The Anomalous Microstructural, Tensile and Aging Response of Thin Cast Sn3.9Ag0.6Cu Lead Free Solder

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Abstract--In this study bulk and thin cast samples were produced with an identical Sn3.9Ag0.6Cu composition. The thin cast material exhibited a much finer as-quenched microstructure than the bulk material with the IMC phase restricted to a thin network. Both the bulk and thin cast materials continually softened during room temperature aging, while both materials initially softened and then subsequently hardened when aged at 120^{0}C and 180^{0}C. The thin cast material was in all cases significantly softer than the bulk material, and responded to aging as if it were bulk material aged at a higher temperature. These results have significant implications for the elevated temperature application of Sn3.9Ag0.6Cu.

Keywords: Sn-Ag-Cu lead free solder, aging response, microstructural changes, tensile properties

INTRODUCTION

Lead-free solder alloys will see increasing use in the future. The NEMI, Sn3.9Ag0.6Cu alloy or a close variant appears to be a leading candidate for broad commercial use. Although aging effects on microstructure and tensile behavior have been studied in bulk Sn3.9Ag0.6Cu solder samples[1-7], the effects of strong reductions in sample size on the development of microstructure and consequent mechanical properties are not well known. This issue is one of increasing importance as the size of electronic solder connections become ever smaller.

Existing research has clearly shown that microstructural development in the bulk Sn3.9Ag0.6Cu alloy is much more complex than that in eutectic 63Sn37Pb. In this study, we investigate how the microstructural development and mechanical properties of bulk and thin cast samples respond quite differently to aging at three different temperatures. The thin cast geometry was developed so that we could produce accurate tensile test samples with a specimen dimension small in comparison to the scale of the bulk microstructure. Restricting a dimension in the thin cast sample resulted in changes in the microstructure of the thin cast material in a way similar to how changes in the dimension of a solder ball from large to small relative to the scale of the bulk microstructure results in strong changes in microstructure. This is an issue of increasing importance as the size of solder balls used in electronic packages will continue to strongly decrease in the future. We will show that the bulk and thin cast samples do exhibit significant differences in thermal-mechanical properties, and as a consequence we may expect that small solder balls will show important performance differences relative to that of large solder balls under elevated temperature service in an electronic package.

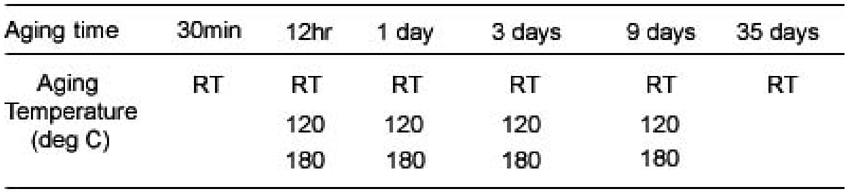
EXPERIMENTAL PROCEDURE

All experimental samples were from the same commercial NEMI Sn3.9Ag0.6Cu alloy (composition given in mass %). Mechanical test samples were vacuum cast inside a conical shaped stainless steel mold in two different thicknesses, 100 μm (thin cast) and 1500 μm (bulk). Figure 1 shows that the conical mold consisted of an outer vessel and an inner plug, the difference in sample thickness was the result of a difference in plug design. All samples shared the same outer vessel. Solid solder was first loaded into the solder well of the cleaned mold, which was then heated under vacuum until the solder completely melted. When the solder melts, the central plug drops into precision alignment as excess molten solder is forced upward and out of the casting vent. This results in a very clean sample with precise thickness. Once the sample material was melted, the mold was removed from the vacuum furnace and rapidly water quenched.

Figure 2 shows the cooling curves measured via thermocouples in contact with the solder from the mid section of the bulk and thin cast samples. The equilibrium solidification temperature of the alloy is 217^0C. The figure shows an initial rapid cooling process of approximately 2.2 seconds followed by a temperature plateau which corresponds to the period of primary solidification. The period of primary solidification is significantly longer for the bulk sample at approx. 2.8 sec. versus 1.3 sec. for the thin cast sample. The figure further shows that there is undercooling during solidification for both types of samples. However the degree of under-cooling is significantly larger for the thin cast samples. The physical requirement for large undercooling to promote the solidification of near ternary eutectic Sn-Ag-Cu alloys has been previously reported[8,9]. The observed differences in the cooling curves are primarily due to the far larger amount of latent heat produced by the larger volume bulk sample which must be transferred through the same wall area as that of the thin cast sample.

After quench, bulk and thin cast samples were aged in an air furnace to the set of conditions listed in Table 1.

Table 1. Aging times at room temperature (RT), 120 and 180^{0}C.



