

A Path to Ductile Low Temperature Solders for Mass Production of Electronic Assemblies?

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ABSTRACT

While alloys based around the Sn-In system provide a great combination of low melting point, high thermal conductivity and ductility, their cost necessarily limits their use to special applications. If the wider electronics industry is to enjoy the benefits of low temperature solders (LTS), environmental, and economic, as well as technical, it will be necessary to develop a database that can provide the confidence the industry needs to use solders based on the Sn-Bi system. Because the fundamental metallurgy of Sn-Bi solders differs in several significant ways from that of other Pb-free solders, establishing that confidence will require systematic studies that will go beyond what was done to provide the electronics industry with the confidence to move from Sn-Pb to the first generation of Pb-free solders. When a solder based on the Sn-Bi system behaves in a way that might compromise its performance in soldering processes, or its reliability in service, the response of the material scientist is to look for additions to the base alloy, sometimes referred to as “dopants”, which could have the potential to improve its performance. Early reports indicated that an addition of Sb mitigated the embrittling tendency of the Bi phase in the microstructure of Sn-Bi solders by refining the eutectic phase. That in subsequent studies it has been found difficult to reproduce that beneficial effect consistently suggests that, in the experiments in which the beneficial effect was observed, there might have been factors additional to the presence of Sb that were contributing to the improved ductility. In this paper we report the results of a systematic study of the behaviour of Sb in a Sn-Bi alloy and consider the implications of the findings for the reliability of LTS solder joints. These results are considered in the context of a wider review of the characteristics that distinguish Sn-Bi alloys from the Pb-free solders on which the industry currently relies.

INTRODUCTION

There are several benefits that a change to solders that require lower process temperature can deliver to the electronics industry:

- A reduction in energy consumption in soldering processes.
- Avoidance of process temperatures in the range in which large ball grid array (BGA) packages warp to the extent that there is an unacceptable incidence of defects in the joints to the package.
- The possibility of
 - Soldering to temperature-sensitive substrate materials compatible with the human body.
 - Using cheaper and possibly more environmentally friendly substrate and packaging materials.
 - Wave or selective soldering of complex high thermal mass through-hole assemblies.

However, advantage cannot be taken of these opportunities unless the industry has confidence that LTS can deliver performance in soldering processes, mechanical properties and reliability in service that is at least comparable with that delivered by the current default Pb-free solder alloy Sn-3.0Ag-0.5Cu (“SAC305”) [1], (all compositions are in wt.% unless otherwise specified). For solder paste, which is likely to remain the form in which a solder alloy is used in the manufacture of advanced electronics, the requirements extend beyond the alloy itself to the chemistry and rheology of the flux medium [1]. The studies reported in this paper have not gone beyond the properties and behaviour of the solder alloy itself.

Factors that distinguish Sn-Bi solders from the Pb-free solders on which the electronics industry now relies are:

- The presence in the microstructure of a substantial volume fraction of nearly pure Bi, which demonstrates a tendency to brittle failure in some circumstances.
- The substantial, but very temperature-sensitive, solid solubility of Bi in the Sn phase.
- The high homologous temperature that Sn-Bi solders are at when they are exposed to the conditions in which electronic circuitry typically operates means that the diffusion processes that drive microstructural change proceed rapidly, introducing a greater degree of instability to solder joints than is the case with the current generation of Pb-free solders.
- The high susceptibility of the Bi atom to electromigration to the anode where its high electrical resistivity can compromise the performance of electronic circuitry.

While all those factors will ultimately have to be taken into account in assessing the suitability of an LTS based on the Sn-Bi system for use in the assembly of advanced electronics, there is one factor that has dominated consideration of whether it is worth pursuing this option for low temperature soldering. That is whether an alloy with a significant volume fraction of Bi in a Sn matrix strengthened by Bi in solid solution can survive the stresses to which solder joints can be exposed in service.

With its rhombohedral crystal structure with limited active slip planes Bi cannot easily accommodate strain and at high strain rates and Sn-Bi alloys with a high Bi content tend to brittle failure (Fig. 1, Fig. 2, Fig.3 (c) and (d)). There is, however, evidence [3] that at low strain rates Bi is able to match the elongation of the Sn phase (Fig. 2(b), Fig. 3(a)). This provides hope of the possibility of ductile Sn-Bi solder.

This basic metallurgy of Sn-Bi alloys is very different from that of the Sn-Ag-Cu and Sn-Cu Pb-free solders on which the electronics manufacturing industry largely relies, Cu and Ag have virtually no solubility in Sn but react with Sn to form intermetallic compounds (IMC) Cu_6Sn_5 and Ag_3Sn . In the form in which they usually occur in the as-soldered microstructure, fine, closely-spaced particles dispersed through the Sn matrix, these IMC account for most of the strength of these solders while not themselves contributing a tendency to brittle failure.

