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The Effect of Strain Rate on the Ductility of Bismuth-Containing Solders

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ABSTRACT
With the identification of bismuth as an addition to lead-free solders that can reduce melting points and provide an additional strengthening mechanism, the electronics industry has moved to solder alloys that differ significantly from those on which it has previously relied for general assembly. Because of its low melting point, its unchallenged non-toxicity, and its unique ability to form intermetallic compounds with most of the substrates across which connections are needed, tin has provided the basis for most of the solders used in electronics manufacturing. The silver and copper additions used to reduce the melting point of tin in the first generation of lead-free solders have almost no solubility in the tin phase and are present in the microstructure as the intermetallic compounds Ag_3Sn and Cu_6Sn_5, which provide, at least temporarily, the bonus of particle strengthening of the tin phase. The nickel addition, which enhances the fluidity of tin-copper solder and can stabilizes the hexagonal form of the Cu_6Sn_5 in all lead-free solders, is largely incorporated into the crystal structure of that intermetallic phase, partly replacing copper in the crystal lattice. Nickel in excess of that requirement forms other intermetallic phases that can provide additional particle strengthening of the tin phase. The matrix of these first-generation lead-free solders is essentially nearly pure tin. As an alloying addition in lead-free solders, bismuth differs from silver, copper and nickel in that it has substantial solid solubility in the tin phase. In solid solution the bismuth strengthens the tin phase, which has made it a popular ingredient in high reliability solder alloys. In that regard, the role of bismuth in lead-free solders is similar to that of lead in tin-lead solders. A critical difference, however, is that while lead in excess of the solid solubility in the tin phase at the prevailing temperature is present in the microstructure as a lead phase with a significant amount of tin in solid solution, bismuth at a level in excess of the solid solubility limit in the tin phase is present in the microstructure as a nearly pure bismuth phase. While the lead-tin solid solution, with its face-centred cubic structure is a tough ductile phase, the bismuth phase, with a rhombohedral crystal structure with limited slip planes, has a tendency to brittle failure. A further complication of solders containing bismuth is that over the range of temperatures to which electronic assembles are exposed in service they are closer to their solidus temperature than solders that do not contain bismuth. That means that the diffusion processes that can drive significant microstructural change proceed relatively rapidly. A consequence is that mechanical properties, which can be very dependent on microstructure, can change within relatively short time frames. In this paper the authors report some preliminary results from a wider study of the effects of bismuth on the properties and behaviour of solder alloys, in particular:
1. How the strain rate sensitivity of established leaded and lead-free solders differs from that of the tin-bismuth eutectic.
2. How a bismuth addition at less than the room temperature solid solubility in the tin phase on one of the established lead-free solders affects the strain rate sensitivity of strength and elongation
3. The relationship between the bismuth content of simple binary tin-bismuth alloys and their hardness and tensile strength.

Key words: Bi additions to Pb-free solders, Sn-Bi alloys, strain rate sensitivity

INTRODUCTION
In the early 1990s, the electronics manufacturing industry was alerted, by a bill introduced to the US Congress, to a growing concern about the use of lead in the manufacture of their products [1]. The initial industry response to that bill was that electronics manufacturing without tin-lead solders and solderable coatings would be difficult, if not impossible, and the bill that was eventually passed applied only to the solder used to seal the joints in piping used for potable water reticulation. However, that bill, and early warnings of a move by the European Union to restrict the use of lead in electronics, prompted the industry and its suppliers to begin to look seriously at lead-free alternatives [2, 3].

It is interesting to note, in retrospect, that although they have no toxicity issues, and have long been known to industry, at that time tin-bismuth alloys were not considered to be suitable candidates for replacing tin-lead solders. One reason for that was that their melting point was thought to be too low for the aggressive environments into which electronics were then being introduced [2]. Additions of bismuth at levels up to about 5% were found to improve life in thermal cycle testing of the tin-silver-copper and tin-copper alloys that had been identified as potential lead-free solder options. However, experience of premature failure in thermal cycling of candidate alloys because of lead contamination meant that these bismuth-containing alloys were not recommended for use, at least in the first phase of lead-free implementation when the risk of such contamination was high. The combination of tin, lead and bismuth creates the opportunity for formation within the microstructure of a eutectic phase with a melting point of about 96˚C, which is well within the temperature range to which solder joints are exposed in service.

As lead-free implementation proceeded to the point where, in large sections of the electronics manufacturing industry, the risk of lead contamination was near zero, attention returned to the strengthening effect that bismuth could contribute to the development of high reliability alloys for application in the increasingly harsh environments in which electron circuitry was being required to operate. Higher reliability lead-free solders with bismuth additions at levels up to around 6 wt% now have a firmly established place in electronics assembly [3].

The use of solder alloys based around the tin-bismuth system, with its eutectic at 57% Bi with a melting point of 139˚C, did not come into consideration for wider application until the electronics manufacturing industry found itself facing challenges that could be met only by solder alloys that could be used with process temperatures substantially lower than the 250-260 ˚C required by the established lead-free solders; no higher than 200 ˚C and ideally lower than that. It is perhaps ironic that the property that had been one of the reasons for the earlier rejection of tin-bismuth alloys as a practicable lead-free alternative, their low melting point, is now the property that has brought them back into consideration.

The new interest in lower temperature soldering processes is being driven [5] by the need to:

- Reduce the incidence of warpage-related defects in large CPU area array packages
- Solder temperature sensitive components such as CMOS optical devices
- Make solder joints to temperature sensitive substrates such as used in medical sensors
- Solder through hole assemblies with high thermal mass components that cannot easily be got to the temperature required to achieve wetting and hole fill with conventional lead-free solders
- Reduce energy consumption in electronics assembly processes

Another factor driving interest in tin-bismuth solders for the assembly of consumer electronics and appliances is that bismuth is generally cheaper than tin. The eutectic alloy is only 43wt% tin compared the 96.5% of “SAC305”. And if a tin-bismuth solder contains silver it is typically 1 wt% or less compared with the 3-4 wt% in “SAC” alloys.

Even before the relatively recent interest in their wider application, solder alloys close to the Sn-57% eutectic found application for making connections to temperature-sensitive components or soldering to temperature sensitive polymer substrates. A eutectic or near-eutectic tin-bismuth solder was included in the product range of most manufacturers of soldering materials. However, the form in which the tin-bismuth solder was usually offered for such applications, solder paste, provides a clue to the challenges that have to be dealt with if these alloys are to be widely used in general electronic assembly. The alloy was usually offered only as solder paste because it could not easily be extruded and then drawn to produce flux-cored wire with the manufacturing processes that were used with tin-lead, tin-copper, and tin-silver-copper solder alloys. In conventional extrusion and wire drawing processes tin-bismuth alloys tend to disintegrate into fragments.

This tendency of these tin-bismuth alloys to brittle failure is attributed to the presence in the microstructure of a bismuth phase, which has mechanical properties rather different from the tin phase that predominates in the tin-silver-copper and tin-copper lead-free solders. That bismuth phase is present whenever the bismuth content of the alloy exceeds the limit of solid solubility in the tin phase at the prevailing temperature (Figure 1). At 25 ˚C the limit of solid solubility of bismuth in tin is 2-3 wt%. As the temperature increases that limit increases to about 21 wt% at the eutectic temperature of approximately 139 ˚C but on cooling to ambient temperatures the bismuth phase precipitates out of the tin phase in ways that significantly affect the properties of the solder.

