silicon discs and diamond pastes of 6-micron, 3-micron, 1-micron and 0.25 micron. Chemical etching was performed using 5% hydrochloric acid/95% ethanol solution. Etching time was 1 minute and immersion type of etching was used. The temperature selected for aging was 150°C and aging time of 10 hours. Samples were exposed to these conditions in a furnace after polishing and etching. The purpose of aging was to get a better understanding of the performance by considering the operating conditions during service.

Optical microscopy with crossed polarized light was used to check the effect of cooling rate on grain size and scanning electron microscopy (SEM) to analyze the microstructure of the specimens qualitatively. In this research JSM5910 (JEOL JAPAN) scanning electron microscope apparatus was used. The SEM images were taken at different locations for identification of clear IMCs. These SEM images were further analyzed by imageJ software to investigate the size of these IMCs.

Mechanical testing

MTS tensile machine equipped with a 5 kN load cell was used to carry out Quasistatic tensile tests at strain rate of 2 × 10-4 s-1 to determine the mechanical properties as a function of cooling rate during solidification.

Results and Discussion

Qualitative microstructure study

The microstructure of the SAC alloy is composed of a soft Sn matrix (almost 90 %) and hard IMCs of Ag and Cu with Sn.[14] LaLonde *et al*.[15] quantified the number of crystallographically independent β-Sn dendrites present in near-eutectic SAC balls as a function of cooling rate and estimated that a single 900-μm diameter solder ball contains on average eight individual β-Sn dendrites, independent of cooling rate. These dendrites are surrounded by the eutectic IMCs.[14]

In this study scanning electron microscope was used to collect the images of each sample at different resolutions, in the initial state and after thermal aging, to investigate the effect of variation in cooling rate over the IMCs size. The "as cast" SEM images are shown in Fig. 1 and "thermally aged" SEM images in Fig. 2 for each sample. The black zone is the matrix that is mainly composed of Sn and the white particles are the IMCs.[11] These IMCs, rich in Ag and Cu, are brittle in nature in comparison with the soft Sn matrix and affect the mechanical properties of lead-free solders.[16] The excessive growth of IMCs also causes coarsening of the alloy. The size of these particles depends on many parameters such as alloy composition, cooling rate, and environmental conditions during service. In order to constrain the size of these IMCs, researchers attempted a change in the cooling rate during the solidification process for few other alloys.[12,13] A fast cooling rate can generate a finer microstructure. By closely examining Fig. 1 & Fig. 2, it can be noticed that the IMCs (white particles) formation and growth are more restricted for the samples with faster cooling rate. So, it is logically expected that the sample with faster cooling rate would have better mechanical properties.

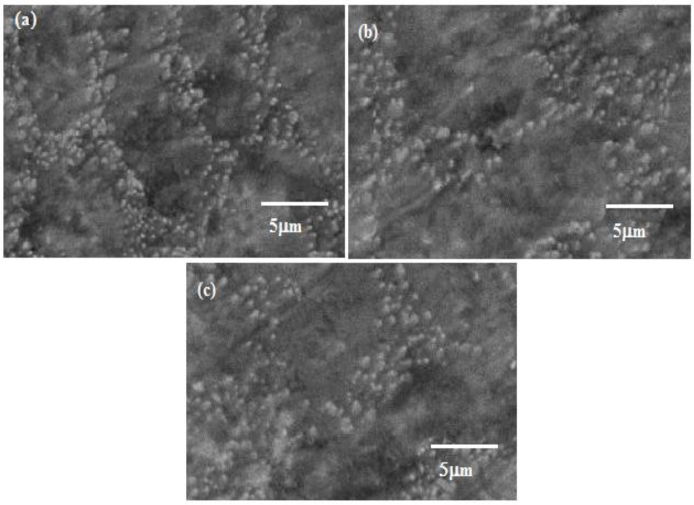

Figure 1: SEM micrographs for as-cast samples, solidified at a cooling rate of: (a) 3°C/s, (b) 6°C/s and (c) 9°C/s

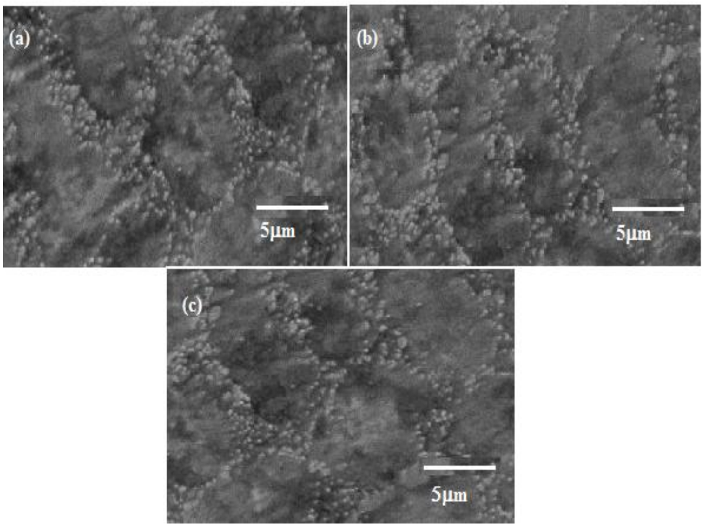

Figure 2: SEM micrographs for thermally-aged samples, solidified at a cooling rate of: (a) 3°C/s, (b) 6°C/s and (c) 9°C/s