In tensile testing at a slow strain rate, as-cast eutectic Sn-57Bi alloys with a high volume fraction of Bi phase, exhibit a high strength and substantial ductility, while at higher strain rates suffer brittle failure [3,4] (Fig. 1).

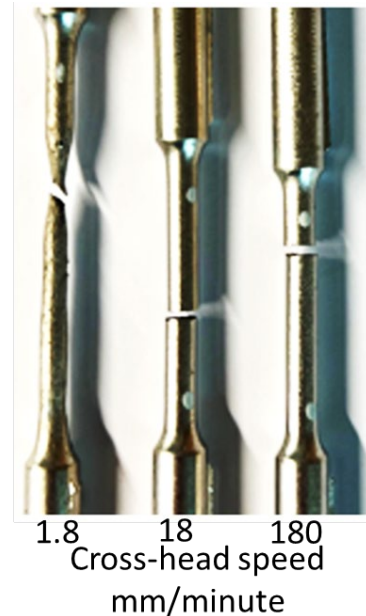


Figure 1. Effect of tensile test crosshead speed on failure mode of as-cast Sn-57Bi alloy. Initial test piece diameter 6mm, gauge length 30mm (Reprinted from reference [3])

In the test pieces that, at the low strain rate, exhibited considerable ductility, it appears that the typically ordered network of eutectic Bi had gradually deformed to accommodate the strain in the Sn matrix rather than suffering brittle fracture (Fig. 2(b) and Fig. 3(a)). When fracture of the test piece eventually occurred, it appears to have been the result of the joining up of cracks at Sn-Bi interfaces formed as a result of grain boundary sliding along those interfaces (Fig. 3(a)). In test pieces which, at the higher strain rates had suffered brittle failure, the fracture appears to have initiated within the Bi phase and then propagated into the Sn phase. (Fig. 3(b), Fig. 3(c))

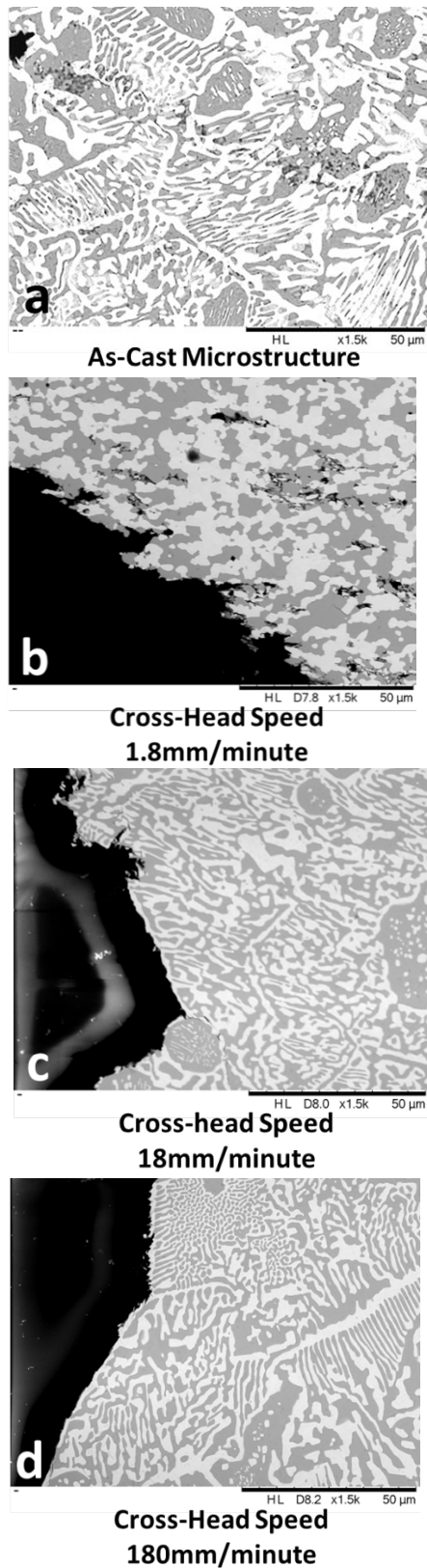


Figure 2. Fracture microstructure at indicated strain rates. (Reprinted from reference [4])

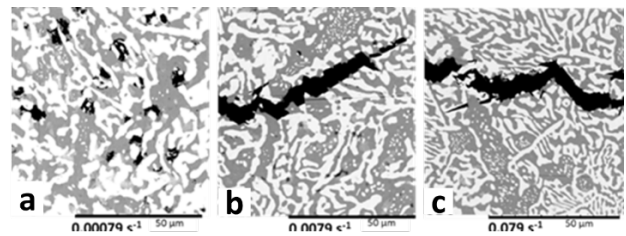


Figure 3. Crack nucleation in Sn-57Bi as a function of strain rate in tensile testing. (Reprinted from reference [4])

An insight into the behaviour of the Bi phase in these tests has been provided by the results of mechanical testing of pure Bi [5]. In tensile and compression testing, pure Bi was found to have no ductility at temperatures below 0°C but as the test temperature increased the elongation increased to a peak of about 35% at a strain rate of about $1.75 \times 10^{-1} \text{ sec}^{-1}$ and about 70% at a lower strain rate of about $1.75 \times 10^{-2} \text{ sec}^{-1}$ at 50°C and then declined to about 30% at the temperature approached 100°C.