Aging time	30min	12hr	1 day	3 days	9 days	35 days
Aging Temperature (deg C)	RT	RT	RT	RT	RT	RT
		120	120	120	120	
		180	180	180	180	

Tensile tests were performed on a MTS 858 testing machine under displacement control. The tensile specimens were machined with a width of 7.6 mm and a gauge length of 20.4 mm. Load and displacement data were recorded and used to determine the true stress/true strain curve. The stain rate is 1.78E-3(1/sec). For each condition, two samples were tested from the same casting. Following tensile testing, separate samples for microstructure investigation were prepared. The samples were aged to the conditions of the tensile test specimens, then metallographically polished and etched. Each metallurgical sample was first ground with SiC papers and then polished with diamond paste. The finest polish size was 0.25 micron. All samples were then etched for three seconds with a 2 vol % hydrochloric acid in ethanol solution. SEM/backscatter electron (BSE) analysis was then performed to identify the microstructures. The SEM machine used was a JEOL JSM 5800-LV, with an accelerating voltage of 20keV.

RESULTS AND DISCUSSION

NEMI Sn3.9Ag0.6Cu alloy after aging at room temperature

Figure 3 shows how bulk and thin cast Sn3.9Ag0.6Cu differ in their microstructural development under room temperature aging. In each case the microstructure consists of a mixture of eutectic regions of dispersed intermetallic compounds (IMC) which surround large, rounded beta-Sn crystals (phases are identified in Fig. 3(a)). The tiny precipitates have been identified as the Ag_3Sn and Cu_6Sn_5 intermetallic phases[1]. A comparison between Figs. 3(a) and 3(c) shows that the large difference in primary solidification time, and the greater degree of under-cooling of the thin cast sample noted in Fig. 2, results in an as-quenched thin cast microstructure which is significantly finer than that of the as-quenched bulk material. In the thin cast sample the beta-Sn grains are small and semi-connected while the IMC eutectic form a thin semi-continuous network. In the bulk sample the IMC eutectic forms a thick continuous network which isolates individual large size beta-Sn grains. A comparison of Figs 3(a) and 3(b) shows that both the beta-Sn and IMC particles significantly coarsen in the bulk sample after 35 days at room temperature. A similar comparison of Figs 3(c) and 3(d) shows that both the beta-Sn and IMC particles also significantly coarsen in the thin cast sample after 35 days at room temperature, however even after 35 days the thin cast microstructure appears finer than the bulk microstructure.

Figure 4 compares the tensile stress versus strain behavior of bulk and thin cast samples at different aging conditions. Figures 4(a) and 4(b) show that both bulk and thin cast materials continually softened during room temperature aging. Increasing the aging time from as-quenched to 35 days reduced the tensile flow strength of the bulk material by 20% from 63.4 MPa to 50.6 MPa, while the tensile flow strength of thin cast material was reduced approx. 18% from 50 MPa to 41 MPa. A comparison between Figs. 4(a) and 4(b) show that the thin cast material is always significantly softer. The thin cast material being approximately 13 MPa softer in the as-quenched condition and 10 MPa softer after room temperature aging for 35 days.

The softening of both the bulk and thin cast alloy correlates with the recrystallization of the large tin-rich grains and the coarsening of the IMC eutectic. Miyazawa and Ariga[2] have shown that aging temperature and time do not influence the lattice constant (a axis) of the tin-rich solid solution, and the solid solubility of Ag in tin-rich solid solution hardly changes. It is thought that the primary hardening mechanism in the alloy is due to precipitation hardening by the IMC particles within the eutectic regions, which becomes less effective as the IMC particles coarsen. The relative softness of the as-quenched thin cast material is therefore the likely result of the disadvantangeous thin semicontinous form of the IMC eutectic regions which precludes effective precipitation hardening. The strength disadvantage of the thin-cast material then persists as the microstructure evolves under extended room temperature aging.

NEMI Sn3.9Ag0.6Cu alloy after aging at 120^{0}C

Figure 5 shows how bulk and thin cast Sn3.9Ag0.6Cu differ in their microstructural development after aging at 120^{0}C. These images should be compared to the as-quenched microstructures shown in Figs. 3(a) and 3(c). Comparisons between Figs. 3(a) and 5(a) and between Figs. 3(c) and 5(c) clearly show strong coarsening of the IMC particles in both the bulk and thin cast material after aging for one day. A further comparison between Figs. 3(a) and 5(a) shows coarsening of the beta-Sn grains in the bulk material, while a comparison between Figs. 3(c) and 5(c) shows at most weak coarsening in the beta-Sn grains in the thin cast material after aging for one day.

Comparisons between Figs. 5(a) and 5(b) and between Figs. 5(c) and 5(d) show very substantial changes occuring in both materials as the aging time increased from one day to three days. Here we see that the IMC particles are significantly more coarse in both the bulk and thin cast materials. A comparison between Figs. 5(a) and 5(b) further shows strong coarsening and partial interconnection of the beta-Sn grains in the bulk material, while a comparison between Figs. 5(c) and 5(d) shows that the coarsening of the thin IMC eutectic network has resulted in the near isolation of individual IMC particles and the interconnection of the beta-Sn phase in the thin cast material.