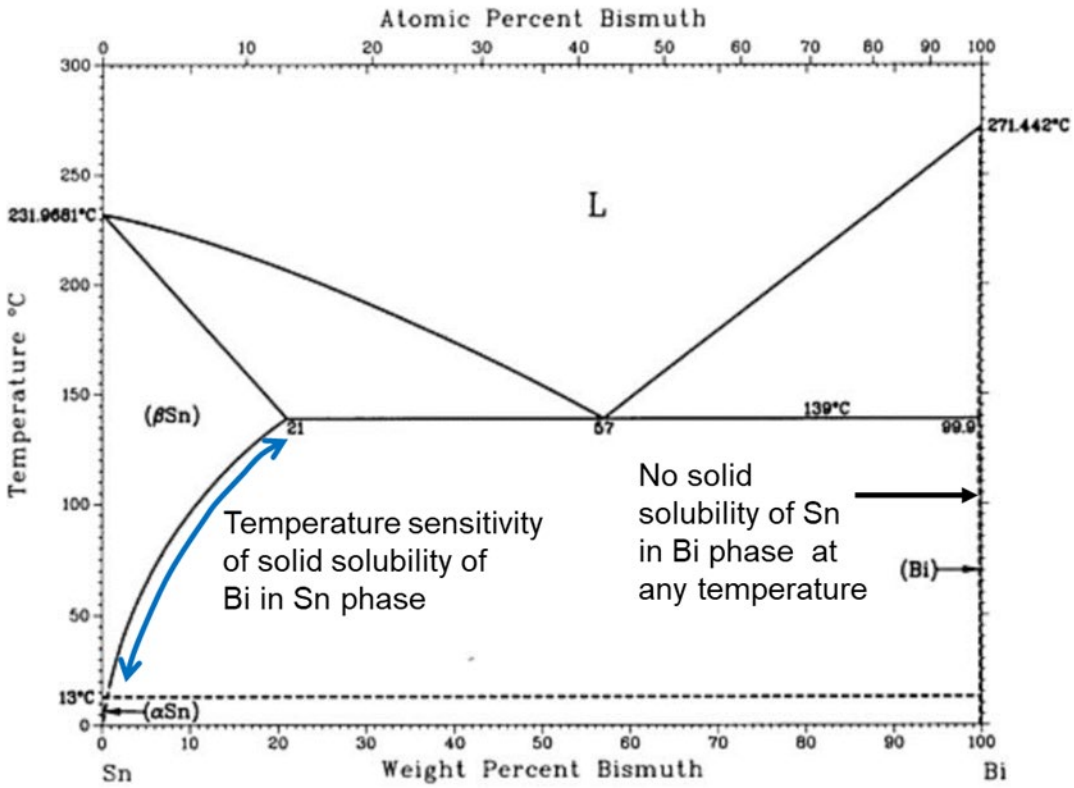


Figure 1. Tin-bismuth phase diagram highlighting the temperature sensitivity of the solid solubility of bismuth in tin [6]

The hardness data in Table 1 provides an indication of the greater resistance to deformation of pure bismuth to deformation than pure tin. In a tin-bismuth alloy, in which both phases are present, the difference would be reduced because of the strengthening effect on the tin phase of the bismuth in solid solution. Nevertheless, it can be expected that the properties of solder alloys that contain bismuth will be affected by the presence of this phase, which responds to stress elastically and plastically in ways different from that of the phase in which it is embedded.

Table 1. Comparison of some properties of tin and bismuth

Property	Sn	Bi
Melting Temperature (˚C)	231.9 [7]	271.47 [7]
Young's Modulus (GPa)	41.6 [8,9]	31.7 [8]
Brinell Hardness	3.9 [8,9]	7.0 [8]

The microstructure of the alloy, in particular the particle size of the bismuth and tin phases, can have a significant effect on the response of bismuth-containing alloy to stress. A fine microstucture can create opportunities for deformation by grain boundary sliding that would not require dislocation movement in the bismuth phase and there are reports of exceptional ductility when the microstructure and strain rate favours that deformation mechanism [4, 9].

Another factor that has to be taken into account when measuring the mechanical properties of tin-bismuth alloys is that the temperatures to which solder joints are exposed in service are closer to the melting point of tin-bismuth solders than that of the established lead-free solders. At these higher homologous temperatures, the diffusion processes that drive microstructural evolution proceed more quickly in tin-bismuth solders than they do in the established lead-free solders. That means that the results of mechanical testing can depend on the time that has elapsed since the test piece was cast, and the thermal excursions to which it might been exposed. The variation in published data on the mechanical properties of Sn-Bi alloys is probably a reflection of that sensitivity of the microstructure to temperature and time, as well as testing conditions (Table 2).

Table 2. Variation in reported tensile test results for tin-bismuth alloys

Composition	Ultimate Tensile Stress (MPa)	Yield Stress (MPa)	Elongation (%)
Sn-34Bi	66.1 [11]	53.3 [11]	23.2 [11]
Sn-52Bi	59.6 [11]	51.0 [10]	53.2 [11]
Sn-58Bi	49.2 [11]	40.6 [11]	15.1 [12]
Sn-58Bi	52.0 [12]	49.0 [12]	35.0 [11]
Sn-58Bi			25.0 [13]

EXPERIMENTAL PROGRAM

In this preliminary exploration of the effect of bismuth on the mechanical properties of solder alloys, three effects of bismuth were examined.

- A comparison of the strain rate sensitivity over three orders of magnitude of the tensile strength of three established solders, leaded and lead-free, with the tin-bismuth eutectic.
- An assessment of the effect of a bismuth addition below the solid solubility limit in the tin phase of one those established lead-free solders
- In simple binary tin-bismuth alloys the relationship between bismuth content, hardness and tensile strength at the slowest of the three strain rates

The work reported in this paper is part of the first stage of a long-term project directed at characterising the effect of bismuth additions on the mechanical properties of the lead-free solder alloys systems and the relationship between the mechanical properties of tin-bismuth alloys and the bismuth content. Although different in application, these two categories of alloys can be considered to be related because once bismuth has been added to a tin-based system there is at least one of the phases that correspond to the two phases in the tin-bismuth system. There is the tin with bismuth in solid solution and, where the bismuth exceeds its solid solubility at the prevailing temperature, a near pure bismuth phase will be present. The bismuth in solid solution affects the mechanical properties of the tin phase and the bismuth phase provides additional barriers to the deformation of the tin phase with consequent strengthening.

The results of this project will be interpreted in terms of the microstructure with the eventual objective of generating a Finite Element Model that takes into account the characteristics of the dominant phases, and the microstructure. One step in the preparation of that model will be determining the nine parameters in the constitutive model proposed in 1982 by Anand [14]. This model has proved to be robust in predicting the performance of solder alloys and has the advantage that the parameters can be extracted from the results of a series of tensile tests over a range of temperature and strain rates.