These researchers [5] noted that the temperature at which the Bi begins to accommodate deformation without brittle failure is also the temperature at which recrystallization begins and they distinguished two stages in that process describe as “subrecrystallization” and “superrecrystallization”. Further research will be required to clarify this effect but these stages might reflect that recognized sequence in the thermal fatigue in conventional Pb-free solder joints [6], i.e., climbing of accumulated dislocations to form subgrains with low angle boundaries, which with further strain evolve into larger grains with high angle boundaries that open up the option of the grain boundary sliding that eventually generated the cracks that cause failure.

Recrystallization has also been identified as a contributor to the ductility of the Sn-Bi eutectic in lap shear testing [7]. The microstructure of the Sn-Bi solder in the band in which deformation was accommodated without brittle failure by recrystallization of the Bi has some similarity with the microstructure close to the ductile fracture in Fig. 2.

ADDITIONS TO SN-BI ALLOYS

Whatever the underlying mechanism might be, the tendency to brittle failure has been the characteristic that has created greatest concern about the suitability of Sn-Bi LTS for applications where high reliability is required. The response to that concern has been an intense effort by electronics manufacturers, soldering materials suppliers, universities and other research organisation, to identify additions to the basic binary alloy that mitigate that tendency to brittle failure [2]. There is also hope that additives can make some contribution to stabilizing microstructure, slowing growth of the interfacial IMC layer and inhibiting electromigration [2].

Additives that have been evaluated for beneficial effects in Sn-Bi alloys can be classified into several categories [2]:

- Those that have no solubility in Sn or Bi but form intermetallic compounds with Sn, which are the first phases to form in the melt and could act as nucleants for the Sn or the Bi that could affect the final microstructure or provide particle strengthening for Sn phase. Additions in that category include Ag, Cu, Ni.
- Those that have some solubility in the Sn and the Bi phases and could be expected to affect their behaviour during solidification and possibly also in the solid state. Sb is the addition in this category that has attracted greatest interest. However, as noted in this paper (Fig. 4) Sb also shares with Ag, Cu and Ni the thermodynamic possibility of forming the SnSb intermetallic in the melt, which could also have the potential of acting as a nucleant for Sn and the Sn-Bi eutectic as well as providing particle strengthening

EFFECT OF SB IN SN-37BI

It had been reported that an addition of Sb increased the ductility of a Sn-Bi alloy, with that effect being attributed to the refinement of the microstructure of the eutectic [8]. However subsequent studies have been unable to confirm that effect. Although a clear link between an Sb addition and the ductility of Sn-Bi alloys was not firmly established there appeared to be sufficient evidence to justify a deeper investigation of the potential of the Sn-Bi-Sb system.

In the work reviewed in this paper, some of the fundamental tools of metallurgical investigation were employed to measure the effect of additions of antimony ranging from 0.2% to 3% Sb on the phases present in a Sn-Bi alloy.[9]

It can be speculated that the ductility of a Sn-Bi alloy could be improved by:

- Improving the ductility of Bi by introducing other atoms into its crystal structure.
- Modifying the morphology of the Bi phase so that its potential brittle failure at high strain rates did not trigger crack propagation into the Sn phase.
- Modifying the deformation response of the Sn phase so that it acts as a buffer against transmission of high speed strain to the Bi phase.

In the work reviewed in this presentation [9], the effects of Sb additions up to 3 wt% on the solidification behavior, the microstructure and crystal structure of hypo-eutectic Sn-37wt%Bi alloys were investigated systematically via cooling curve analysis, scanning electron microscopy (SEM), and electron probe microanalysis (EPMA). Calculations of phase diagrams (CALPHAD) and density functional theory (DFT) simulations were employed to predict the phases and the crystal structures in the alloys. In-situ synchrotron powder X-ray diffraction (PXRD) was used to study the dissolution and precipitation of the Bi

phase in real-time, and to reveal other phase and crystallographic changes at temperatures and timeframes relevant to conditions encountered during assembly and service of electronic devices.

