

MICROALLOYED Sn-Cu Pb-FREE SOLDER FOR HIGH TEMPERATURE APPLICATIONS

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require any of the materials or substances listed in Annex II (of the Directive)

- is scientifically or technical impracticable
- the reliability of the substitutes is not ensured
- the total negative environmental, health and consumer safety impacts caused by substitution are likely to outweigh the total environmental, health and safety benefits thereof.”

ABSTRACT

While the search continues for replacements for the highmelting-point, high-Pb solders on which the electronics industry has depended for joints that maintain their integrity at high operating temperatures, an investigation has been made into the feasibility of using a hypereutectic Sn-7Cu in this application. While its solidus temperature remains at 227°C the microstructure, which has been substantially modified by stabilization and grain refining of the primary Cu₆Sn₅ by microalloying additions of Ni and Al, makes it possible for this alloy to maintain its integrity and adequate strength even after long term exposure to temperatures up to 150°C. In this paper the results of a study of microstructural evolution during elevated temperature aging and in particular the growth of intermetallics at the interface between Cu and Ni substrates will be reported as well as the results of elevated temperature mechanical testing.

INTRODUCTION

While susceptibility to tin whisker growth remains a barrier to the transition to Pb-free technologies in some applications, there is now general acceptance by the electronics industry that there are reliable alternatives to the Sn-37Pb and Sn-36Pb-2Ag solders that were previously used for the majority of electronic assembly. There has, however, been ongoing concern about whether Pb-free alternatives can be found to the high-Pb solders that have traditionally been used in applications where the solder joint is required to operate at elevated temperature [1].

At the time the EU Directive on the Restriction of Hazardous Substances in Electrical and Electronic Equipment (“RoHS”) came into force in 2006, the lack of a proven alternative to these high-Pb solders was acknowledged by Exemption 7 of Annex III granted to “Lead in high melting temperature type solders (i.e. leadbased alloys containing 85% by weight or more lead)”. However, it was made clear that this exemption would remain only while “the elimination or substitution via design changes or materials and components that do

A recast of the Directive issued in June 2011 includes the statement that for such exemptions “the maximum validity period which may be renewed shall... be 5 years from 21 July 2011”. The inference from this statement is that there is an expectation that alternatives to the use of solders with a lead content of 85% or more will be found before 21st July 2016.

As well as providing adequate strength in the same temperature range at that in which the high-Pb solder has been used, ideally it should be possible to form a joint with the alternative material with process temperature no higher than those used with the high-Pb solders.

The most widely used high-Pb solder has been the Sn-95Pb alloy, which has a melting range with a liquidus temperature around 365°C and a solidus temperature around 304°C and is typically reflowed at a peak temperature around 380°C [1,2].

Alternatives to the high-Pb solders that have been considered include conductive adhesives based on resins that can survive elevated temperature and nano materials which can be sintered at temperatures comparable with the process temperature used with the high-Pb solders. While these alternative materials can undoubtedly provide solutions in many applications, the advantages of a solder joint have prompted a search for a Pb-free alloy that would work as a solder with characteristics similar to that of the high-Pb solder it has to replace.

Most of the search for a Pb-free solder that could replace the high-Pb solders has been directed at finding an alloy that has a similar solidus temperature to that of the Sn-95Pb alloy and compositions that meet or exceed that criterion in the Au-Sn, Bi-Ag, Zn-Sn and Zn-Al systems have been identified with

some finding commercial application [1, 2]. However, all of these alloys have disadvantages compared with the Pb-Sn alloy if not in terms of cost then in mechanical properties or susceptibility to corrosion.

Problems with these alternative alloys prompted a reexamination of the actual requirements of the solder in applications where the high-Pb alloys have been used to determine whether there were situations where variants on more conventional Pb-free alloys might be suitable.

Although the solidus temperature of one of the most commonly used high-Pb solder, Sn-95Pb, is around 304°C, in one of the common applications of this alloy, the attachment of silicon dies to substrates, the joint is typically at temperatures around 150°C with a peak around 200°C. The solidus temperature of alloys in the Sn-rich end of the Sn-Cu system is 227°C so that temperatures in the range 150-200°C represent homologous temperatures of 0.846 and 0.946 respectively, at which the strength of the alloy would be expected to have declined dramatically.

In the Sn-Cu system (Figure 1) [3] there is the possibility of increasing the volume of second phase, which would be expected to have a strengthening effect on the alloy, even at such high homologous temperatures, by increasing the Cu content of the alloy. Beyond about 7.6% the first phase to freeze out of the melt is Cu_3Sn which with compositions up to about 38% Cu would then undergo a peritectic reaction to form Cu_6Sn_5 as the cooling progresses. While higher Cu content alloys might have potential, in the study reported here the Cu level will be limited to a maximum of 7% so that the primary second phase, Cu_6Sn_5 , forms from the melt in a single stage.