Figure 6 compares tensile data from bulk and thin cast samples for various aging times at 120^{0}C. The figure shows that both the bulk and thin cast materials initially soften and then subsequently harden. The minimum flow strength occurs after one day, and then both materials measurably harden as the aging time is increased up to nine days. A comparison between Figs. 6(a) and 6(b) shows that the thin cast material is in all cases significantly softer than the bulk material. The reason for the strength advantage of the bulk material is not absolutely clear, however we observe that the hardening rate of the bulk material is clearly higher. This indicates that the bulk material has more effective dislocation generation and interaction mechanisms which in turn result from a stronger IMC microstructure.

The initial softening and subsequent hardening of both materials suggests that two distinct mechanisms are simultaneously at play, a rapid softening mechanism superimposing with a slow hardening mechanism. The rapid softening clearly correlates with strong coarsening of the IMC particles. The slower hardening mechanism is unclear, however it appears reasonable, given the strong coarsening and interconnection observed in the beta-Sn grains, that the hardening response is due to an intrinsic increase in flow strength in the beta-Sn grains.

NEMI Sn3.9Ag0.6Cu alloy after aging at 180^{0}C

We next examine how the microstructure of Sn3.9Ag0.6Cu changes with time as the aging temperature is increased to180^{0}C. Figure 7 shows that the samples aged at 180^{0}C show processes of IMC coarsening, beta-Sn growth and IMC dispersion similar to those observed in the 120^{0}C aging studies. However, the increase in temperature resulted in increasing the rate at which these processes occur. This in turn resulted in more complete IMC dispersion at the end of three days.

Figure 8 compares tensile data from bulk and thin cast samples for various aging times at 180^0C. The figure shows that, similar to what was observed at 120^0C, both the bulk and thin cast materials initially soften and then subsequently harden. Again, the minimum flow strength occurs after one day, and then both materials measurably harden as the aging time is increased up to nine days. A comparison between Figs. 8(a) and 8(b) again shows that the thin cast material is in all cases significantly softer than the bulk material. Now however, there is less difference in hardening rate between the two materials and greater difference in initial yield strength.

A comparison between Figs. 5(d) and 7(b) shows that the microstructure of a bulk sample aged three days at 180^0C is similar to the microstructure of a thin cast sample aged three days at 120^0C. A further comparison between Figs. 6(b) and 8(a) shows that the flow strength of a bulk sample aged three days at 180^0C is similar to the flow strength of a thin cast sample aged three days at 120^0C. Therefore, we may observe that the thin cast material responds as if it were bulk material aged at a higher temperature.

SUMMARY AND CONCLUSIONS

In this study thin cast and bulk type samples were produced with an identical Sn3.9Ag0.6Cu composition. A comparison was then made of the differing microstructural and tensile properties response to aging. From this work a number of important conclusions can be drawn.

1] The bulk and thin cast microstructures both consisted of a mixture of eutectic regions of dispersed intermetallic compounds (IMC) within a predominately tin matrix, and large beta-Sn crystals. *The thin cast material exhibited a much finer as-quenched microstructure than that of the bulk material with the IMC phase restricted to a thin network*. The modified microstructure of the thin cast material has very important mechanical implications, since the primary means of strengthening this alloy is through the development of relatively thick bands of fine IMC particles.

2] In both the bulk and thin cast material the beta-Sn and IMC particles significantly coarsen after 35 days at room temperature, however even after 35 days the thin cast microstructure appears finer than the bulk microstructure. Both the bulk and thin cast materials continually softened during room temperature aging, *however the thin cast material was always significantly softer*.

3] The bulk and thin cast differed in their response to aging at 120^0C. After three days the bulk material shows strong coarsening and partial interconnection of the beta-Sn grains, while the coarsening of the IMC particles in the thin cast material resulted in the near isolation of individual IMC particles and the interconnection of the beta-Sn phase. Similar behavior is observed during aging at 180^0C.

4] Both the bulk and thin cast materials initially soften and then subsequently harden when aged at 120^0C and 180^0C, *however the thin cast material is in all cases significantly softer than the bulk material*. The initial softening and subsequent hardening of both materials suggests that two distinct mechanisms are simultaneously at play, a rapid softening mechanism superimposed with a slow hardening mechanism. The rapid softening clearly correlates with strong coarsening of the IMC particles. The slower hardening mechanism is unclear, however it appears reasonable, given the strong coarsening and interconnection observed in the beta-Sn grains, that the hardening response is due to an intrinsic increase in flow strength in the beta-Sn grains.

5] The microstructure of the bulk material aged three days at 180^0C is similar to the microstructure of a thin cast sample aged three days at 120^0C. Furthermore, the flow strength of a bulk sample aged three days at 180^0C is similar to the flow strength of a thin cast sample aged three days at 120^0C. Therefore, we may observe that *the thin cast material responds as if it were bulk material aged at a higher temperature*. We expect that this is a general characteristic of small scale Sn3.9Ag0.6Cu samples including industrially important small scale solder balls, if so, this result has important implications for the elevated temperature application of Sn3.9Ag0.6Cu.