In this paper the results of two of these preliminary investigations will be reported.

- The sensitivity of the alloys listed in Table 3 to the strain rate in tensile testing at ambient temperature
- The relationship between the tensile strength and hardness and the bismuth content at ambient temperature of simple binary tin-bismuth alloys (Table 4).

To ensure comparability, the test pieces for both test regimes were prepared in the same way and tested on the same tensile testing machine under the same conditions.

Table 3. Chemical Analysis of Tensile Tested Lead-free Solders (wt%)

Nominal Composition	Cu	Pb	Ag	Bi	Ni	Ge
Sn-0.7Cu-0.05Ni	0.640	0.025	<0.001	0.005	0.053	0.006
Sn-3.0Ag-0.5Cu	0.520	0.030	3.10	0.012	0.003	<0.001
Sn-1.5Bi-0.7Cu-0.05Ni	0.697	0.033	<0.001	1.53	0.053	0.006
Sn-57Bi	0.002	0.012	0.001	57.7	<0.001	<0.001
Sn-37Pb	0.001	37.401	0.003	-	-	-

Table 4. Nominal Composition of Binary Tin-Bismuth Alloys

Bi wt%	0	10	20	30	37	40	50	57	70
Sn wt%	Remainder								

EXPERIMENTAL METHOD

An issue that has made it difficult to compare tensile test results for different alloys and from different laboratories is uncertainty about the design and manufacturing method of the test pieces and history of thermal exposure between the times of manufacture and test [15]. One of the objectives in the work reported here was to try to minimize that source of variability.

There is a view that when measuring the properties of solder alloys for the purpose of assessing the likely reliability in service of solder joints made with those alloys, the dimensions and microstructure of the test piece should be relatable to those of typical solder joint. For the purpose of this investigation, however, priority was given to:

- A geometry that would make it possible to accurately measure actual strain rates
- A method of manufacturing test pieces that provides some assurance of mechanical integrity
- Consistency in the cooling and ageing conditions that can have a great effect on the microstructure.

On the basis of those considerations the decision was made to use a test piece based on the ASTM Standard E8/E8M [16]. The design of the mould, which produces two test pieces with each pour, follows the basic principles of casting design to minimize the likelihood of, shrinkage cavities or cracks (Figure 2). The split mould was machined from solid aluminium.

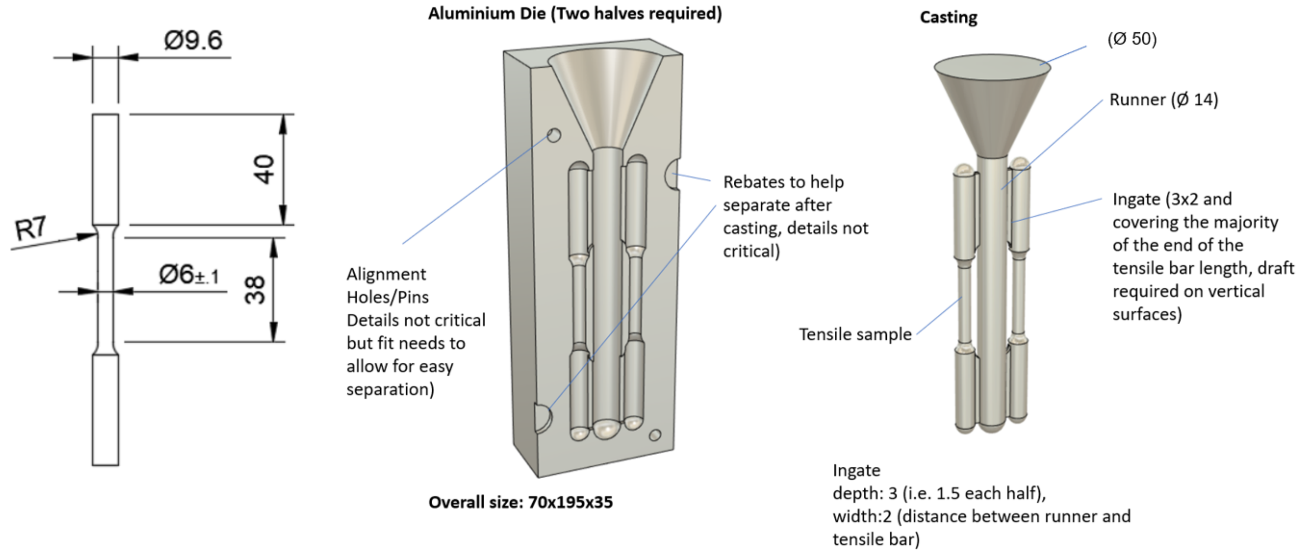


Figure 2. Tensile test piece dimensions, mould and casting from which the test pieces were recovered

To make the alloys, the carefully weighed pure metals were placed in a boron nitride coated clay-graphite crucible and brought to a temperature of approximately 200˚ C above the liquidus temperature of the target alloy for at least one hour, with regularly stirring. The molten alloy was poured into the mould in a way that minimized the likelihood of air entrainment and allowed to cool naturally. For consistency of cooling conditions, after each casting the mould temperature was stabilized to 120˚C before the next test piece was cast. The cast test piece was left in the mould for 7 minutes to cool and then removed and allowed to air cool. The typical cooling curve for a Sn-57Bi alloy, collected from the central runner bar, is shown in Figure 3. Test pieces were inspected for visible casting defects before being cleared for testing. A separate sample was sectioned from the 14mm diameter runner bar for hardness testing.