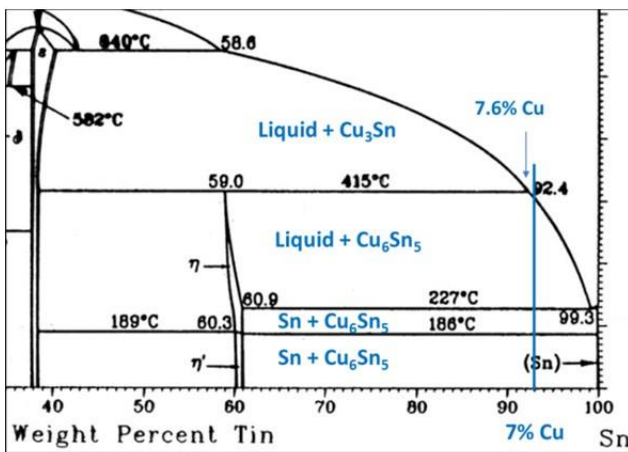


Figure 1. Sn-rich corner of the Sn-Cu Equilibrium phase diagram [3]

MODIFIED HYPEREUTECTIC Sn-Cu ALLOYS

In Sn-Cu alloys with Cu in the range from about 0.9% to 7.6% Cu, the first phase to precipitate is primary Cu_6Sn_5 , which would typically form as coarse prismatic crystals

reflecting its hexagonal-close-packed crystal structure. Grains of intermetallic compound (IMC) of that size and spacing would probably not be very effective in strengthening the matrix to achieve a measurable increase in strength at a high homologous temperature and may even be a source of weakness. IMC such as Cu_6Sn_5 are hard and resistant to deformation and in bulk form might tend to crack, which in turn might initiate cracking in the Sn matrix.

The likelihood that an alloy with such a high Cu content would have the mechanical properties desirable in a solder would be greater if the Cu_6Sn_5 phase were in the form of fine dispersed grains and an investigation of possible grain refiners was undertaken [4].

For a given volume fraction of Cu_6Sn_5 the grain size is determined by the number of nuclei activated during the solidification process. There are two recognized methods for increasing the number of nuclei: heterogenous nucleation and constitutional undercooling [4].

Heterogenous nucleation is achieved by introducing into the system a particle on which the Cu_6Sn_5 can grow. In the absence of such heterogenous nuclei, particles of Cu_6Sn_5 must form directly from the melt, a process that requires a high energy input which can come only from undercooling. Even with substantial undercooling the number of nucleations tends to be small and consequently the Cu_6Sn_5 particle size large.

Constitutional undercooling relies on the build-up of a concentration of solute ahead of the advancing solid-liquid interface during solidification. The freezing point of the liquid with that increased solute concentration is lowered so that the effective undercooling that provides the driving force for homogeneous nucleation is increased.

In a series of experiments reported elsewhere [4] trace level additions (500ppm) of a selection of elements were added to Sn-4Cu to determine their effect on the nucleation and hence the particle size of the Cu_6Sn_5 . Alloys were prepared by melting Sn-4Cu in a boron-nitride-coated clay-graphite crucible in an electric furnace at 450°C with additions made either as pure metals or master alloys. After alloying samples were collected in small boron-nitride-coated stainless steel cups and allowed to cool in air. Representative samples were subject to thermal analysis in the set-up illustrated schematically in Figure 2 [4].

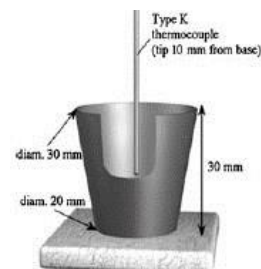


Figure 2. Thermal analysis set up

A typical thermal analysis result is presented in Figure 3 [4].

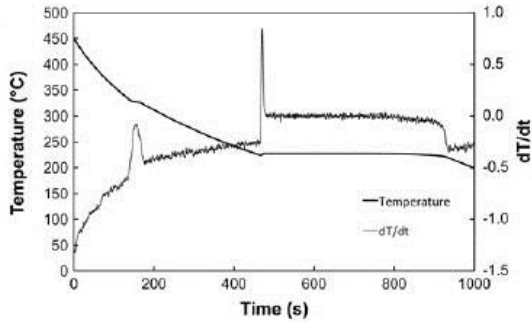


Figure 3. Cooling curve and differential for Sn-4Cu alloy

The addition elements were selected mainly on the basis of their low solubility in β -Sn, which would promote constitutional undercooling, or their low solubility in Cu_6Sn_5 which would mean that they would be likely to form a separate intermetallic phase on which the Cu_6Sn_5 could nucleate. The exceptions to those criteria were Ni and Ge which are key ingredients in a widely-used family of Sn-Cu alloys. In these alloys the Ni stabilizes to room temperature and below the hexagonal form of the Cu_6Sn_5 , the stable form of which at those temperatures is otherwise monoclinic [5-7]. The Ge is an anti-oxidant, reducing drossing on the molten metal and discoloring oxidation during reflow. These additions were included in the initial study to confirm that they did not themselves affect Cu_6Sn_5 nucleation.