EXPERIMENTAL METHODS

Selecting the base alloy

Because of good performance in laboratory testing and successful industrial trials of a proprietary alloy [10], Sn-37wt% Bi was chosen as the base alloy in this study. Where the primary reason for using an LTS is avoidance of solder joint defects that result from package warpage, the requirement is only that reflow soldering processes can be carried out with a peak temperature of less than 200°C, Sn-37Bi has a liquidus of 174°C, which allows for a superheat of 25°C without exceeding that limit. The proprietary alloy has trace additions of other elements but in the experiments reported in this paper the starting point is the unalloyed binary Sn-37Bi.

As a reference, Thermo-Calc[®] was used to generate an equilibrium phase diagram for Sn-37B-xSb that predicts, on the basis of known data, the likely phases present as a function of Sb content and temperature [11] (Fig 4).

Sample fabrication

Sn-37wt%Bi-xwt%Sb alloys, where x=0.2, 0.5, 1.0, and 3.0, were prepared by melting measured quantities of pure Sn and a high purity Sn-5wt%Sb master alloy and holding at 450°C for one hour before casting into a steel mould preheated to 150°C. This resulted in a solidification time comparable with that of solder joints during the manufacture of an electronic assembly.

Thermal analysis

The temperature was tracked during cooling in air of 60g samples in graphite crucible from 450°C to 100°C to identify the liquidus and eutectic temperature. Note was also taken of any recalescence, the temperature rise during solidification, that results from release of latent heat.

Observation of microstructure and phase compositions

Prepared cross-sections were examined in scanning electron microscopy (SEM) and electron probe microanalysis (EPMA), which provides better energy resolution than energy dispersive X-ray spectroscopy (EDS), making possible the deconvolution of the closely spaced Sn and Sb characteristic peaks when the Sb is present in low concentrations. Compositions were analysed at 5 points in each phase field with the average and range reported.

Crystal structure as a function of temperature

The effect of heating and cooling on the crystal structure of the phases present in these alloys was tracked using powder X-ray diffraction (PXRD) in the Australian Synchrotron. The high temporal resolution enabled by the high flux synchrotron radiation makes possible the study of changes in the crystal structure during heating and cooling at rates

similar to those to which solder joints could be exposed in service. PXRD patterns were collected at 10°C steps between 30°C and 200°C with a heating rate between steps of 30°C/minute. The PXRD patterns were analysed to obtain the lattice parameters of each of the phases detected in the samples, which include the tetragonal β -Sn, trigonal Bi, rhombohedral Sb and cubic SnSb intermetallic compound.

Density Functional Theory (DFT) Calculations

Based on the crystal structures identified by synchrotron PXRD, DFT calculations were performed to model the interactions occurring between Sn-Sb and Sn-Bi-Sb in the Sn phase to determine the stability of each structure.

RESULTS

Microstructure and crystal structure of Sn

The equilibrium Sn-37Bi-Sb phase diagram (Fig. 4) predicts that during cooling of molten Sn-37Bi, primary Sn with Bi in solid solution freezes out first and the liquid remaining at the 139°C eutectic temperature freezing isothermally in coupled growth of Sn and Bi eutectic structure. When Sn freezes from a liquid it usually does so in the form of dendrites and that is what happened in this sample. The equilibrium Sn-Bi phase diagram predicts that as the alloy cools from the eutectic temperature the solid solubility of Bi in Sn falls, with Bi in excess of that limit precipitating out of solution onto the eutectic Bi or as particles within the Sn phase.

The calculated phase diagram predicts the appearance at room temperature of the SnSb intermetallic compound in all four of the Sn-37Bi alloys that have an Sb addition.

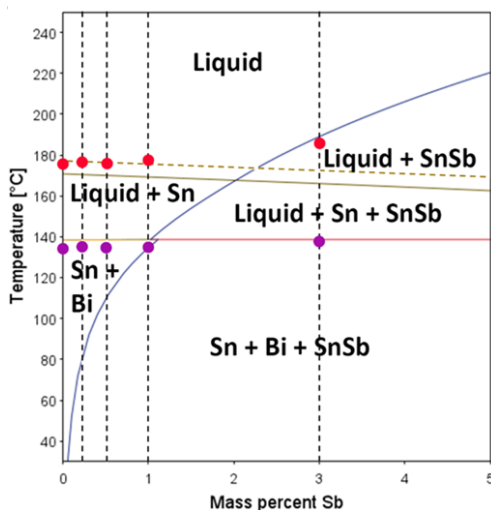


Figure 4. Section of the Sn-Bi-Sb phase diagram at a composition of Sn-37Bi-xSb. (Reprinted from reference [9])

Cross-sections of the tested alloy are presented in Figure 5.