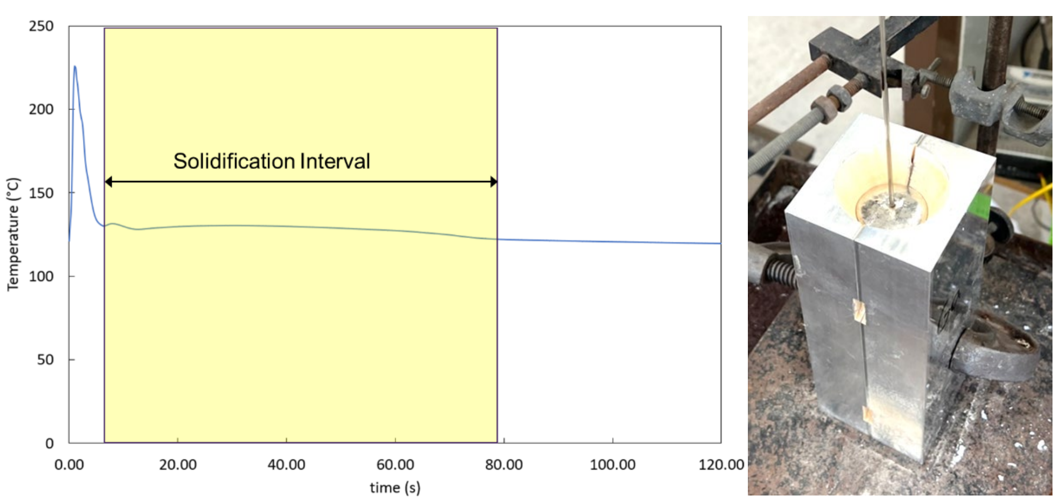
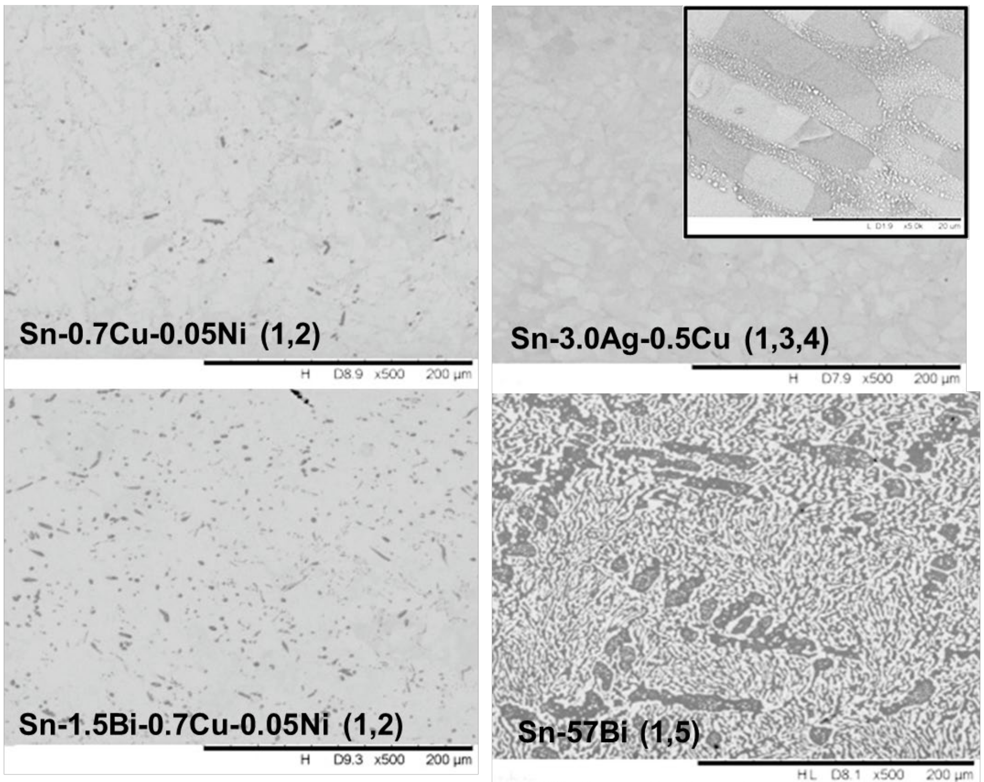


Figure 3. Typical cooling curve for cast test piece and thermocouple monitoring

The microstructure of the lead-free solders listed in Table 3 are presented in Figure 4 with the dominant phases listed.

The microstructure of the binary tin-bismuth solders in Table 4 are presented in Figure 5.



Major Phases Present: 1. β-Sn, 2. $(Cu,Ni)_6Sn_5$, 3. Cu_6Sn_5, 4. Ag_3Sn, 5. Bi

Figure 4. Microstructure of lead-free solders tested

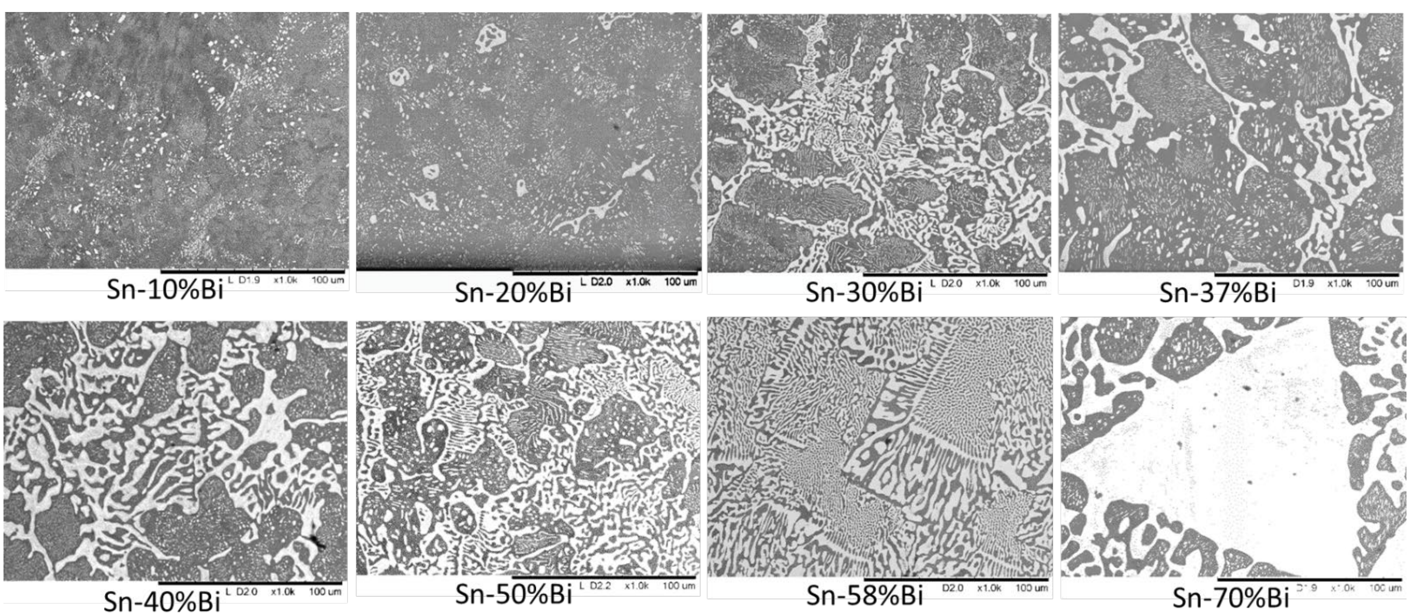


Figure 5. Microstructure of tin-bismuth alloys tested

Tensile testing was carried out at room temperature on an Instron 5584 machine with mechanical grips and a 10kN load cell. Testing was performed at a constant cross-head speed and strain was monitored using an Instron Advanced Video Extensometer 2 (AVE2). Five individual tests were carried out for each composition and test condition. Hardness was measured using a Leco 800AT hardness tester at a load of 19.6N and a dwell time of 10 seconds.

Test conditions for the solders listed in Table 3 are set out in Table 5.

Table 5. Tensile test conditions. 5 repeats for each condition

Temperature (~25 ˚C)			
Cross Head Speed (mm/min)	1.8	18	180
Strain Rate (s^{-1})	0.00079	0.0079	0.079

Test conditions for the series of tin-bismuth alloys in Table 4 are set out in Table 6

Table 6. Tensile and Hardness test conditions for tin-bismuth alloys

Method	Equipment	Test Conditions (~25 ˚C)
Tensile test	Instron 5584	Cross Head Speed 1.8 mm/min
Macro Hardness	Vickers Macroindentation Tester	Load: 19.6 N
		Dwell time: 10 s
		Repeats: 6
		Indenter: Diamond
		Lens: x10

On the basis that, although test pieces were free of visible defects, there may be some internal defects that would affect elongation, of the five samples tested in each condition only the results for the three samples with greatest elongation were used (Figure 6).

