EFFECTS OF COMPOSITION AND ISOTHERMAL AGING ON THE MICROSTRUCTURE AND PERFORMANCE OF ALTERNATE ALLOY Pb-FREE SOLDER JOINTS

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ABSTRACT
Alloy composition, reflow profile and thermal history are all known to affect the microstructure and mechanical properties of Sn-Ag-Cu based solder joints. Secondary precipitates such as Ag3Sn and Cu6Sn5 interact with dislocations in the Sn grain matrix and thus affect the creep resistance of Sn-Ag-Cu solder alloys. The size, number and arrangement of these strengthening precipitates determine the thermomechanical response of a Sn-Ag-Cu solder joint in service. During typical service, solder joints age with time, temperature and cyclic loading. As the secondary precipitates coarsen, their number density decreases, increasing their spacing and reducing their effectiveness at impeding dislocation motion. This microstructural evolution with aging can degrade the mechanical performance of solder joints and the reliability of the solder interconnects. Sn-Ag-Cu solder strengthening can also be achieved through solid solution alloying elements such as Bi and Sb. Such solid solution strengthening can retain much of its effectiveness after extended aging.

Systematic investigations of the effects of alloy composition and isothermal aging on solder microstructure and shear fatigue were performed on various Pb-free alloy solder joints. The microstructures of these alloys were examined in 20mil diameter solder joints. Isothermal shear fatigue testing was performed on individual solder joints formed with carefully controlled thermal histories. Such testing has been shown to be a relatively quick and reliable method of screening alloys for reliability.

Shear strength, microstructure, and shear fatigue lifetimes of different alloy solder joints were correlated with composition and thermal history. Increasing Ag concentration was observed to increase the area fraction of pseudo-eutectic phase regions and the room temperature shear fatigue life. Shear fatigue life was also observed to decrease with aging time. The rate of degradation with aging increased with increasing Ag content. Alloys containing Bi and other minor elements exhibited less degradation upon aging.

Key words: Microstructure, Isothermal shear fatigue life, surface finish, solid solution and reliability

INTRODUCTION
The adoption of near eutectic Sn-Ag-Cu solders (e.g. SAC305) as replacements for SnPb solder in microelectronic interconnects has resulted in greater efforts to improve their mechanical properties (e.g. creep and fatigue resistance) [1-11] Varying the processing parameters of Sn-Ag-Cu solder joints affects their initial microstructure after reflow, their mechanical properties, and hence their lifetime during service. Important examples include changes in composition, surface finish, solder volume and the cooling rate from the melt during reflow. In particular, the volume fraction of the near eutectic phase, Ag3Sn precipitate number, size, and arrangement (Fig. 1) affect the mechanical response of Sn-Ag-Cu near eutectic solder joints, and their reliability [1, 5].

Figure 1. A scanning electron micrograph of a near eutectic Sn-Ag-Cu alloy (SAC387). The near eutectic phase can be seen, along with β-Sn dendrites. Some examples of Ag3Sn and Cu6Sn5 precipitates in the near eutectic phase are labeled.

The initial microstructure of Sn-Ag-Cu interconnects has a strong influence on their thermomechanical response during device use, particularly at earlier times. Immediately after reflow, the bulk microstructure of the Sn-Ag-Cu solders joints includes near eutectic SnAgCu (secondary precipitates Ag3Sn and Cu6Sn5) surrounded by beta Sn dendrites (Fig. 1) [3]. The Ag3Sn particles, especially the
smaller ones (<40µm), have the most significant effect in impeding dislocation motion and thus limiting strain. The dominant role of Ag₃Sn over Cu₆Sn₅ precipitates in the strengthening of Sn-Ag-Cu solders is due to their prevalence and small size [1, 2]. The number density of the small Ag₃Sn precipitates is a strong contributing factor to the enhancement of the creep and fatigue resistances of the Sn-Ag-Cu solder joints. Microstructural investigations of Sn-Ag solder joints by Keller et al [1] identified the volume fraction of the near eutectic SnAgCu (the inter-dendritic regions occupied by small Ag₃Sn and Cu₆Sn₅ precipitates) as one of the most important aspects in the mechanical properties of Pb free solder joints [1, 12]. Their study reported a linear relationship between the Ag concentration and the volume fraction of the near eutectic SnAgCu. The study also correlated increased shear strength with increased volume fraction of the near eutectic SnAgCu regions. Consistent with the axiom that increasing the number density of small precipitates in Pb free solder increases creep resistance, the ATC life time of Sn-Ag-Cu solder joints have been reported to increase monotonically with Ag concentration (Fig. 2) [4, 13]. Similar trends have been observed in shear fatigue tests (Fig. 3). Previously, we have reported that the isothermal shear fatigue lifetimes of near eutectic Sn-Ag-Cu solder joints increased monotonically with Ag concentration, more than doubling upon an increase in Ag concentration from one to four percent [5].