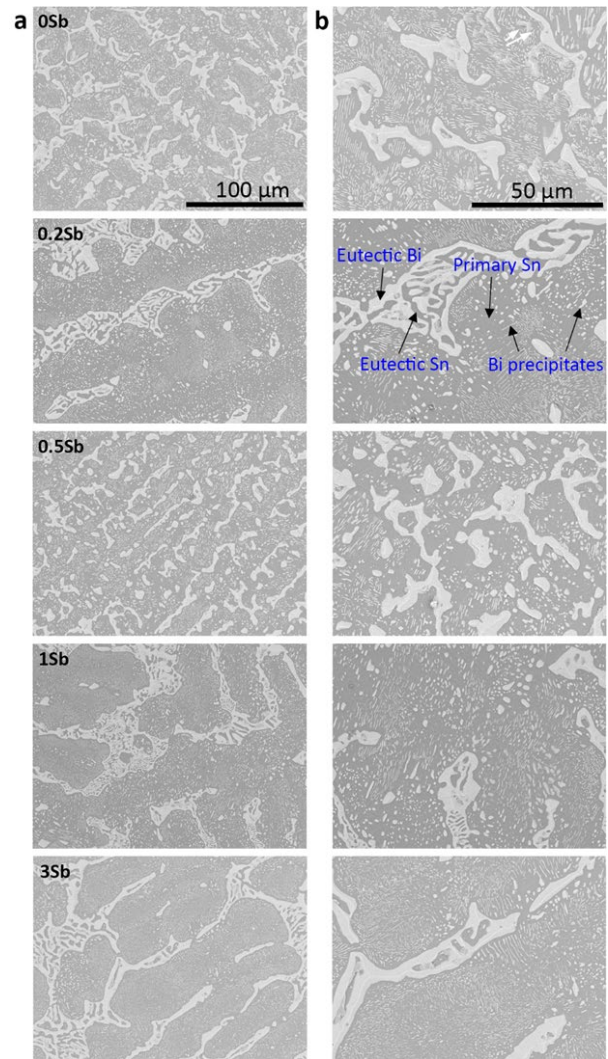


Figure 5. SEM images of cast samples Sn-37Bi, Sn-37Bi-0.2Sb, Sn-37Bi-0.5Sb, Sn-37Bi-1Sb, Sn-37-3Sb, at lower magnification (a) and higher magnification (b). (Reprinted from reference [9])

The lower magnification images in Fig. 6 appear to be consistent with previous reports that the lowest dendrite secondary arm spacing in Sn-57Bi alloys occurs with an Sb addition of 0.5%. However, although some attempts had been made to prepare these samples under similar conditions, the cooling could not be accurately controlled so that the differences in the microstructure could be due to differences in the cooling rate. The microstructures of samples used for thermal analysis, in which the cooling rate was carefully controlled, did not show that trend (Fig. 6). There is no clear relationship between dendrite arm spacing and Sb content.

However, an effect that can be observed in the samples cooled under controlled conditions is that the spacing of the Bi phase that has precipitated out of solid solution in the Sn phase as the temperature fell after solidification is smaller.

(Fig. 6b) That effect could be the result of Sb promoting the nucleation of the Bi phase.