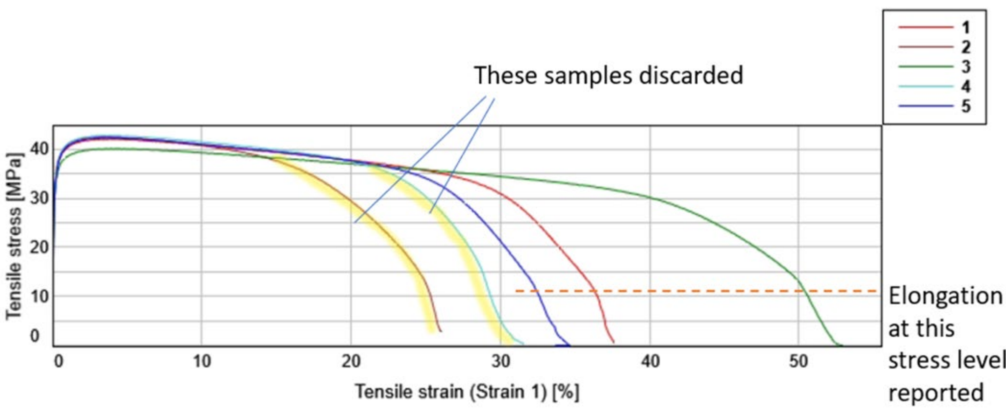


Figure 6. Typical tensile stress strain plots showing criteria for selecting 3 results out of 5 repeats and method of defining elongation.

RESULTS & DISCUSSION

The yield strength (0.2% proof stress) and ultimate tensile strength at the three strain rates are plotted in Figure 7.

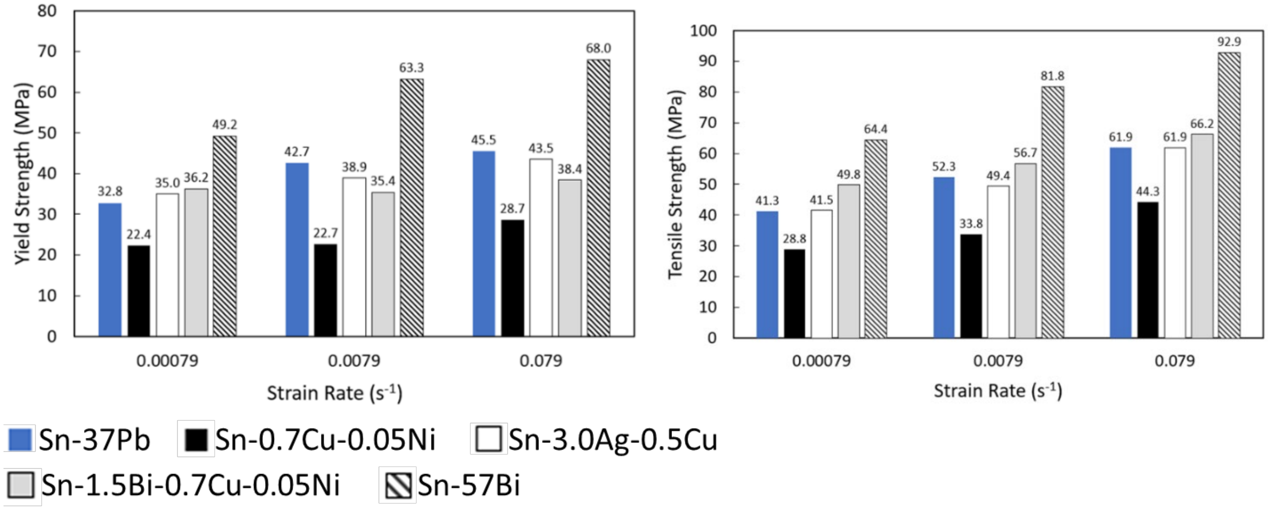


Figure 7. Yield Stress (0.2% Proof Stress) and Ultimate Tensile Strength as a function of strain rate.[17].

Over the range of strain rates tested, the response of all the alloys in Table 3 closely followed the expected power law relationship (Figure 8), but the effect of a substantial volume of bismuth phase can be seen in the effect of strain rate on elongation (Figure 9). The macroscopic appearance of the fracture can be seen in Figure 10, while the microstructure in the fracture area of the Sn-57Bi alloy is shown in Figures 11.

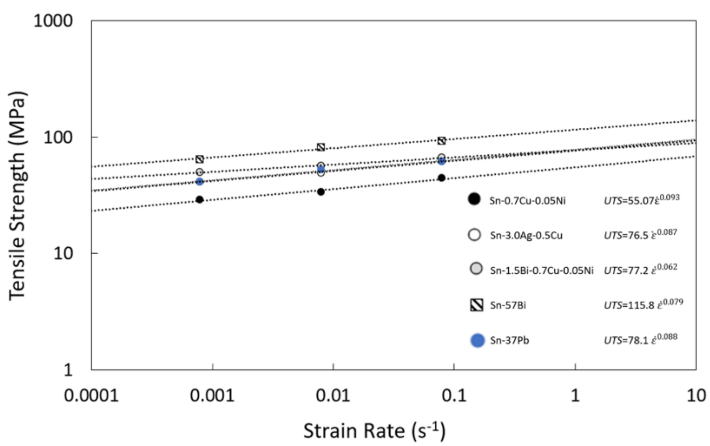


Figure 8. Logarithmic plot of Ultimate tensile strength as a function of strain rate [17].

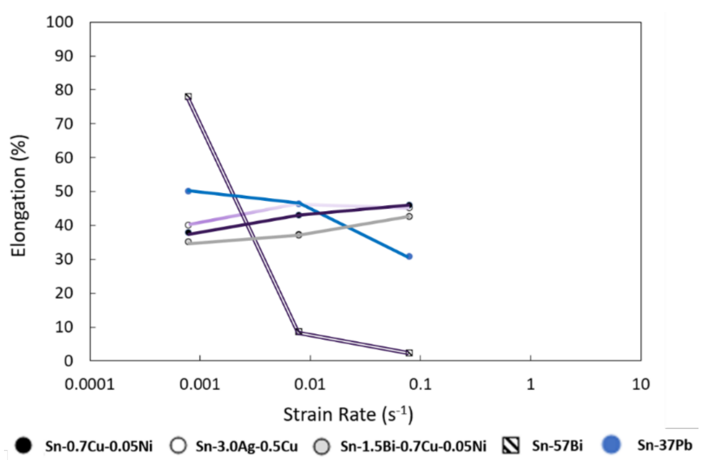


Figure 9. Elongation as a function of strain rate [17].