The conclusion of this series of experiments was that Al is the element has by far the most powerful effect on Cu_6Sn_5 nucleation (Figure 4) [4].

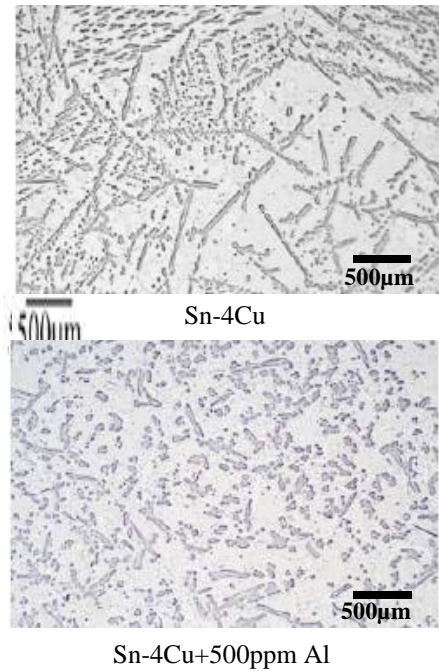


Figure 4. Effect of Al addition on Cu_6Sn_5 morphology

It was found that Ni and Ge additions of 500ppm and 600ppm respectively did not affect the grain refining effect of Al and because of the beneficial effects those additions have on the performance of Sn-Cu alloys further experiments were carried out with alloys with Ni and Ge levels optimized for performance in that regard.

Experiments with increasing levels of Al in a commercial Sn-4Cu alloy indicate that the optimum addition is around 250ppm (Figure 5) [4].

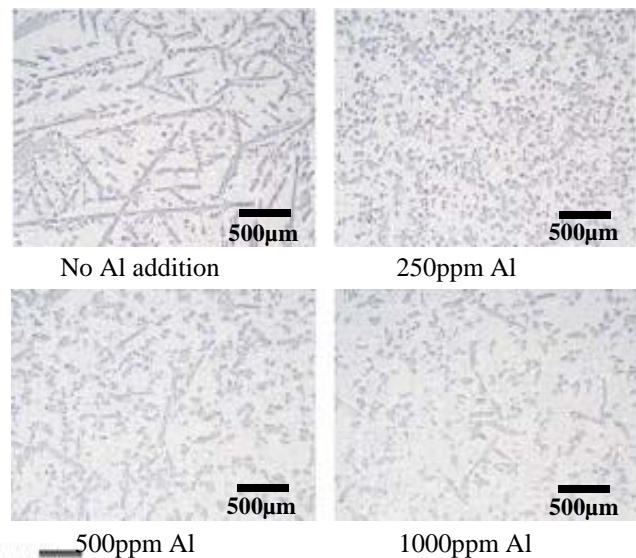


Figure 5. Effect of Al level on refining of Cu_6Sn_5 in commercial Sn-4Cu alloy with additions of Ni and Ge

The conclusion of an analysis of the relative contributions of an Al addition to constitutional undercooling and

heterogenous nucleation [4] was that the latter is the more likely cause of the observed refining of the Cu_6Sn_5 . Evidence to support that conclusion is provided by the discovery of particles of an Al-Cu intermetallic compound in the centre of Cu_6Sn_5 crystals (Figure 6) [4].

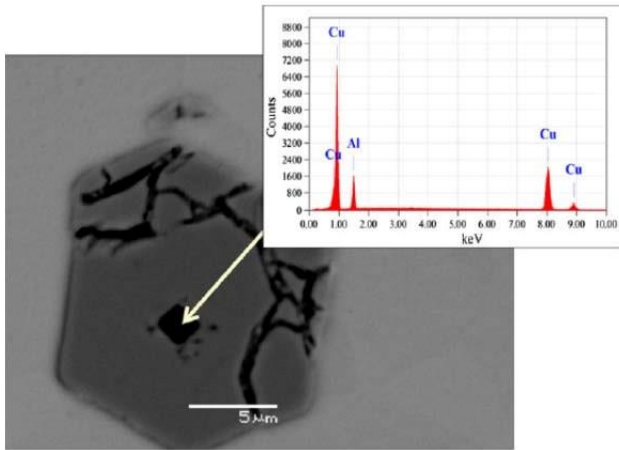


Figure 6. Al-Cu intermetallic inside a Cu_6Sn_5 crystal formed from Sn-4Cu

Observations in thermal analysis indicate that the temperature at which the Cu_6Sn_5 phase starts to form from the Sn-4Cu alloy (determined by the first differential) falls with increasing levels of Al addition (Figure 7) [4]. Since this behavior is not consistent with heterogenous nucleation it is hypothesised that this is the result of a reduction in the level of Cu in the liquid, and hence a reduction in the liquidus temperature, because of the formation of the Al-Cu nucleants.