ACKNOWLEDGMENTS

The authors gratefully acknowledge the support of the Semiconductor Research Consortium under contract 2001-NJ-892 and the efforts of our SRC program monitor Harold Hosack.

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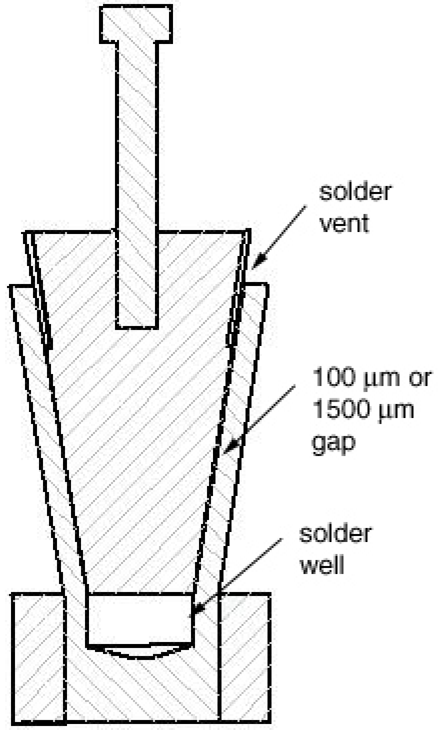

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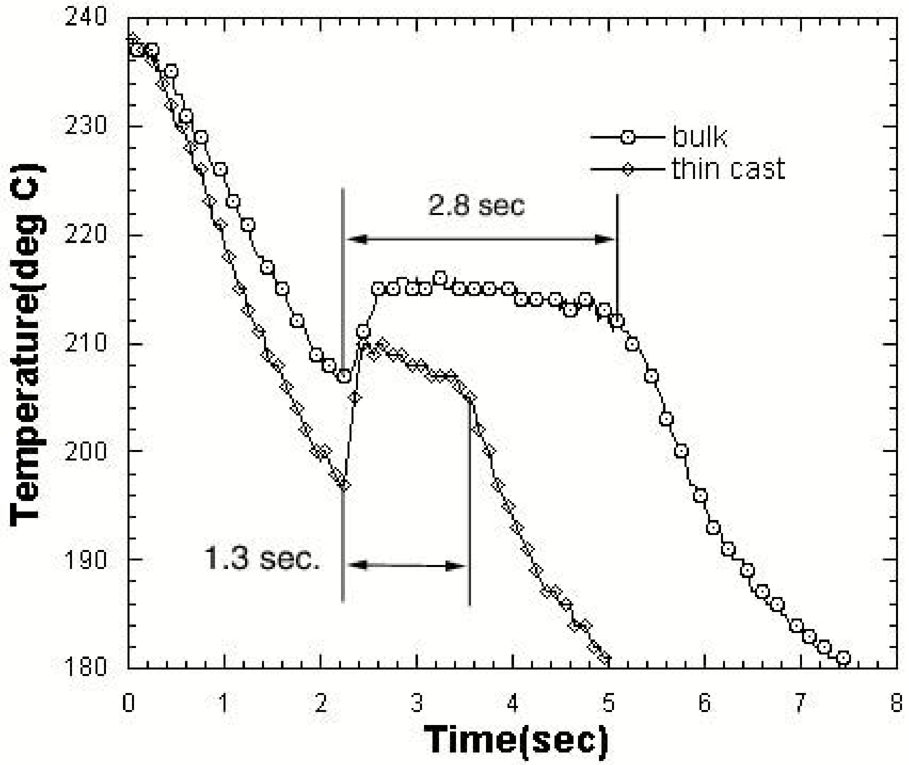
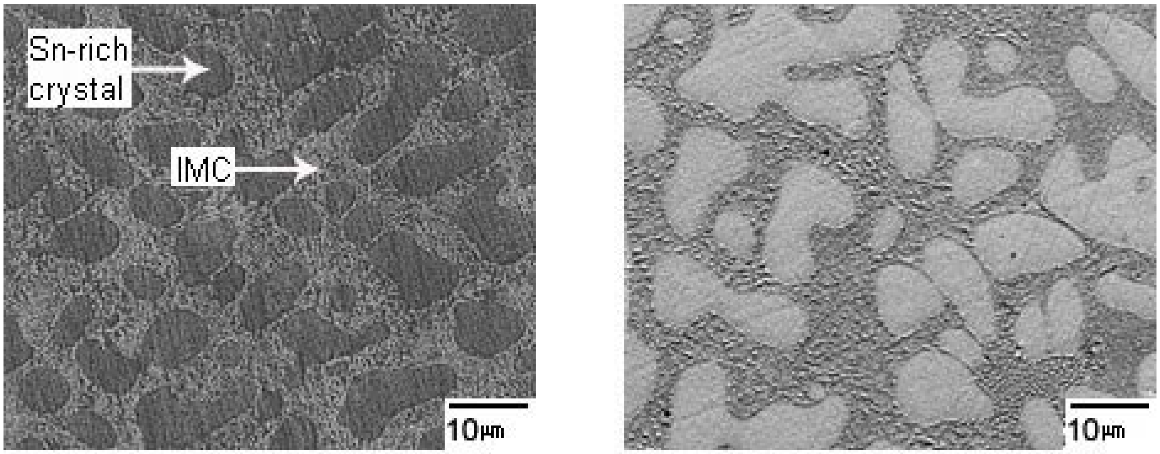
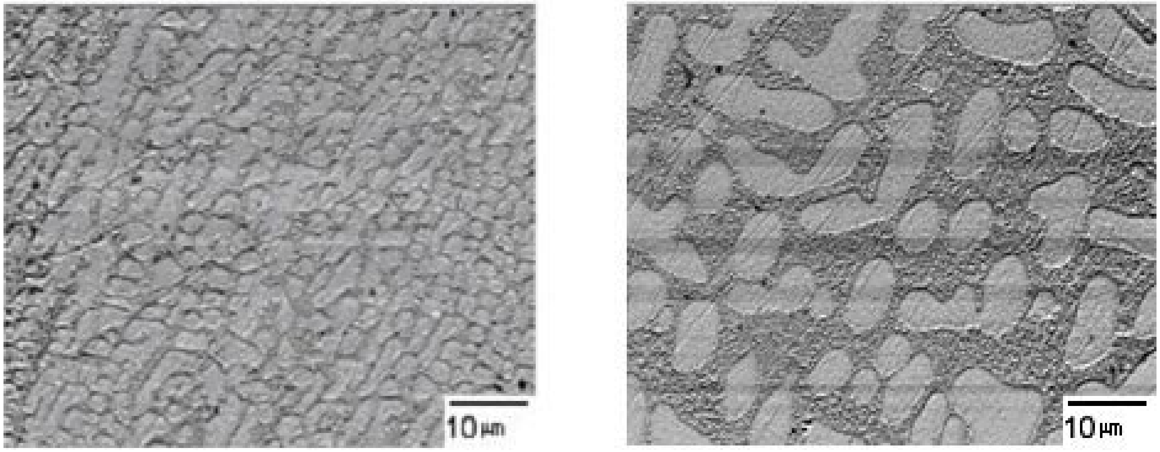