Figure 2. A plot of the characteristic lifetime versus Ag concentration in the solder joint, during accelerated thermal cycling of thin chip array ball grid array (CTBGA) SnAgCu solder joints. [The data is from Ref. 4]

Solute atoms can also be effective in impeding the movement of dislocations, and thus in strengthening Pb free solders by limiting strain [14, 15]. Large differences in size between the atoms of the matrix and those of alloying elements can enhance this solute strengthening mechanism. In an effort to improve the microstructure and mechanical properties of Sn-Ag-Cu solder joints, such other alloying options have been explored, [6] including one to six percent additions (1-6wt. %) of different elements, such as Bi and Sb, which display extended solubility in Sn (Fig. 4). Such changes in composition can have significant effects on reliability performance. For example, the Knoop hardness of Sn-xBi has been reported to increase monotonically with Bi concentration [7, 8]. In another example, Miric et al [2010] have shown that alloying Sn-Ag-Cu with Ni, Bi, and Sb (to form the Innolot alloy) results in higher shear strength than classic Sn-Ag-Cu solders after thermal cycling at -40 to 125°C for 1000 cycles and 2000 cycles [16].

Figure 3. Weibull plots showing the effect of composition on the room temperature shear fatigue life of solder joints on Cu-OSP substrates [The data is from Ref. 5].

Figure 4. (a) Bi-Sn phase diagram [The diagram is from Ref.9]

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Effects of Aging on the Life Time of Sn-Ag-Cu Solder Joints

When in service, Pb free solder joints undergo significant microstructural evolution, both in the bulk and at the interfaces, due to temperature changes, mechanical loading, and electrical current. The precipitates in the Sn matrix coarsen, and the thickness of IMC at the interface increases. The coarsening of the Ag$_3$Sn and Cu$_6$Sn$_5$ precipitates decreases their effectiveness in impeding dislocation motion. The creep and fatigue resistance of the solder joints thus drops with service time, culminating in reduced strength and fatigue life. Simply aging a solder joint at an elevated temperature will also speed this coarsening process. For instance, a study conducted by Zhou et al. (2014), reported that the characteristic life of SAC105 and SAC305 upon ATC cycling with a profile of -40°C to 125°C, decreased with pre-aging time at a temperature of 125°C (Fig. 5) [19]. Changes in microstructure, and degradation in mechanical properties (e.g. shear strength, Tensile strength, yield stress, hardness, and strain rate), ATC life, and shear fatigue life of Sn-Ag-Cu upon aging have been reported by other researchers [18-22].

Figure 5. A plot of characteristic life versus aging time for 10mm ball grid array (BGA) SAC105 and SAC305 packages aged at a temperature of 125°C [The data is from Ref. 19].

On the other hand, the microstructure of Pb free solders with elements such as Bi and Sb which are in equilibrium in solid solution in Sn would be expected to be more stable during aging. In fact, previous work has found that the properties of solder alloys containing Bi are more stable during aging, such as a recent study of the creep resistance of a Sn based alloy containing 2.5% Bi and 0.9% Cu. It was reported that solid solution strengthening improved resistance to the effects of aging [23].

In the present study, the effects of both changes in solder composition, and aging time, on room temperature shear fatigue performance were examined. In particular, the Ag composition in SAC solder was varied from zero to four weight percent. The effects of the addition of substitutional alloying elements such as Bi and Sb were also studied. Focus was on the effect of these compositional changes on isothermal shear fatigue performance, and on the effects of composition on changes in the shear fatigue performance after aging. Results were correlated with changes in the microstructure and shear strength of the solder joints. The present study compares the effect of aging on the mechanical properties of SnAgCu/Cu solder joints, with the effect of aging on the mechanical properties of Pb free solder/Cu joints containing dispersoids such as Bi. Thus this study examines the efficacy of room temperature shear fatigue tests in revealing the effect of varying Pb free solder joint processing on mechanical response.