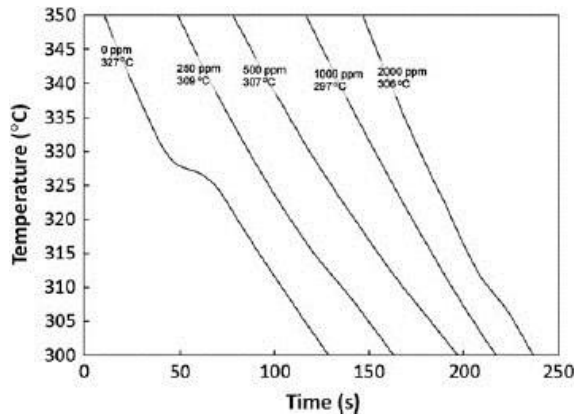


Figure 7. Fall with Al level of the temperature at which formation of Cu_6Sn_5 commences in Sn-4Cu alloy

Real time observation of the solidification of Sn-4Cu with and without the addition of 250ppm Al have revealed the effect of the Al addition on the nucleation of Cu_6Sn_5 (Figure 8) [4].

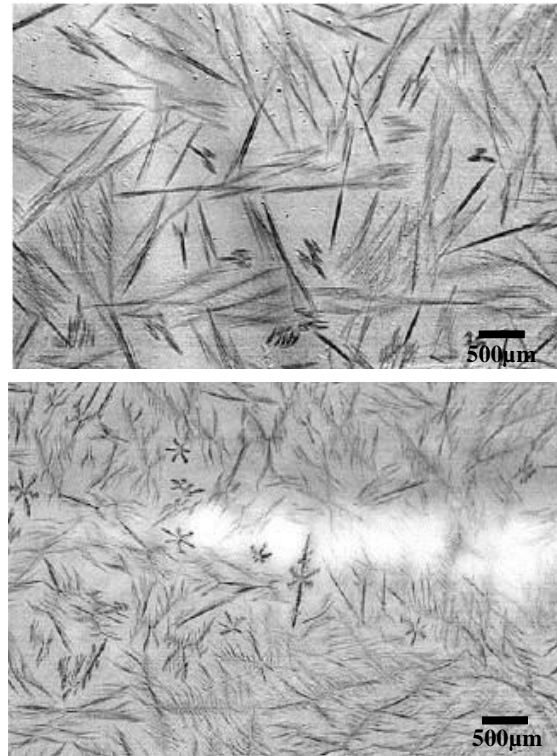


Figure 8. Still images from real time video of the solidification of Sn-4Cu (top) and Sn-4Cu+250ppm Al observed in the synchrotron beam line

PROPERTIES OF MODIFIED Sn-7Cu

With a mechanism for refining the Cu_6Sn_5 phase in the Sn4Cu alloy confirmed experiments were carried out to determine the potential of an Al-modified Sn-7Cu-0.05Ni alloy [9], which as explained earlier has close to the maximum Cu content possible if the Cu_6Sn_5 phase is to be formed directly from the melt rather than partly from a peritectic reaction.

In addition to its effect on the Cu_6Sn_5 grain size the Al addition refines the Sn grain size of the reflowed alloy (Figure 9). This suggests that the Cu_6Sn_5 is facilitating the nucleation of the Sn.

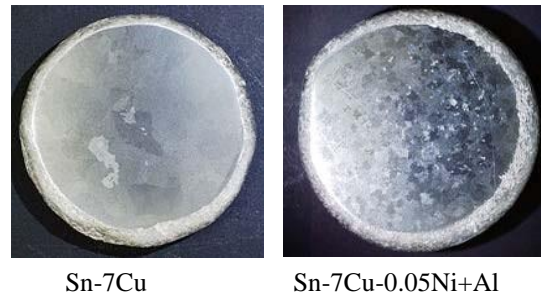


Figure 9. Solder surface reflowed and slow cooled on copper substrate revealing Sn grain refining effect of Al

Bulk samples were prepared by casting the alloy into a metal mold (Figure 10). To assess the effect of cooling rate on properties, cooling to the mold was adjusted to achieve fast

and slow cooling. The actual cooling rate was measured by monitoring the temperature in the gage length of the test piece as indicated in Figure 10 and the results are plotted in Figure 11.