Figure 2. Temperature versus time measured by a thermocouple in contact with the solder during water quench.



(a) as quenched(bulk)

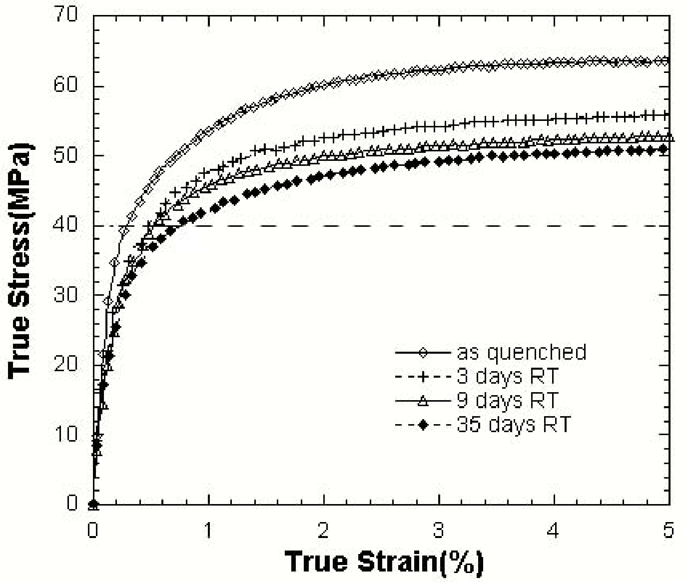
(b) 35 days RT(bulk)



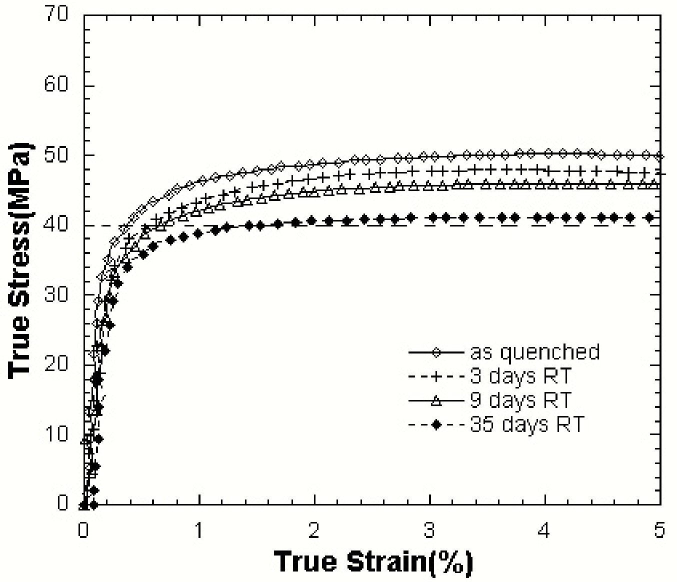
(c) as quenched(thin)

(d) 35 days RT(thin)

Figure 3. SEM-BSE micrographs of bulk and thin cast Sn3.9Ag0.6Cu lead free solder samples in the as-quenched and as-room-temperature-aged condition.