EXPERIMENT

Ball Shear and Shear Fatigue Test

Solder joints of different Pb free alloys were assembled by reflowing 20mil (500µm) diameter solder spheres on 16mil (400µm) solder mask defined pads. Flux was deposited on the Cu-OSP pads by stencil printing process prior to placing the solder spheres. The boards were designed such that parts (small enough to fit in the DSC pan) containing a single solder joint could be diced and placed in the Differential Scanning Calorimeter for the second reflow Fig. 6. The populated boards were reflowed in a forced convection oven in nitrogen atmosphere at a peak temperature of 245°C for 60 seconds. A precise reflow profile was performed on each solder joint in the Differential Scanning Calorimeter, and a measurement of the solidification temperature of each individual solder joint was performed.

Figure 6. Shows (a) Printed Circuit board on which solder joints were built (b) a Printed Circuit Board with a square area delineated by dashed red lines with only one solder bump which is placed in the differential scanning calorimeter (DSC) after dicing.

Although the effects of thermal history on shear fatigue performance were not factored in this paper, the work is in progress and results will be published later.

Shear Strength

The shear strength was determined for as-assembled solder joints. Low speed (0.7mm/s) shear testing of the joints was performed with a Dage4000+ bond tester. The shear height during the tests was 10% of the solder ball height. This shear height was within JEDEC’s recommended shear height range, which specifies a value less than 25% of the solder ball height. The shear strength measurements served to gauge the strength of each alloy, and as a criterion of choosing a suitable load for use in the shear fatigue tests.
The shear tool was placed behind the solder joint as in Fig. 8c. The sample was translated against the tool, pushing the solder joint until shearing from the pad occurred. As the test progressed, the applied shearing force (load) was measured.

**Room Temperature Shear Fatigue Test**

Shear fatigue tests were performed on individual solder joints after individual reflow in the DSC. The solder joints were attached to a testing block which was mounted on a fixture in the Dage4000+ bond tester (Fig. 7a and 7b). The solder joints were then loaded in shear at a height of 36µm above the pad’s surface and at a load rate of 350µm/s, up to a maximum load of 350g (the applied load for the shear fatigue tests for all the alloys was calculated as approximately 44% of the shear strength of SAC305 joints on Cu-OSP surface finish). The loading direction was reversed at the end of each half cycle. This controlled shear cycling was continued until the solder ball completely failed.

![Figure 7.](image)

**Figure 7.** (a) Dage4000+ with sample block mounted to a fixture with an arrow pointing to the shear fatigue tool (b) the sketch of the shear fatigue tool (c) The sketch of the set up for the ball shear test.

Selected samples were mounted in epoxy, cross sectioned, and metallographically polished to 0.02 µm colloidal silica. Bright field optical microscopy was used to examine the morphology of samples and the growth of intermetallic compounds after annealing. Cross polarized images of each ball were taken to identify the number of Sn grains in each solder ball. A high resolution Zeiss 55 capable of variable pressure (VP) scanning electron microscope (SEM) equipped with an energy dispersive spectrometer (EDS) was used for backscattered and secondary electron imaging, and for chemical analysis. Analysis of volume fraction of the inter-dendritic phase (Fig. 8) was performed using image analysis software.

A scanning electron microscopy (SEM) image of SAC305 on Cu substrate showing how the volume fraction of the near eutectic phase can be quantified using Axiosvision© or ImageJ© software.

![Figure 8.](image)

**Figure 8.** A scanning electron microscopy (SEM) image of SAC305 on Cu substrate showing how the volume fraction of the near eutectic phase can be quantified using Axiosvision© or ImageJ© software.

**RESULTS**

**Effects of Composition on microstructure of Sn-Ag-Cu solder joints.**

Increases in the Ag composition of SnAgCu/Cu solder joints resulted in clear increases in the volume fraction of the near eutectic phase (Figs. 8-10). Scanning electron microscopy (SEM) micrographs of cross sections of Pb free solder/Cu solder joints with different solder concentrations generally revealed Sn dendrites surrounded by near eutectic material (e.g. Fig. 9). The area fraction of this interdendritic mixture of Sn and precipitates (such as Ag3Sn) increased as the Ag concentration increased. Fig. 9 portrays a stark example of this evident dependence, more than half of the SEM micrograph for SAC405/Cu reveals near eutectic material, while for SAC105/Cu micrograph this fraction is much lower.