Figure 10. Set-up for casting bulk solder test pieces

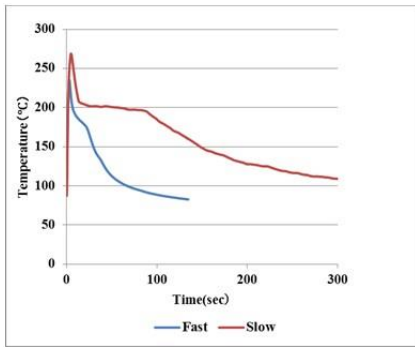


Figure 11. Fast and slow cooling rates for bulk solder test pieces

The effect of cooling rate on tensile strength and elongation for the Al-modified Sn-7Cu-0.05Ni alloy measured at 20°C with a cross-head speed of 1mm/s is apparent in Figure 12. The strength of the Sn-7Cu alloy is significantly affected by the cooling rate while elongation remains unchanged. The strength of the Sn-95Pb alloy is lower but is not significantly affected by cooling rate. Elongation of the Sn95Pb is greater than that of the Sn-7Cu alloy particularly with the faster cooling rate.

The difference between the strength of the fast and slow cooled samples of Sn-7Cu-0.05Ni+Al is probably a reflection of the difference in microstructure (Figure 13).

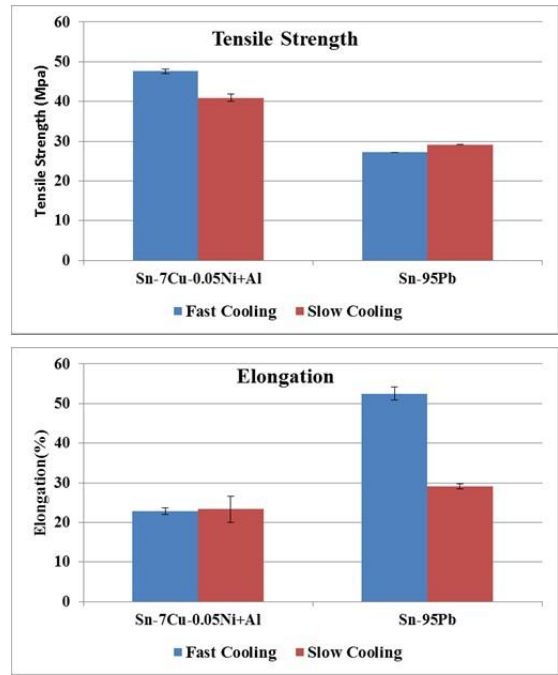


Figure 12. Tensile strength and elongation of Sn-7Cu-0.05Ni+Al and Sn-95Pb at fast and slow cooling rates

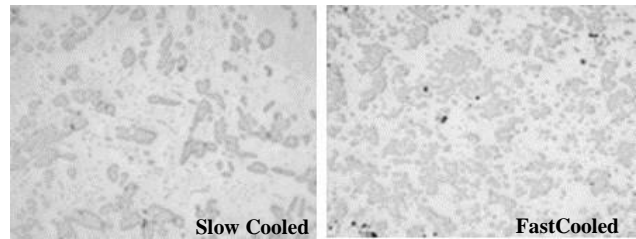


Figure 13. Microstructure of Sn-7Cu-0.05Ni+Al in the gage length of slow and fast cooled bulk tensile test pieces

For mechanical testing of solder joints cast ingots were rolled into 400µm foil from which 5mm square preforms were cut for the formation of a lap joint between two pieces of 1mm thick copper (Figure 14). The test pieces were assembled with an activated rosin flux and reflowed for 30 second at temperatures of 260°C, 300°C, 340°C, 380°C and 420°C. Since this alloy is being evaluated as an alternative to Sn-95Pb, for comparison purposes test pieces were assembled with this alloy with a reflow temperature of 330°C.

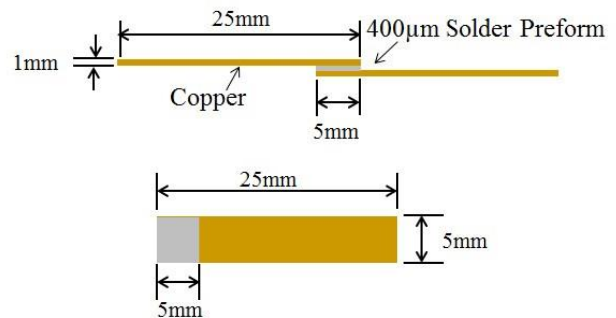


Figure 14. Shear test piece

Tests were performed at a cross-head speed of 1mm/s at 25°C, 100°C, 150°C, 200°C, 220°C and 230°C. Typical stress strain curves are shown in Figure 15.