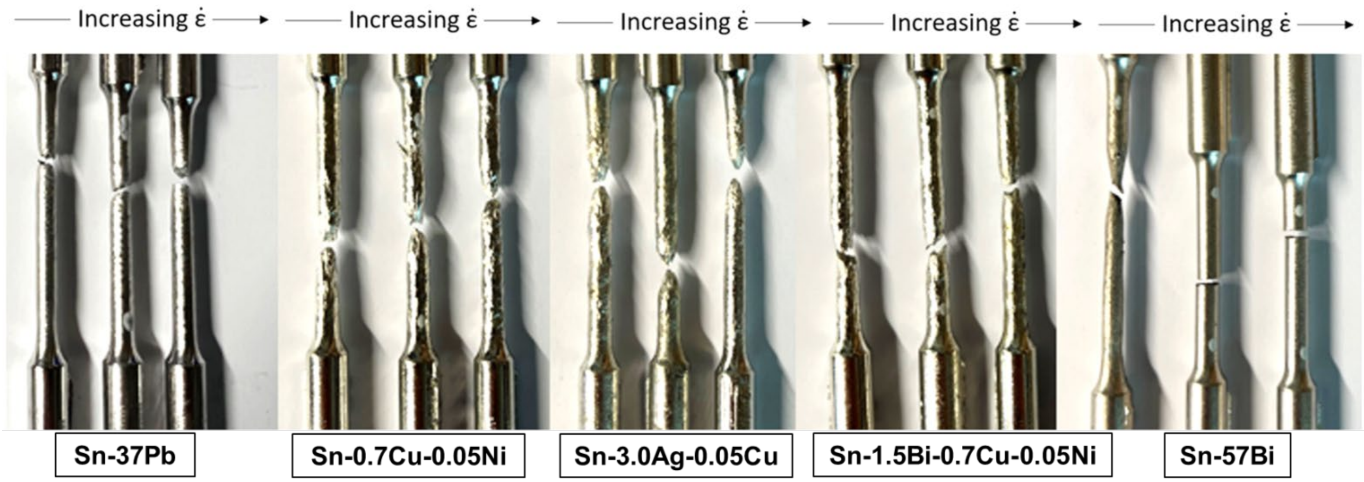


Figure 10. Character of strain and fracture as a function of alloy and strain rate

A clue to the reason for the dramatic decrease in elongation and the transition to brittle fracture in the Sn-57Bi alloy is provided in the cross-sections of the fracture area (Figure 11).

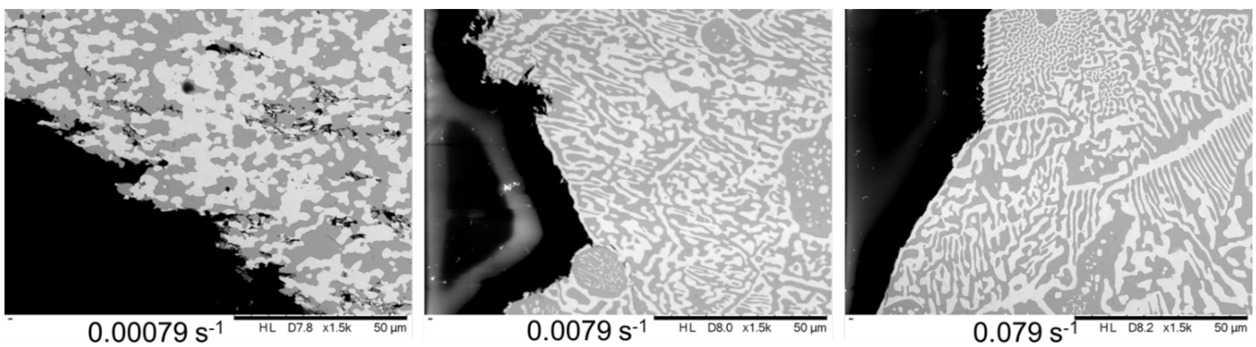


Figure 11. Microstructure close to the fracture of Sn-57Bi at the indicated strain rates.

To investigate further the effect of strain rate on the failure of the Sn-57Bi alloy, the tensile tests at strain rates of 0.00079 $^{s-1}$, 0.0079 $^{s-1}$ and 0.079 $^{s-1}$were interrupted at strains of 30%, 3% and 2% respectively (Figure 12) and the microstructure in the region of the impending failure examined (Figure 13).

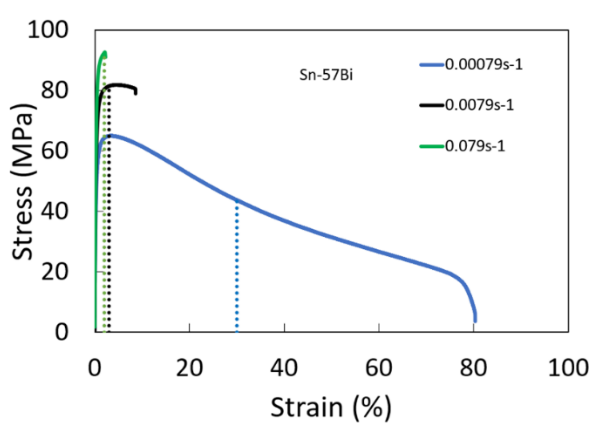


Figure 12. Tensile tests of Sn-57Bi stopped before failure. Solid lines show what would have been a completed test. Dashed lines indicate the point at which the test was interrupted to investigate damage initiation in the microstructure.

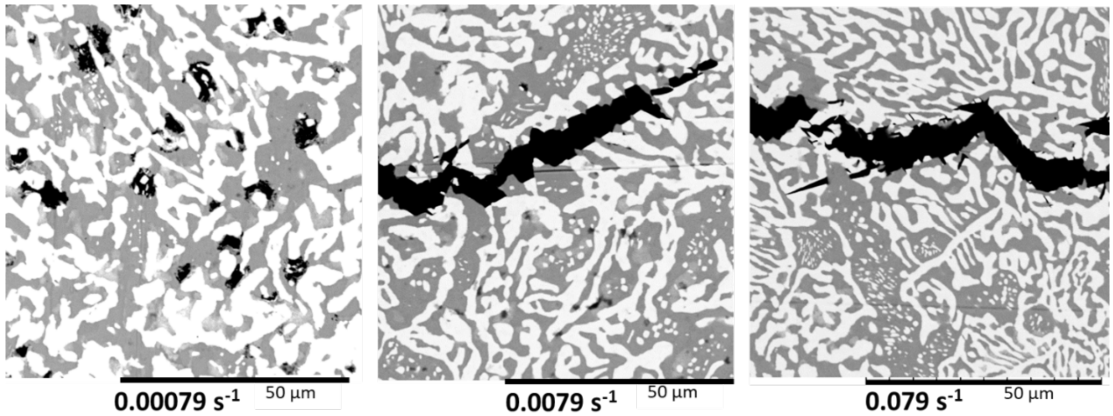


Figure 13. Damage initiation in the microstructure of Sn-57Bi before fracture.

The results of tensile testing at a strain rate of 0.00079 s^{-1} of the binary tin-bismuth alloys listed in Table 4 are plotted in Figure 14 and the corresponding elongations in Figure 15 with the microstructure of the corresponding alloys in the as-cast condition.