A quantitative examination of the dependence of the volume fraction of the near eutectic SnAgCu material on the Ag concentration in SnAgCu/Cu solder joints was conducted (Fig. 10). The area fraction of the near eutectic SnAgCu material was measured (Fig. 8) for a number of SEM micrographs of cross sections of samples for each of four different Ag concentrations. A plot of the volume fraction determined from these measurements versus Ag concentration is presented in Fig. 10. A linear dependence of volume fraction on Ag concentration was observed. Thus the SEM electron micrographs (e.g. Figs 8 and 9) indicate a linear dependence of the number of small precipitates in the solder joints on Ag concentration (the nature of the near eutectic SnAgCu material did not change significantly with Ag concentration). Thus creep resistance of the solder, and corresponding mechanical strength would be expected to increase with Ag concentration, consistent with previous observations.
strength of SAC/Cu solder joints was observed to increase linearly with Ag content. Furthermore, the value of the shear strength of a SN100C/Cu solder joint was 46 MPa, consistent with its zero Ag concentration in an linear fit to the shear strength of SAC/Cu solder joints versus Ag concentration.

The addition of elements that form solid solutions with Sn at relatively high concentrations (e.g. Bi, see Fig 4), increased the shear strength of solder joints (Fig. 11). For instance, the observed shear strength for an Innolot/Cu solder joint was 90 MPa. Innolot solder adds 3.0wt.% Bi and 1.4wt.% Sb (and 0.1%Ni) to SAC366. In comparison, the shear strength of SAC405/Cu solder joints was found to be less: 72MPa. The Bi and Sb provide further dispersoid strengthening to the solder matrix. In another example, the shear strength of SnCuNiBi which contains 1.5wt.%Bi was found to be higher; 62MPa as compared to that of non Bi containing SN100C, 46MPa.

The Shear Strength of Pb Free Solder/Cu joints
A systematic variation of the shear strength of near eutectic SAC/Cu solder joints with increasing Ag content was observed (Fig. 11) for a number of different solder/Cu joints. For instance, the Ag content, x, was varied from 1 wt.% to 4wt% in SACx05/Cu solder joints. The shear fatigue lifetime of individual solder joints was observed to be sensitive to changes in solder composition, and to aging times. At time zero, the shear fatigue lifetime of near eutectic SnAgCu/Cu solder joints increased with Ag concentration (Fig. 12(a), Fig. 13). Examining the Weibull plots in Fig. 12(a) for different solder joints, it can be seen that the lifetimes for SAC305/Cu solder joints are systematically higher than those for SAC105/Cu solder joints, and both are much higher than that of SN100C/Cu, which has a Ag concentration of zero. Examining a plot of the characteristic lifetime versus Ag concentration for SAC/Cu solder joints, this trend is clear. The room temperature shear fatigue lifetime increases rapidly with Ag concentration for these SAC/Cu solder joints, as can be seen for the zero time points in Fig. 13. Given the clear correlation between the shear fatigue lifetime and Ag concentration (Fig. 10), it is evident that the shear fatigue lifetime is correlated with this volume fraction. This is consistent with the concept that the creep resistance of the solder matrix is increased by the addition of Ag, Bi, and Sb.

Figure 9. Scanning electron microscopy (SEM) images of (a) SAC105 and (b) SAC405 solder joints on Cu substrate.

Figure 10. A plot of volume fraction of the near eutectic SnAgCu material (interdendritic region filled with Ag3Sn and Cu6Sn5 precipitates) versus Ag concentration for SnAgCu/Cu solder joints.

Figure 11. Plot of shear strength of 20mil solder joints on Cu-OSP surface finish versus Ag concentration in various solder alloys.

Room Temperature Shear Fatigue of Pb Free Solder Joints
Values of the shear fatigue lifetime of individual solder joints were observed to be sensitive to changes in solder composition, and to aging times. At time zero, the shear fatigue lifetime of near eutectic SnAgCu/Cu solder joints increased with Ag concentration (Fig. 12(a), Fig. 13). Examining the Weibull plots in Fig. 12(a) for different solder joints, it can be seen that the lifetimes for SAC305/Cu solder joints are systematically higher than those for SAC105/Cu solder joints, and both are much higher than that of SN100C/Cu, which has a Ag concentration of zero. Examining a plot of the characteristic lifetime versus Ag concentration for SAC/Cu solder joints, this trend is clear. The room temperature shear fatigue lifetime increases rapidly with Ag concentration for these SAC/Cu solder joints, as can be seen for the zero time points in Fig. 13. Given the clear correlation between the volume fraction of the near eutectic SnAgCu material and Ag concentration (Fig. 10), it is evident that the shear fatigue lifetime is correlated with this volume fraction. This is consistent with the concept that the creep resistance of the solder matrix is increased by the addition of Ag, Bi, and Sb.
solder increases with the number of smaller precipitates in the solder.

Evidence of the efficacy of the addition of dispersoids in solid solution in Sn was evident in room temperature shear fatigue results (Figs. 12 and 14). For instance, the addition of 3%Bi and 1.4%Sb to a Sn based, 3.6%Ag alloy (to make Innolot, which also contains 0.15%Ni) resulted in more than a factor of two increase in the shear fatigue lifetime for Innolot/Cu solder joints (Fig. 12(a)).