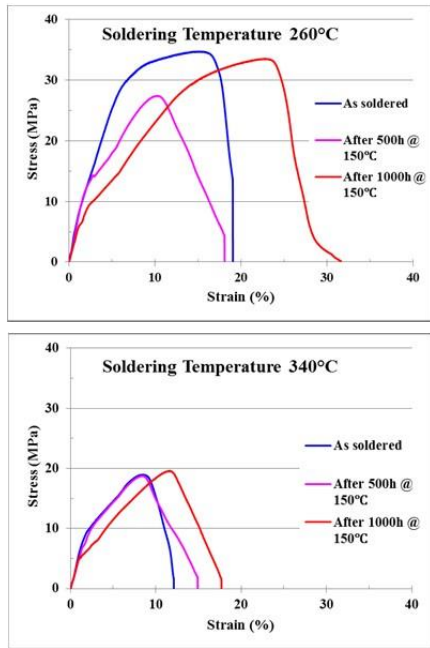


Figure 15. Typical shear stress-strain plots for Sn-7Cu-0.05Ni+Al lap joints at 25°C as a function of soldering temperature and aging

While soldering temperature has an effect on joint strength the additional effect of thermal aging is minimal (Figure 16). The reduction in strength with aging temperature parallels the coarsening of the Cu_6Sn_5 (Figure 17). However, since it is clear from Figure 17 that the copper substrate is fully wetted at a soldering temperature of 260°C, it is not necessary to use the higher soldering temperatures required with solders with a higher solidus temperature. The presence of particles of undissolved Cu_6Sn_5 at temperatures below the liquidus does not appear to interfere with the soldering process.

In aging at 150°C, coarsening of the Cu_6Sn_5 occurs and also growth of the interfacial intermetallic layer with the appearance of the Cu_3Sn phase between the Cu and Cu_6Sn_5 (Figure 18). While the total thickness of IMC seems similar for all solder temperatures, after aging for 1000 hours at

150°C the proportion of Cu_3Sn is greater in the joints soldered at lower temperatures. 0.05Ni alloy maintains a strength advantage over Sn-95Pb

through to 200°C and under the conditions of this test the Al-modified Sn-7Cu-

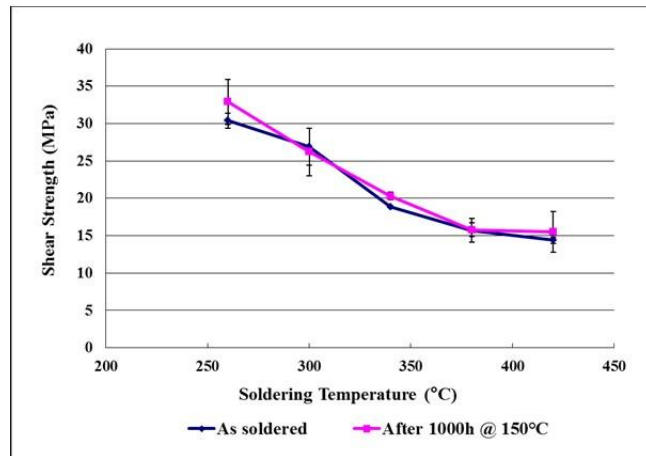
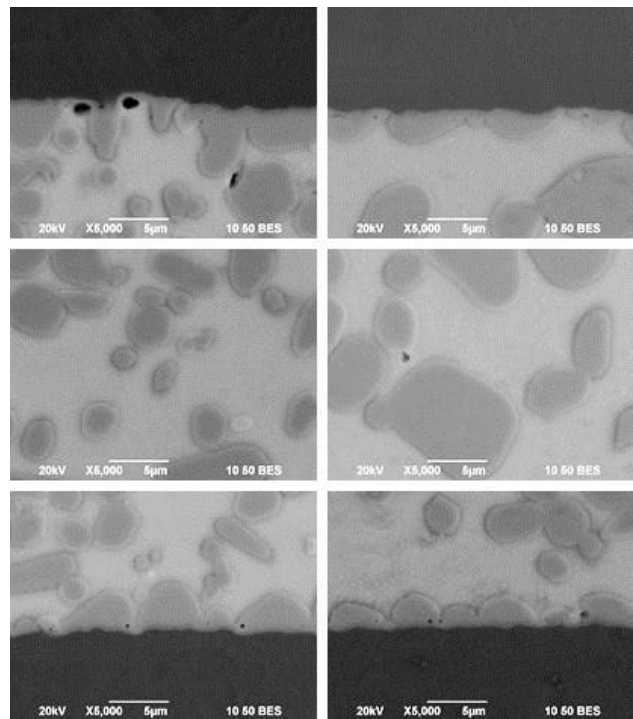
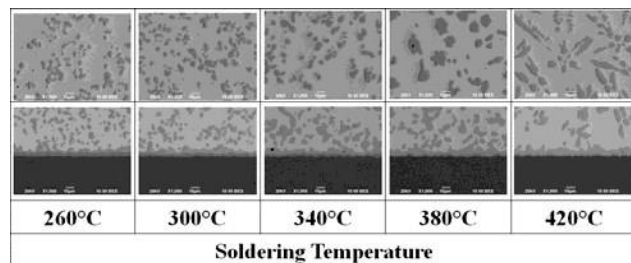


Figure 16. Effect of soldering temperature and aging on shear strength of Sn-7Cu-0.05Ni+Al



matches the strength of the Sn-95Pb even at 220°C, only 7°C below its solidus temperature. In testing after 1000 hours aging at 150°C the shear stress at 25°C dropped only 6.3%.