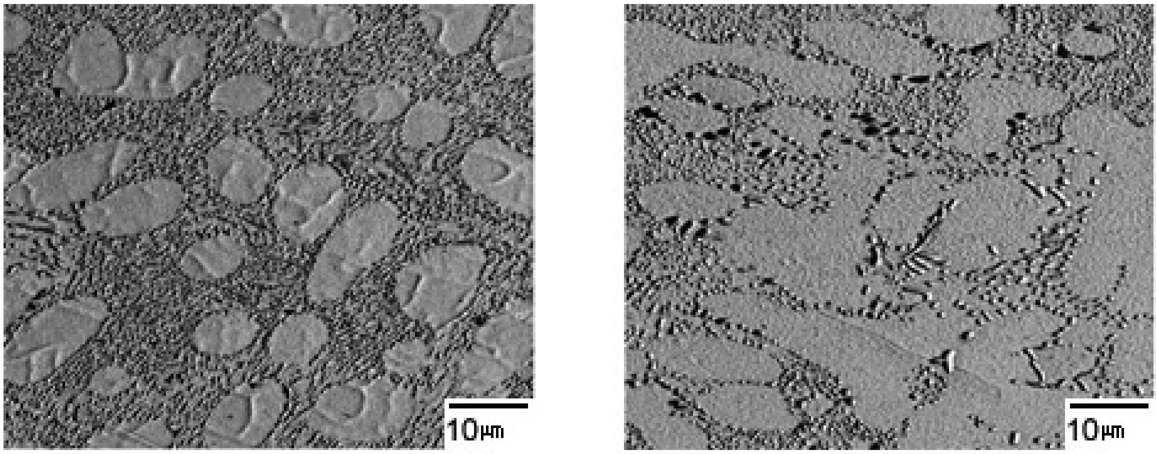


(a) Bulk samples.

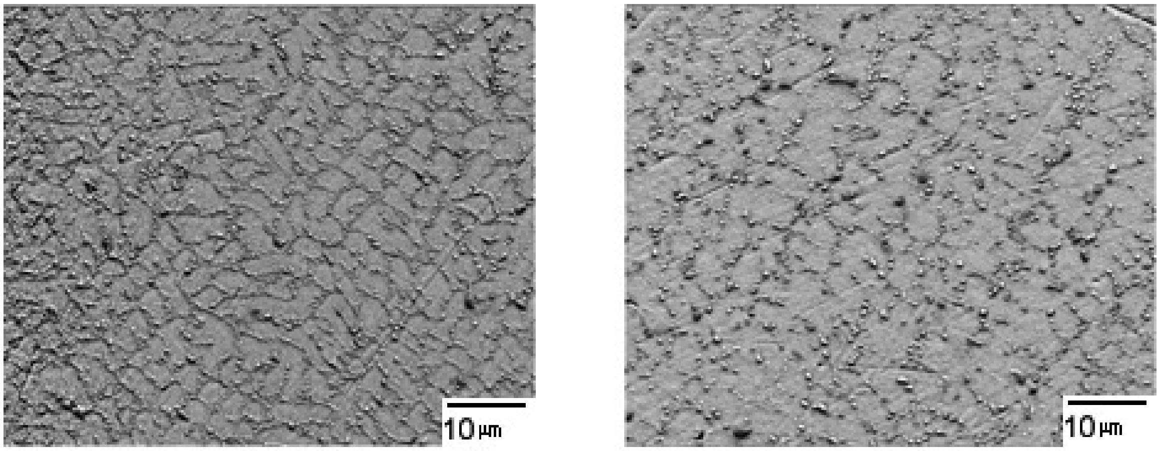


(b) Thin cast samples.

Figure 4. Comparison of room temperature tensile data from bulk and thin-cast Sn3.9Ag0.6Cu materials after aging at room temperature.