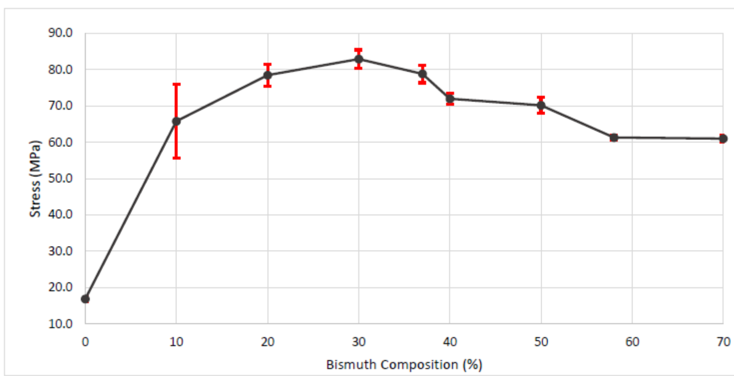


Figure 14. Ultimate tensile strength at a strain rate of 0.00079 $^{s-1}$ of tin-bismuth alloys as a function of bismuth content.

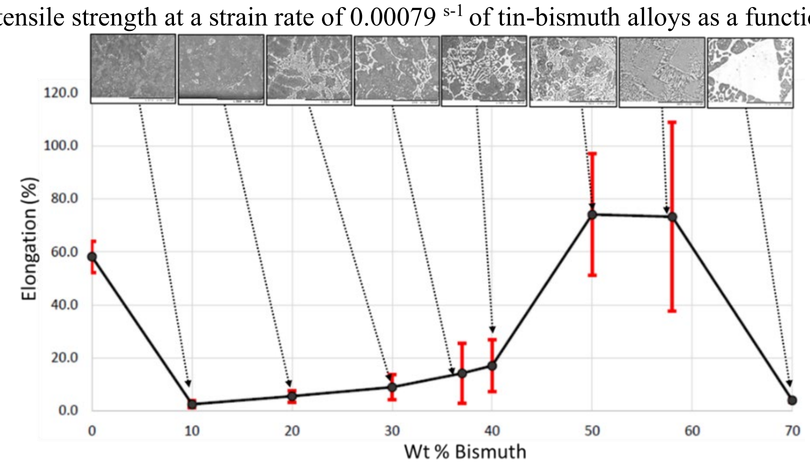


Figure 15. Elongation at a strain rate of 0.00079 $^{s-1}$ of tin-bismuth alloys as a function of bismuth content.

The hardness of two of the alloys in Table 4, Sn-37Bi and Sn-57Bi as a function of ageing time at room temperature is plotted in Figure 16.

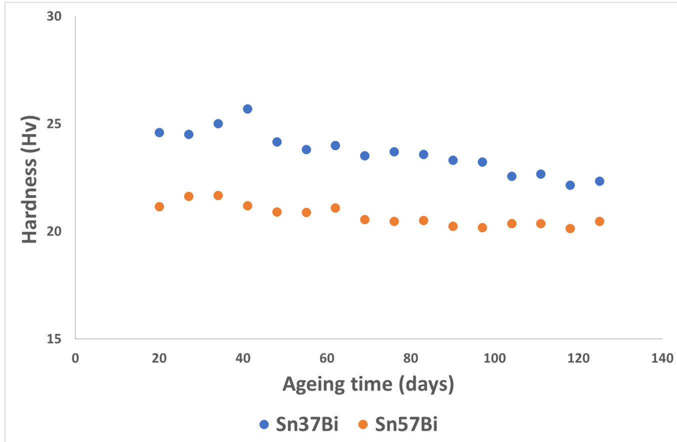


Figure 16. Hardness of representative tin-bismuth alloys as function of aging time at room temperature

DISCUSSION
The objective of the research project, of which the work described in this paper is a part, is been to develop an understanding of the effects that bismuth can have as an addition to established lead-free solders and as an ingredient in tin-bismuth alloy. Given the reputation that bismuth has as a cause of embrittlement in solder alloys there has been a particular interest in identifying the conditions under which brittle failure occurs.

While there is still much further work required, there are some useful conclusions that can be drawn from the results reported here.

As the results in Figure 17 show, as an additive to an established lead-free solder, below the level of maximum solubility, bismuth is a powerful strengthener, albeit strain rate dependent (Figure 17) without compromising ductility (Figure 9).

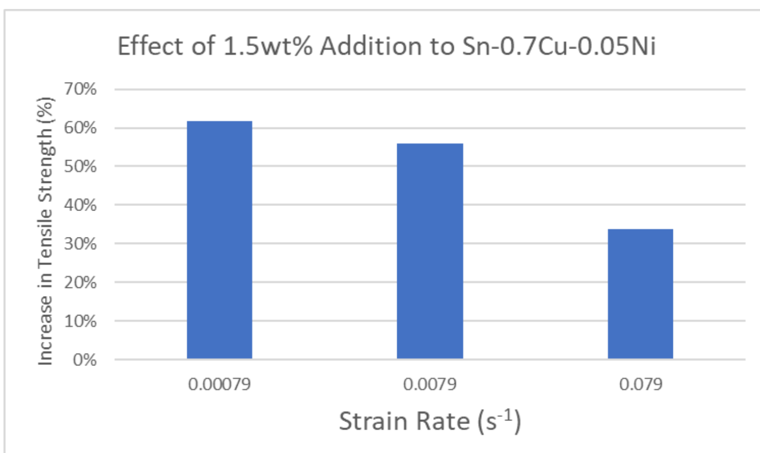


Figure 17. Effect of 1.5Bi addition SN-0.7Cu-0.05Ni on tensile strength

That all the alloys tested at strain rates that varied over three orders of magnitude follow the power law relationship between tensile strength and strain rate provides some reassurance that the presence of bismuth does not take an alloy outside the scope of current experience of solder alloy behavior.

On the transition of the Bi-57 alloy to brittle failure at higher strain rates (Figures 9 and 10) the microstructure in the area of fracture (Figure 11 and 13) provides a basis for a possible explanation.

- At the highest strain rate (0.079 s^{-1}) it is clear that after failure the microstructure of the tin-bismuth eutectic is undisturbed, being more or less identical with that of the as-cast test piece (Figure 4). The fracture has occurred through the bismuth phase with no evidence of significant deformation in the tin phase.
- At the lowest strain rate (0.00079 s^{-1}) the as-cast eutectic microstructure has been completely broken down, most likely by dynamic recrystallization during the tensile test. Most of the considerable deformation that occurred before fracture is a combination of microstructural rearrangement and deformation of the tin phase. The absence of cracking within the bismuth phase suggests that it

has not made much contribution to the bulk deformation of the test piece apparent in Figure 10, and the facture at these low strain rates occurs by the coalescence of voids in the tin phase.

- At the intermediate strain rate (0.0079 s^{-1}) the as-cast eutectic microstructure is largely undisturbed but there is evidence of some deformation in the tin phase that was not apparent in the test piece that failed at the highest strain rate. Nevertheless, the fracture has occurred mainly in the bismuth phase, or at the interface between the bismuth and tin phases.