Figure 17. Coarsening of Cu_6Sn_5 phase in Sn-7Cu-0.05Ni+Ag reflowed on a Cu substrate with increasing

soldering temperature **Figure 19.** Stability of Sn-7Cu-0.05Ni+Al microstructure of lap joint to copper formed by reflowing a 400 μ m preform

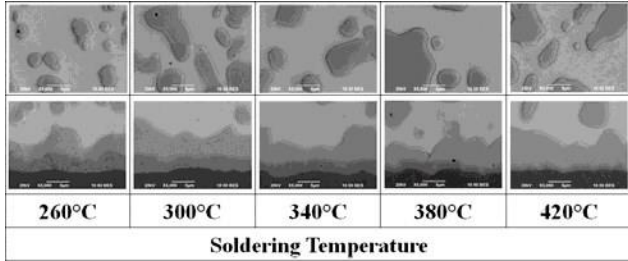


Figure 18. Coarsening of Cu_6Sn_5 phase and growth of the interfacial intermetallic layer in Sn-7Cu-0.05Ni+Al joints reflowed at the indicated temperature and aged for 1000 hour at 150°C

Reflowed 1 x 30s

Reflowed 2 x 60s

of lap joint to copper formed by at 260°C

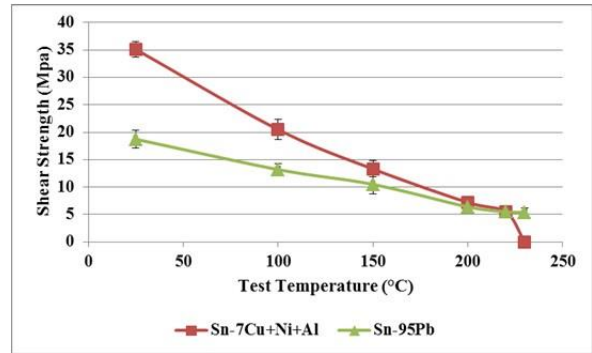


Figure 20. Shear strength of lap joints to copper of Al-modified Sn-7Cu-0.05Ni and Sn-95Pb as a function of test times and multiple reflow cycles (Figure 19). temperature, cross-head speed 1mm/s

While there is some deterioration as a result of aging the

strength is probably sufficient for die attach and other applications where the function of the joint is mainly to provide an electrical and thermal connection rather than to carry a mechanical load.

The strengthening effect of the higher Cu content is

Testing over the temperature range to which die attach solders are likely to be exposed (Figure 20) indicate that despite operating at a higher homologous temperature,

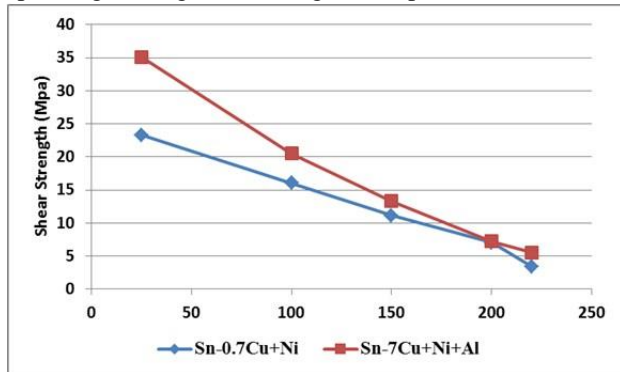


Figure 21. Shear strength of lap joints to copper of Almodified Sn-7Cu-0.05Ni and Sn-0.7Cu-0.05Ni as a function of test temperature, cross-head speed 1mm/s

powder particle size that a smooth sphere could be formed. As can be seen in Figure 21, that criterion was met in Grade D4 powder (20-38 μ m) with perhaps the fast cooling rate and the high surface area: volume ratio also contributing to the fine grains size of the Cu_6Sn_5 .

As with joints formed by reflow of a preform (Figure 19) the microstructure of joints formed with Sn-7Cu-0.05Ni paste (Figure 23) is affected by soldering conditions.