Grain size

It has been known that adding a surface-active element, such as rear earth, to an alloy can increase the activation energy for the diffusion of the boundaries of grains so that it restrains the grain boundary from moving.[17] Aiming to eliminate the adverse effects, caused by slow cooling, the effect of faster cooling rate on grains size was examined in this study. Optical microscopy with cross polarized light was used to examine the grains. With the help of cross polarized light, grains can be observed as different shades under the microscope. A representative image for each sample is shown in Fig. 3. A much significant decrease in the grain size for the samples with faster cooling rate can be seen. Grain size was measured and is plotted, as a function of cooling rate, in Fig. 4 for the "as cast" and "thermally aged" samples. A significant decrease in average grain size can be noticed due to cooling the alloy at a faster cooling rate. This improvement can be attributed to a reduction in grain size as well as diffusion of grain boundaries due to adding the RE element. Almost no change in grain size was experienced due to thermal aging.

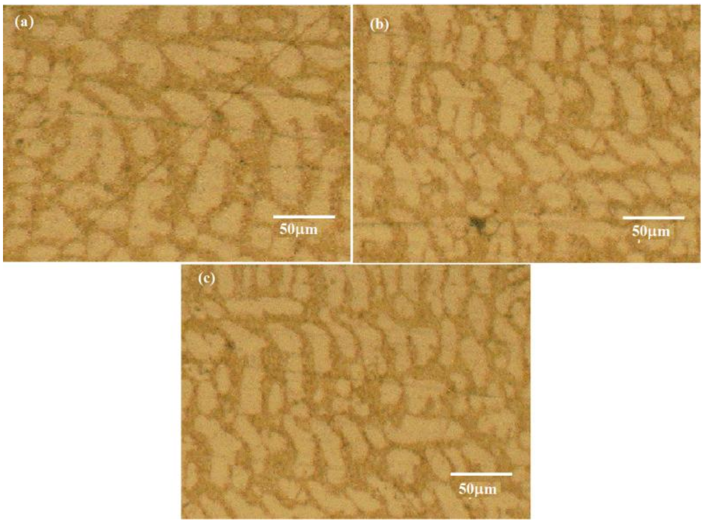

Figure 3: Optical microscopy images with samples solidified at a cooling rate of: (a) 3°C/s, (b) 6°C/s and (c) 9°C/s

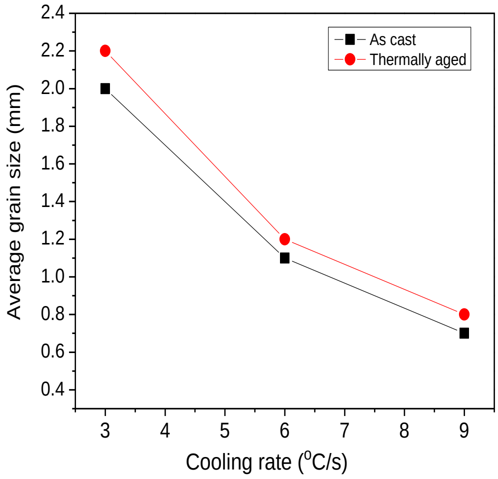

Figure 4: Average grains size versus cooling rate during solidification

Plastic deformation is due to the motion of dislocations. Thus, the strength (resistance to deformation) can be improved by impeding this dislocation movement, which will hinder the onset of plasticity. Reducing the grain size, by applying a faster cooling rate, is the most feasible way for this alloy to improve the strength because the smaller grains create more obstacles per unit area to the movement of dislocation, often without any sacrifice in toughness. The relationship between grain size and strength has been explained by the Hall-Petch relationship.[18] This is based on the fact that it is difficult for a dislocation to pass into another grain, especially if it is very misaligned.

Particle size

ImageJ software was used in this study to measure the average IMCs particle size. The data obtained is provided in Table 1 at 5000x magnification. It is seen that the IMCs particle size is greatly reduced for the sample with faster cooling rate. It is clearly seen that the undue growth of IMCs is avoided by apply a suitably faster cooling rate. The IMCs, rich in Ag and Cu, are brittle in nature in comparison with the soft Sn matrix and affect the mechanical properties of lead-free solders.[16] Moreover, solid-state intermetallic compound (IMC) growth behavior plays an important role in the solder joint reliability.[19] As these IMCs are greatly reduced in size, it is logically expected that the mechanical properties would improve for the alloy with faster cooling rate.