On the basis of the evidence provided by one half of the fracture surface, as in Figure 11, it is difficult to determine whether the free surface is the result of intergranular or transgranular failure. In an attempt to resolve that question, separate tensile tests performed on Sn-57Bi alloys at the same three strain rates, 0.00079 s-1, 0.0079 s-1 and 0.078 s-1 were stopped prior to failure after total strains of 30%, 3% and 2% respectively. The microstructure of regions showing evidence of damage at those strain rates is shown in Figure 13. At the lowest strain rate, Figure 15(a), there is evidence of recrystallization of the formerly complex regular Sn-Bi eutectic with interfacial voids present. At the medium strain rate, Figure 15(b), cracks can be seen to pass through the bismuth phase with little associated deformation, and the tin phase is able to deform and bridge the crack tip until it fails, leaving a slightly ragged interface. At the highest strain rate, Figure 15(c), there is less deformation of tin phase visible but it can be seen that the bismuth phase still appears to fracture first, with a small "island" of tin phase remaining across a region of cracked bismuth phase.

The pattern of response to strain rate described above provides a model for the relationship between strain rate and the failure of tin-bismuth alloys with a significant volume fraction of bismuth. The key factor appears to be whether the externally imposed stress is applied at a rate fast enough to force the flow stress of the tin phase in which the bismuth is embedded beyond the point at which it can drive brittle failure of the bismuth phase. That suggests that strategies that increase the resistance of the tin phase to deformation might protect the bismuth phase from the stress that triggers brittle fracture and improve ductility and impact resistance
Although tensile test results for the series of binary tin-bismuth alloys are available only for the slowest strain rate, the elongation data (Figure 13) shows a strong effect of microstructure on ductility. That the reduction in elongation is greatest at the lowest bismuth addition (10wt%) but then starts to recover as the bismuth level increases toward the eutectic composition before declining again at the proportion of primary bismuth increases, indicates that the relationship between the presence of bismuth and ductility is complex. The microstructure of the two phases appears to be critical and it appears that the fine dispersion of the bismuth phase that occurs in the eutectic can be an advantage, at least at low strain rate used in the testing reported here.

Although not explored in the experimental work reported in this paper, microstructures that favor grain boundary sliding as another way of accommodating high strain rate deformation have been shown to provide a way of reducing the likelihood of alloys with a significant volume fraction of bismuth phase failing in a brittle manner. However, another aspect of the behavior of tin-bismuth alloys referred to earlier, the high rate of diffusion driven process at the high homologous temperature to which solder alloys are exposed in electronic circuitry could mean that such microstructures would be difficult to maintain unless some form of stabilization, such as grain boundary pinning, could be introduced.

The change in the hardness of the Sn-37Bi and Sn-57Bi during room temperature ageing (Figure 16) is a clear demonstration of one of the characteristics of tin-bismuth alloy identified in the introduction to this paper; the relatively rapid rate of microstructure evolution that occurs because these alloys are at a high homologous temperature even in ambient conditions. Although the microstructural evolution that occurs during this room temperature ageing is not reported in this paper, on the basis of other experience it can be expected that variations in hardness will result from the relative contributions of solid solution and precipitation strengthening mechanisms. Any hardness increase that may occur as a result of the precipitation of the bismuth phase from the tin phase that was left in a supersaturated condition after freezing under non-equilibrium conditions will need to be considered in combination with the decreasing hardness occurring as a result of the reduction in solute strengthening in the tin phase. The slow decline in hardness evident in Figure 16 is also likely to be the consequence of coarsening of the microstructure that can occur during long term ageing at high homologous temperatures. The detailed study of these mechanisms at different time scales in dynamic and cyclical heating environments is the subject of ongoing work

CONCLUSIONS

Although there remains much work to be done to fully characterize the behavior of solder alloys that contain significant amounts of bismuth the results reported here could provide the basis for improving the robustness of low melting point tin-bismuth alloys.

FUTURE WORK

The scope of the research program that has provided the data reported in this paper is extending to cover a wider range of compositions, test temperature, and strain rates, with a view to the development a model that it is hoped will provide a basis for the formulation of low temperature solders with higher reliability. This work might also contribute to the identifications of ways of increasing the stability of high reliability solder alloys in which the strengthening effects of bismuth play a role.

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REFERENCES

1 US Congress S.2637-Lead Exposure Reduction Act of 1990 101st Congress (1989-1990)

2. M. Warwick "Implementing lead free soldering- European Consortium Research", *Journal of Surface Mount Technology, 1999-smtnet.com*

3. Richard Coyle et al. "Enhancing thermal fatigue reliability of Pb-free solder alloys with additions of bismuth and antimony" *SMTAI 2020*

3. T.A. Siewert et al. "Database on lead-free solders", *2001 Proceedings. 51st Electronic Components and Technology Conference*

4. J.L Freer Goldstein and J.W. Morris Jr, "Microstructural Development of Eutectic Bi-Sn and Eutectic In-Sn During High Temperature Deformation "*Journal of Electronic Materials*, Vol. 23 No.5, 1994

5. M. Tsuriya, Lim Sze Pei, D. Locker, Wei Keat, K. Sweatman, F. Lee , "Low Temperature Materials for 1st Level Interconnect in Semiconductor Packaging". *ICEP 2022 Conference Proceedings*,

6. ASM International. (1992). *ASM Handbook Volume 3: Alloy Phase Diagrams.* ASM International.

7. MatWeb, LLC. (2022). *Material Property Data*. Retrieved from MatWeb: https://matweb.com/

8. Gale, W. F., & Totemeier, T. C. (2004). *Smithells Metals Reference Book.* Elsevier Butterworth-Heinemann.

9. Wang, Chuan Ting, He, Yong, Terence G Langdon, "The significance of strain weakening and self-annealing in a superplastic Bi–Sn eutectic alloy processed by high-pressure torsion ", *Acta Materialia*, Volume 185, 15 Feb 2020, p 245-256

10. ASM International. (1992). *ASM Handbook Volume 3: Alloy Phase Diagrams.* ASM International.

11. Silva, B. L., Silva, V. C., Gracia, A., & Spinelli, J. E. (2017). Effects of Solidification Thermal Parameters on Microstructure and Mechanical Properties of Sn-Bi Solder Alloys. *Electronic Materials*, 1754 - 1769.

12. Wang, F., Chen, H., Huang, Y., Liu, L., & Zang, Z. (2019). Recent progress on the development of Sn-Bi based low-temperature Pb-free solders. *Materials Science: Materials in Electronics*, 3222-3243.

13. Mei, Z., & Morris, J. W. (1992). Characterization of Eutectic Sn-Bi Solder Joints. *Journal of Electronic Materials*, 599-607.

14. L. Anand, "Constitutive Equations for the Rate-Dependent Deformation of Metals at Elevated Temperatures," 1982, *Transactions of the ASME*, Vol, 104, January 1982, 12-17

15. "A review of mechanical test method standards for lead-free solders." NPL Report

16. ASTM Standard E8/E8M - 21 (2016) "Standard Test Methods for Tension Testing of Metallic Materials", ASTM International, West Conshohocken, PA, 2021

17. Qichao Hao, Xin Fu Tan, Stuart McDonald, Keith Sweatman, Takatoshi Nishimura, Tetsuro Nishimura, Kazuhiro Nogita "Comparison of the Mechanical Properties of Conventional Pb-free Solders and Eutectic Sn-Bi Solder," *2022 International Conference on Electronics Packaging (ICEP)*, 2022, pp. 173-174, doi: 10.23919/ICEP55381.2022.9795406.