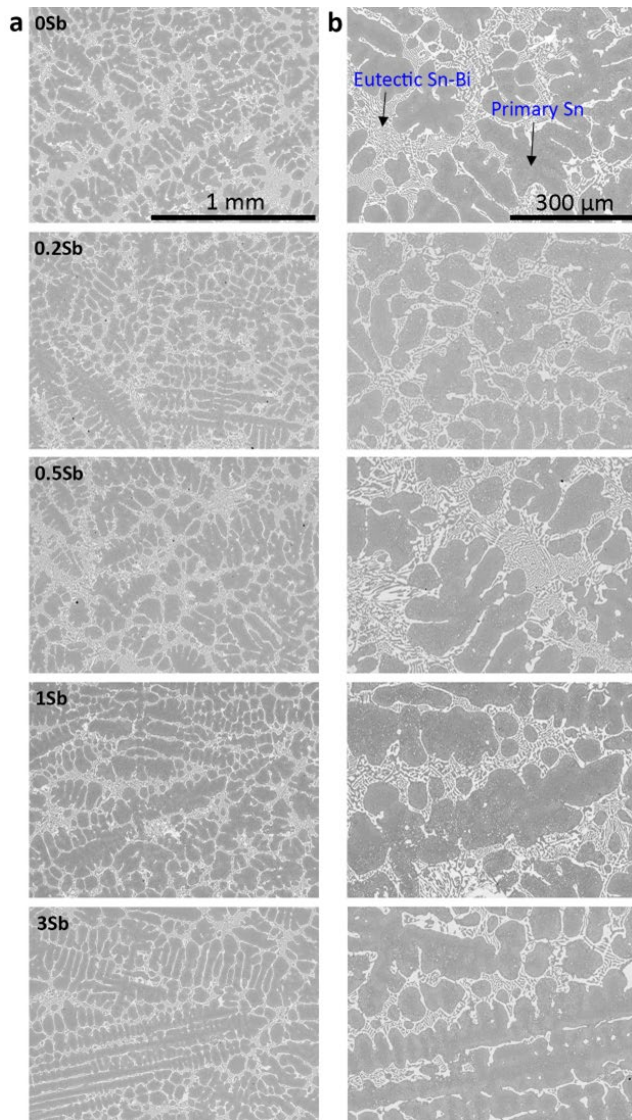


Figure 6. SEM images of samples used in cooling curve analysis Sn-37Bi, Sn-37Bi-0.2Sb, Sn-37Bi-0.5Sb, Sn-37Bi-1Sb, Sn-37-3Sb, at lower magnification (a) and higher magnification (b). (Reprinted from reference [9])

Synchrotron PXR phase detection

While the PXR patterns (Fig. 8) show the presence of Sn and Bi phases in all samples, the SnSb phase was detected only in the Sn-37Bi-3Sb alloy.

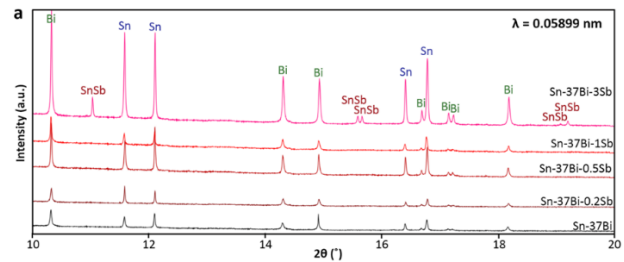


Figure 7. Room temperature synchrotron PXR patterns of samples stored at room temperature for six months to reach equilibrium. (Reprinted from reference [9])

EPMA phase detection

Because the atomic numbers of Sn (50) and Sb (51) are very close the contrast in SEM images is very low. In EPMA mapping (Fig. 8) the SnSb appears as high intensity spots within the Sn phase only in the Sn-37Bi-3Sb alloy. Both the calculated Sn-37Bi-xSb equilibrium phase diagram (Fig.4), and Scheil (non-equilibrium) solidification predict that no SnSb phase freezes out of liquid during cooling so that if it forms, it does so by precipitation within the solidified Sn phase as it cools to room temperature. Only in the alloy with 3% Sb is the driving force sufficient to nucleate the SnSb phase in the melt.

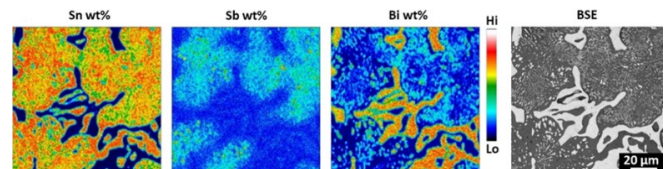


Figure 8. EPMA Sn, Sb and Bi maps of Sn-37Bi-3Sb and BSE image of the mapped area. (Adapted from reference [9])

EPMA and element distribution

EPMA indicates that the concentration of Sb in Sn increases almost linearly with increasing wt% Sb in the alloy, while Sb can be detected in the Bi phase only in the Sn-37Bi-3Sb alloy.

There is wide variation in Sb levels measured by EPMA in the Sn-37Bi-3Sb alloy because results depend on whether or not the reading was taken on a field containing a particle of SnSb. The concentration of Bi in solution in the Sn is relatively constant at around 3.8wt% irrespective of the Sb concentration, but the spread of concentrations increases with increasing wt% Sb in the alloy, again probably because of the presence of particles of SnSb phase.

Thermal Analysis

Although the calculated phase diagram predicts three solidification events as the Sn-Bi-Sb alloys cool, SnSb, Sn and eutectic Sn-Bi, the SnSb was not detected in the cooling curves obtained. That is presumably because the volume of the SnSb phase is small. However, SnSb could be showing its presence by its effect on the solidification temperature of the Sn and Sn-Bi eutectic phases in the 3%

Sb sample. The temperature at which the primary Sn solidifies in this experiment is greater than that predicted by the Thermo-Calc TCSD4: Solder Alloy v4.0 2021b database (Fig.5) and that could be due to the use in those calculations of an earlier Sn-Bi phase diagram in which the eutectic composition was identified as 52% Bi rather than the more widely published 57%.