**Effect of Aging on Lifetimes: Precipitate Hardening compared to Solid Solution Strengthening**

The room temperature shear fatigue lifetime of SAC/Cu solder joints decreased precipitously upon aging at a temperature of 125°C (Fig. 12 and 13). Aging times ranged from 1100 h to 4200 h, but large drops were observed at the shortest aging times for all SAC compositions. For instance, the lifetime of SAC405/Cu solder joints dropped from 1973 to 640 cycles after aging at 1100h at a temperature of 125°C. While a clear composition dependence of the shear fatigue lifetime was observed before aging, this effect was muted after aging, even for intermediate aging times. After aging for 4200 h, the range in lifetimes for SAC105 to SAC405/Cu solder joints was only between 122 and 227 cycles, in contrast to the range from 308 to 1973 cycles before aging (Fig. 13). Values of lifetimes for these SAC/Cu solder joints have decreased to the level of that of SN100C/Cu solder joints (Fig. 12(c)).

**Figure 12.** Weibull plots showing isothermal shear fatigue performance for sets of 20mil solder joints of five alloys on Cu-OSP substrate, for different aging times (a) as-reflowed, (b) aged at 125°C for 2520 hours (c) aged at 125°C for 4200 hours.
Figure 14. Bar charts reveal the effect of aging on the room temperature shear fatigue characteristic life time of different SAC alloys. The aging temperature was 125°C. An expanded version of the bar charts for SAC305 and SnNiCuBi is provided.

In contrast to the large decreases in shear fatigue lifetimes for SAC/Cu solder joints after aging, the shear fatigue of solder joints with Pb free alloys containing alloying elements such as Bi were fairly stable. Such solder joints revealed much smaller changes upon long term aging (Figs. 12 and 14). Lifetimes of Innolot/Cu solder joints (Figs. 12 and 14(a)) decreased by a factor of two after 4200 h of aging to a lifetime of 501 cycles, a stark contrast to the lifetime of 227 cycles for SAC305/Cu solder joints after 4200 h aging. Furthermore, lifetimes of SnCuNiBi/Cu solder joints revealed an increase in shear fatigue lifetime after aging at 125°C for 4200 h (Fig. 14b). This may indicate that the arrangement of Bi atoms in the solder can be optimized with specific thermal treatment.

The differences in behavior of SAC/Cu solder joints and those solder joints containing elements such as Bi are consistent with the fact that Sb and Bi are in equilibrium in solid solution in Sn at relatively high concentrations at moderate temperatures (e.g. more than 10% Bi at a temperature of 125°C, Fig. 4). While small Ag3Sn precipitates are effective at hindering dislocation motion, after prolonged aging these precipitates coarsen and their efficacy lessens. In contrast, 3% of Bi or Sb are in equilibrium in solution in Sn at a temperature of 125°C, so such aging would not be expected to cause these additions to lose their ability to hinder the movement of dislocations.

Even at operating temperatures, these elements remain in solid solution (for instance, at 60°C, a 3% addition of Bi to Sn would not be expected to precipitate out of solution) [6, 24-30].

SUMMARY
Measurements of the room temperature shear fatigue lifetime of individual solder joints were observed to be sensitive to changes in solder composition and to aging times. While the dependence of the shear fatigue lifetime on solder composition echoed that of the shear strength on composition, the variation of the shear fatigue was much more sensitive. This variation was distinct, unambiguous and large. Shear fatigue measurements also clearly illustrated the variation of the thermomechanical properties of these solder joints with aging. The efficacy of room temperature shear fatigue measurements was clearly illustrated.

The dependence of the thermomechanical properties of near eutectic SnAgCu/Cu solder joints on Ag concentration was clearly illustrated. The volume fraction of the interdendritic phase was found to increase linearly with Ag concentration for these joints. In a corresponding fashion, the shear fatigue lifetime increased strongly with Ag concentration.

The addition of Bi or Sb to Sn based solder alloys increased their shear strength and shear fatigue lifetimes. Furthermore, these mechanical responses were less sensitive to the effects of long term aging than those for near eutectic SAC alloys. The shear fatigue lifetimes of SnAgCu/Cu solder joints decreased dramatically upon aging at a temperature of 125°C, while solder/Cu joints with Sn based solders containing solid solution dispersoids were relatively stable. In fact, room temperature shear fatigue lifetimes of a SnNiCuBi solder increased upon aging.

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