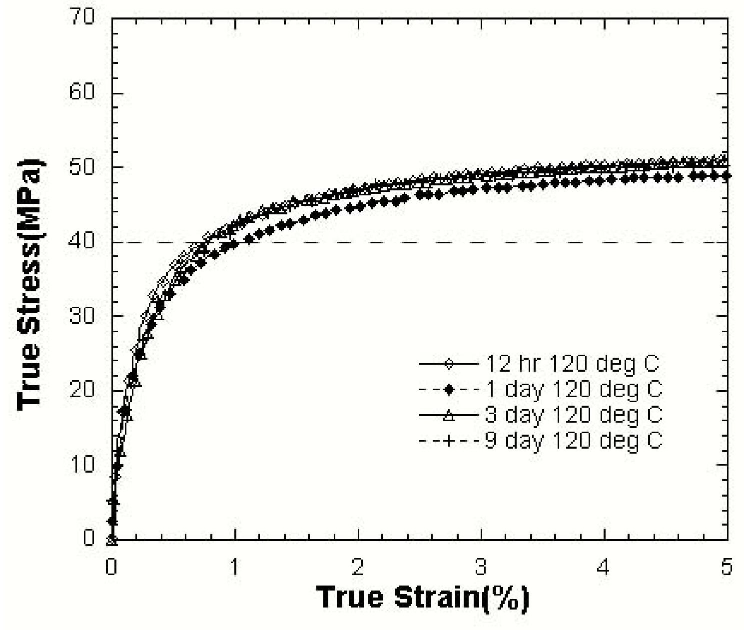


(a) 1 day at 120 deg C(bulk) (b) 3 days at 120 deg C(bulk)



(c) 1 day at 120 deg C(thin) (d) 3 days at 120 deg C(thin)

Figure 5. SEM-BSE micrographs of bulk and thin cast Sn3.9Ag0.6Cu lead free solder samples in the as-120^{0}C aged condition.



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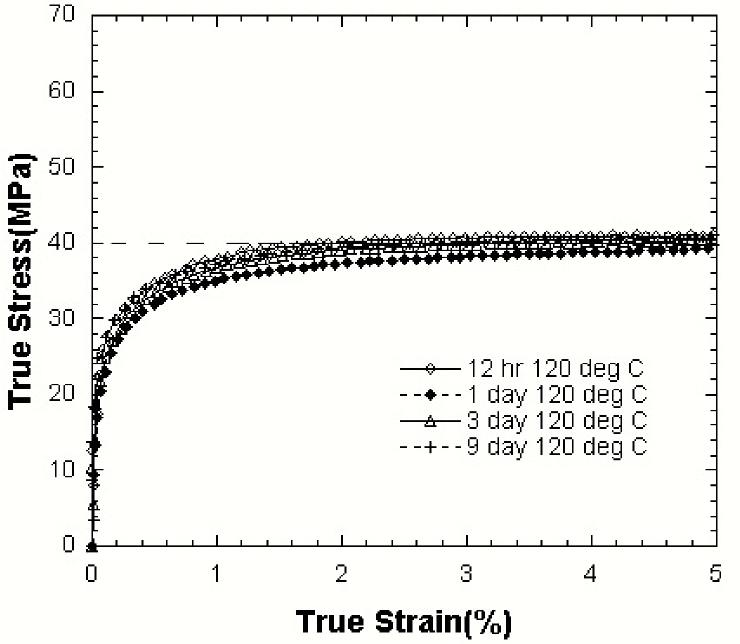

(b) Thin cast samples.

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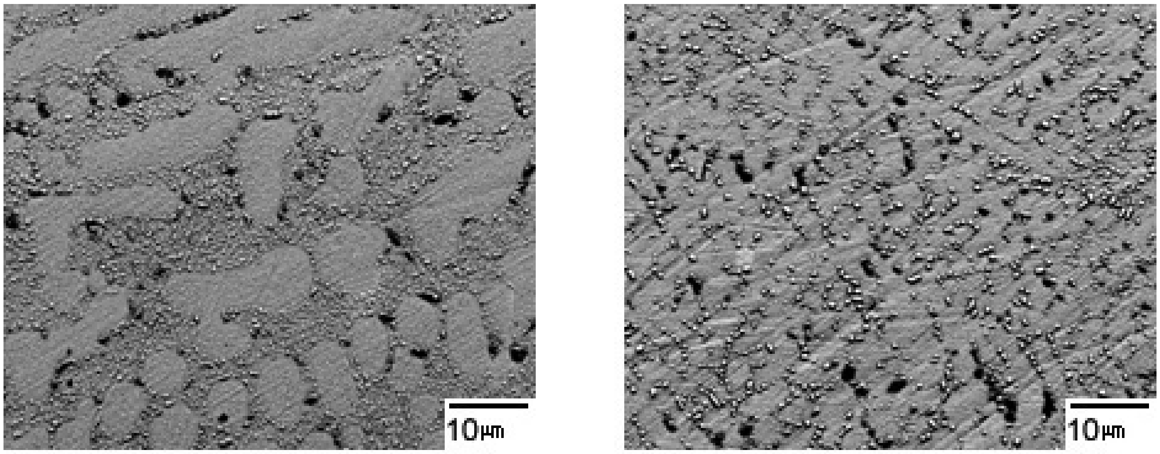
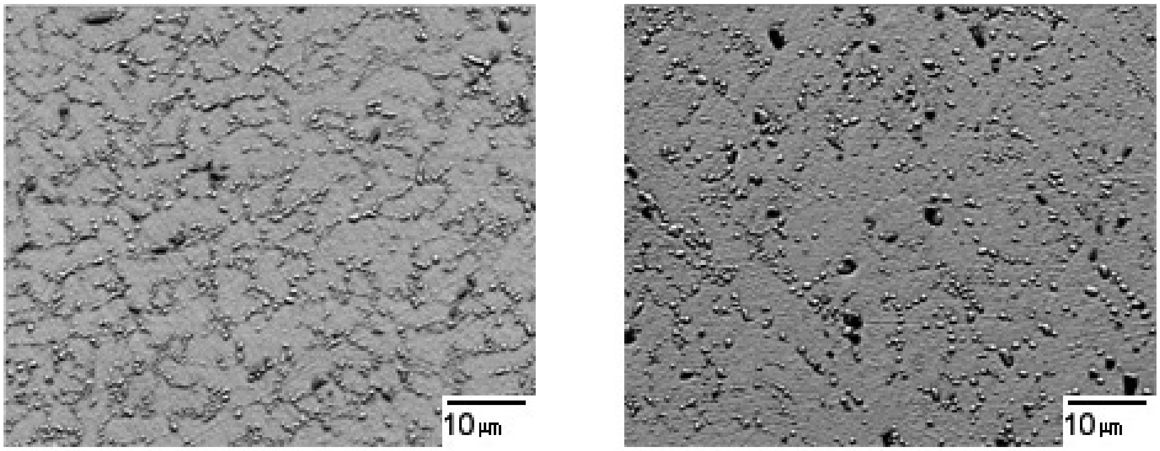