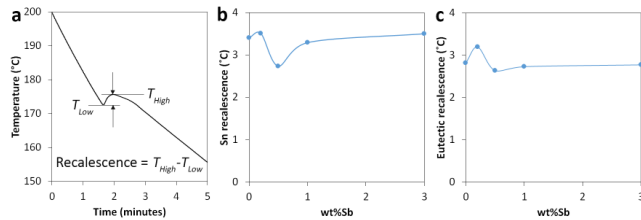


Figure 9. Definition of recalescence (a) and amount of undercooling during the solidification of the primary Sn (b) and the eutectic (c). (Reprinted from reference [9])

Recalescence is a temporary increase in the temperature of a cooling metal when latent heat is released as the phase begins to solidify at a temperature lower than the equilibrium melting point of the phase (supercooling). It was found (Fig.9) that for both the primary Sn phase and the Sn-Bi eutectic, while the addition of 0.2% Sb resulted in a small increase in recalescence, 0.5% Sb reduced the recalescence of both phases to less than that of the base Sn-37Bi alloy. Increasing the Sb to 1% resulted in a return of the recalescence of the primary Sn to near that of the base Sn-37Bi, but did not have so much effect on the eutectic recalescence. The total amount of SnSb phase that can form depends on the amount of Sb, but it is only SnSb that freezes from the melt that can have an effect on Sn nucleation and that was observed only in the alloy with 3% Sb.

The calculated phase diagram indicates that the SnSb phase should be present in the Sn-37Bi-3Sb alloy below about 190°C, which is before the Sn begins to solidify. That prediction was confirmed by holding the Sn-37Bi-3Sb at 230°C for 2 hours to ensure that any SnSb has melted and then held at 180°C for 4 hours to allow the low density SnSb phase to grow and float to the surface. Cross sectioning of the sample after cooling to room temperature revealed blocky SnSb intermetallic particles, confirming that the formation of this phase is thermodynamically viable at 180°C.

Change in lattice parameter with temperature

The changes in the lattice parameters with temperature of the Sn and Bi phases were tracked using synchrotron PXRD. The changes are the result of two effects; normal thermal expansion, and changes in solid solubility with temperature. The atomic radius of Sn is 1.45Å and of Bi is 1.60Å. The unit cell volume of Sn increases with increasing Bi in solid solution as the temperature increases and since the solubility of Bi in Sn is high, there is a parabolic increase in the unit cell volume. However, the presence of Sb has little effect on the trend (Fig.10).

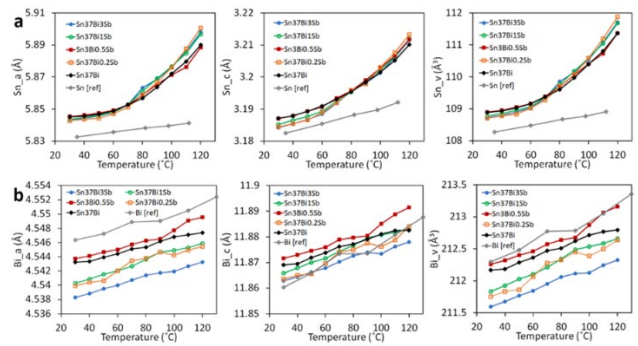


Figure 10. Rietveld refined lattice parameters and cell volumes of (a) Sn and (b) Bi from 30°C to 120°C. (Reprinted from reference [9])

The unit cell volume of Bi decreases with increasing Sn in solid solution but the changes in solid solubility of Sn in Bi with respect to temperature is small so there is not the parabolic increase with temperature that occurs with the Sn phase. While the presence of Sb has little effect on the lattice parameter of the Sn(Bi) solid solution as a function of temperature, the presence of Sb has a significant effect on the lattice parameters of the Bi phase, even though Sb has no solubility in Bi at concentrations of 1 wt% and below. That raises the question of what had caused this effect and a possible explanation is that the variation in the morphology of the Bi phase affects the diffusion distance and the rate at which the Sn can find its way into the Bi.

An alternative explanation is that this effect could be only a consequence of the uncontrolled cooling rate. The holding time at each temperature might not be sufficient to allow thermodynamic equilibrium to be achieved.

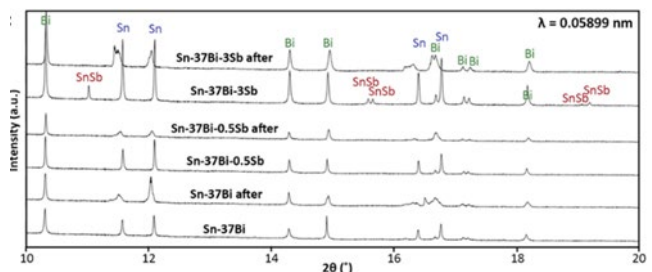


Figure 11. PXRD patterns at room temperature immediately after the step heating experiment. (Reprinted from reference [9])

Precipitation of Bi and SnSb

The PXRD patterns of Sn-37Bi, Sn-37Bi-0.5Sb and Sn-37Bi-3Sb obtained at 30°C immediately after the stepped heating experiment (Fig. 11) show differences from the patterns of those alloys before the stepped temperature experiment (Fig. 7), in which the samples had been stored at room temperature long enough (6 months) to have reached thermodynamic equilibrium.