Table 1: Particles size analysis at 5000X

Cooling rate (°C/s)	Image magnification	Count	Total area (pixels)	Average size (pixels)
3	5000x	4281	26970	6.3
6	5000x	4258	20865	4.9
9	5000x	4227	17331	4.1

Mechanical properties

Many researchers have already attempted to determine the mechanical properties of Sn-Ag and SAC lead-free solder alloys.[20, 21] As cooling rate is an important processing parameter that affects the microstructure of the solder and, therefore, influences mechanical behavior[22], the impact of faster cooling rate over these properties is investigated in this study. Yield stress and tensile strength are presented in Fig. 5 & Fig. 6 for the "as-cast" and "thermally aged" samples respectively, with 5 % error bars. A great increase in both yield stress and tensile strength can be seen. Mechanical properties like yield stress, tensile strength and creep behavior of most of the materials are influenced by their microstructures.[14] Since the microstructure becomes more refined with faster cooling rate during solidification, so a good set of these properties is logically expected. This increase in strength can be attributed to a decrease in average grain size as well as a decrease in average IMCs particle size. It can also be noticed that an increase in yield stress is more than an increase in tensile strength. This is due to the fact that decrease in grain size hinders the onset of plasticity which directly assures an increase in yield stress.

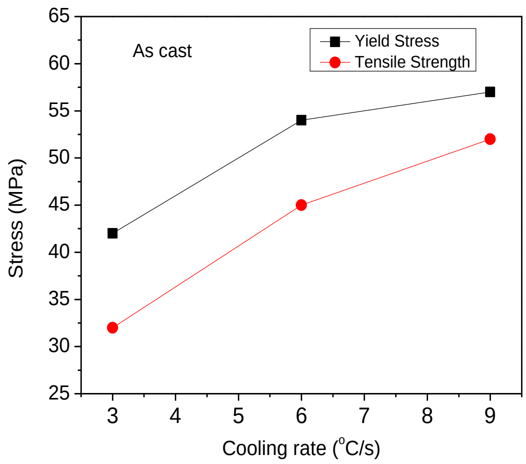

Figure 5: Yield stress and tensile strength for as-cast samples versus cooling rate during solidification

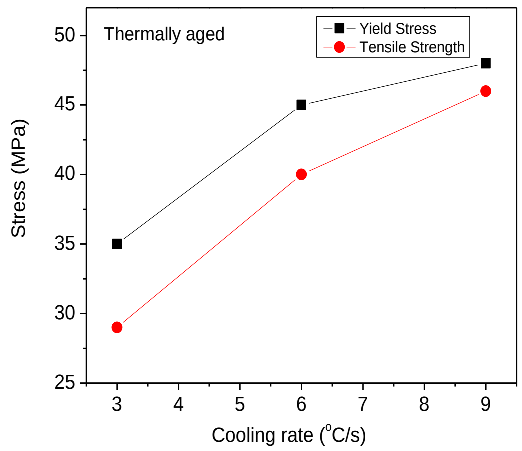

Figure 6: Yield stress and tensile strength for thermally-aged samples versus cooling rate during solidification

One very important point to note is that as the cooling rate increases, elongation to failure decreases. The difference in tensile strength and yield stress values is directly related to elongation to failure. As ductility is the ability to undergo substantial plastic deformation before failure, elongation to failure is a measure of the ductility of a material. In other words, it is the amount of strain it can experience before failure in tensile testing. A ductile material will record a high elongation. Brittle materials tend to show very low elongation because they do not plastically deform. One of the main mechanism by which plastic deformation takes place is the slip of dislocations. Evidently anything that makes the slipping of dislocations difficult, results in lowering of ductility. Grain boundary is one of the major hurdles to the movement of dislocations. For smaller grains, large grain boundary area exists per unit volume. Hence, a smaller grain size results in lowering of ductility. One can conclude that ductility decreases as cooling rate increases, which is consistent with the findings by Mei *et al*.[23]

An examination of Fig. 5 & Fig. 6 reveals that there will be very small difference in elongation to failure between samples with cooling rates 3°C/s and 6°C/s, unlike the sample with cooling rate 9°C/s, which will observe quite a noticeable decrease in elongation to failure. It can be concluded that there will be negligible difference in ductility level between the first two lower cooling rate samples but the sample with cooling rate 9°C/s will experience a decrease in ductility to an undesirable level. So it seems logical to stop at this point and not increase the cooling rate any more, otherwise the ductility will decrease to an unacceptable level. Also, since the sample with cooling rate 6°C/s experiences an appreciable increase in yield stress and tensile strength without a noticeable decrease in ductility, it is logical to select 6°C/s to be an optimum cooling rate for solidification of La-doped SAC alloys.

Conclusion

An extensive study was carried out to suggest improvements in the properties of lanthanum-doped SAC alloy by eliminating the adverse effects of the slow cooling rate application. The effect of faster cooling rate on various desirable properties for a solder joint was investigated. Several conclusions can be made. An overly slow cooling rate leads to excessive grain growth as well as excessive IMCs growth. A suitably faster cooling rate during solidification greatly reduces grain size, controls the IMCs formation and growth, and refines the microstructure of the alloy. A fine microstructure provides a better set of mechanical properties than a coarse microstructure, even for the same composition but different cooling rate. Yield stress and tensile strength were found to be better to a great extent for the alloy with faster cooling rate than slowly cooled alloy. These properties have not been previously achieved for any lead free solder, working at this temperature (150°C). An optimum cooling rate for solidification of La-doped SAC alloys seems to be 6°C/s, as beyond this a rapid drop in ductility was observed.

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