For flexibility of application a solder alloy should be available in paste form and a question was whether the Cu_6Sn_5 particles in the 7% Cu alloy would be fine enough in relation to the

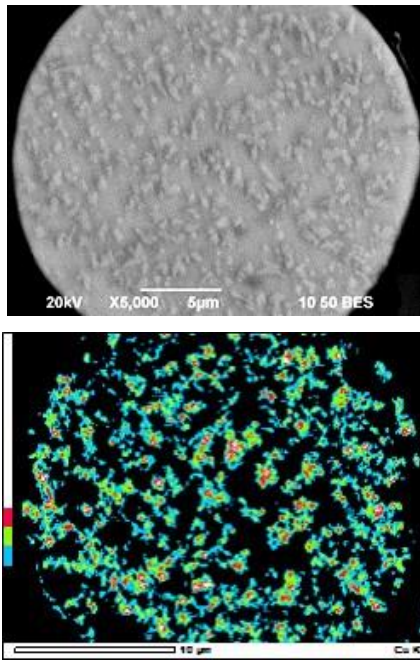
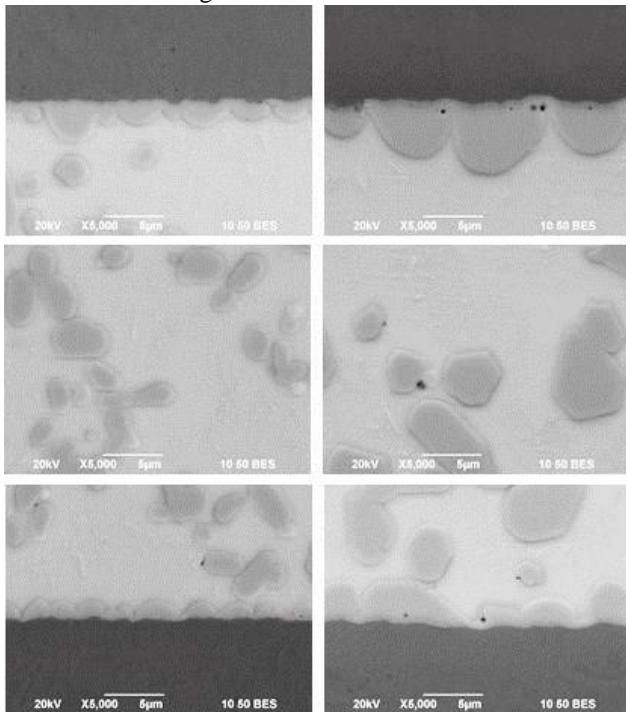


Figure 22. SEM image and EDX element mapping of Cu of D4 grade Al-modified Sn-7Cu-0.05Ni powder

In preparation for thermal cycling studies to be reported later, silicon dies have been reflowed to a Cu substrate with Sn-7Cu-0.05Ni+Al and Sn-95Pb (Figure 24). The better wetting of the Sn-Cu alloy could be contributing to the lower incidence of voiding.



Reflowed 1 x 30s Reflowed 2 x 60s **Figure 23.** Stability of Sn-7Cu-0.05Ni+Al microstructure of lap joint formed by reflowing paste at 260°C

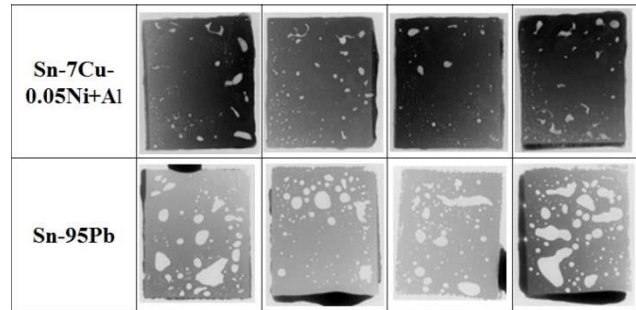
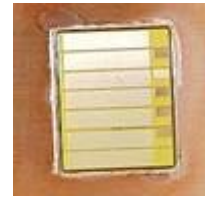


Figure 24. Voiding in solder joint between silicon chip and Cu substrate reflowed with 400μm preform

CONCLUSIONS

The results reported here indicate that a Sn-7Cu alloy in which the particle size of the primary Cu_6Sn_5 phase has been refined by an addition of Al appears to have strength at least comparable with that of Sn-95Pb at temperatures up to 220°C. The reduction in strength that occurs as the Cu_6Sn_5 coarsens suggests that the relatively high strength of the Sn7Cu alloy results from the fine dispersion of Cu_6Sn_5 particles that results from the controlled addition of Al.

FUTURE WORK

Given the clear evidence of a relationship between strength and the Cu_6Sn_5 particle size an attempt will be made to quantify the particle size distribution and relate it to mechanical properties and reliability.

ACKNOWLEDGEMENTS

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