Notable differences are:

- Sn peaks broadened, and shifted to smaller 2θ because of large Bi concentration gradients left in the samples after the large changes in solid solubility during the stepped heating, with insufficient time for the Bi to precipitate.
- In contrast to the 4-hour isothermal holding experiment, the SnSb intermetallic predicted by the calculated phase diagram was not detected in the Sn-37Bi-3Sb in the PXRD experiment. The PXRD experiment suggests that SnSb is very difficult to nucleate in the molten solder under sufficiently fast cooling rates, probably because of a very high solid-liquid interfacial energy which requires a large undercooling. Thermo-Calc simulations calculate solid-liquid interface energies at 140°C of 0.0158 J.m² for Sn and 0.0329 J/m² for SnSb and Sn is notoriously difficult to nucleate from the melt without substantial undercooling. However, the fact that Sn solidification did begin at a higher temperature suggests that SnSb could be acting as a nucleant.

DFT Atomistic Simulation

The objective of this simulation was to calculate the stability of Sn when Bi and Sb are in solid solution. A 512 atoms Sn supercell, Sn₅₁₂, was used as a starting model.

Assuming no Bi is dissolved in Sn, the effect of the solid solution of Sb in Sn was modelled with Sn_{512-z}Sb_z. The result of these calculations is that, the addition of 0.25 wt% Sb to Sn-37Bi (which results in 0.4 wt% in the Sn phase, or $z=2$) gives a negative energy of formation, ΔE_f of -0.72meV/atom, which means that the alloyed Sn is more thermodynamically stable than pure Sn. When the Sb addition to Sn-37Bi is increased to 0.5 wt% ($z=4$) the ΔE_f is positive, which means that the Sn structure becomes less stable.

Applying this method to consider the dissolution of Bi in Sn, the model was Sn_{512-y}Bi_y. EPMA indicated that around 3.8 wt% Bi is in solid solution in Sn at room temperature. On that basis the closest simple model would be Sn₅₀₀Bi₁₂ (4.05 wt% Bi). Models Sn₄₈₈Bi₂₄, (7.97 wt% Bi) and Sn₄₈₀Bi₃₂ (10.50 wt%) were built to simulate higher concentrations of dissolved Bi at higher temperatures.

Combining the two models above, the Sn-Bi-Sb model was Sn_{512-y-z}Bi_ySb_z with $y=12, 14$ and 32 and $z=2, 4$ and 8 with the positions of Bi and Sb atoms selected to maintain tetragonal crystal symmetry. The energy of formation, ΔE_f of all Bi-containing samples are positive with the value increasing with Bi content and with Sb content. That means that the formation of higher Bi concentration Sn structures require higher energies or high temperatures, which is consistent with the phase diagram and experimental observations. The energy of formation increases further with the Sb concentration, which means that the stability of the system is low.

CONCLUSIONS

There are fundamental differences between the basic metallurgy of solder alloys based on Sn-Bi and that of the current generation of Pb-free solders. That means that the criteria for reliability developed for the current generation of Pb-free solders do not necessarily apply to Sn-Bi solders.

Confidence in Sn-Bi as solders for the assembly of high reliability electronics will depend on the development of a deeper understanding of the behaviour of these alloys and, in particular the behaviour of the Bi phase that is the distinguishing feature of their microstructure. Evidence from historic studies suggests that it would be worth investigating the role that recrystallization might play in ductile deformation of Bi. Also, worth investigating would be whether a fine eutectic creates a microstructure more conducive to a ductile response to stress.

In the study of the behaviour and effect of Sb additions to a hypoeutectic Sn-Bi alloy referenced in this paper [9]:

- Sb preferentially dissolves in the primary Sn phase, and only dissolves in Bi and forms SnSb when the concentration is above the solubility limit in Sn.
- The undercooling of the SnSb phase is large during nonequilibrium solidification at the Sb concentrations investigated.
- The temperature sensitivity study of the lattice parameters of Sn and Bi shows significant changes in the lattice parameters of Sn due to the dissolution of the larger Bi atoms at higher temperatures.
- The effect of Sb on the lattice parameters of Sn varies with temperature due to the wide range of Bi concentrations at different temperatures that can influence the Sn-Bi-Sb atomic interactions.
- DFT calculations show the enthalpy of formation during the dissolution/precipitation of Bi is the lowest in the 0.5 wt% Sb sample.

A clear correlation between these results and Sb-induced refinement of the Sn-Bi eutectic was not established although the effects that Sb was found to have could in certain conditions have that outcome.

FUTURE WORK

The results obtained in the study reported in this paper suggest that any effect of Sb on the microstructure an Sn-Bi alloys is very sensitive to the cooling rate. This will be explored in experiments in which the cooling rate is more carefully controlled.

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