(a) 1 day at 180 deg C(bulk)

(b) 3 days at 180 deg C(bulk)



(c) 1 day at 180 deg C(thin)

(d) 3 days at 180 deg C(thin)

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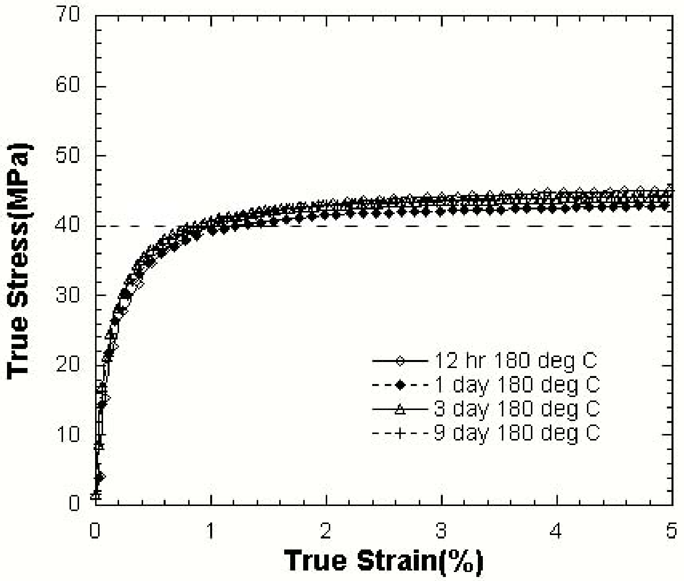
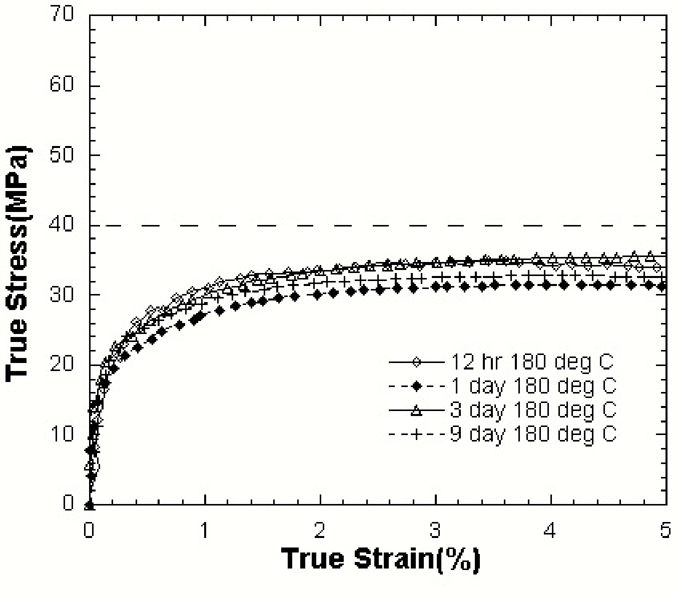


(a) Bulk samples.



(b) Thin cast samples.

Figure 8. Comparison of room temperature tensile data from bulk and thin-cast Sn3.9Ag0.6Cu materials after aging at 180^0C.