

## Grain Refinement for Improved Lead-Free Solder Joint Reliability

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### Abstract

The very small solder joints that now account for an increasing proportion of the connections on which modern electronics depends are typically made up of only a few grains, sometimes only a single grain. This combined with the high degree of anisotropy in the mechanical properties of the body-centred tetragonal beta-tin crystal is a significant factor in determining the response of the joint to the strain to which it is subject in service, with consequent implications for reliability. The superior reliability in joints with multiple small grains of random orientation suggests that it would be advantageous if the solder alloy could be made to solidify with that fine grain structure. In the study reported in this paper the effect of trace additions of selected elements on the grain structure of pure tin and lead-free solder alloys was observed. The elemental additions were chosen on the basis of previous research as well as an analysis of relevant binary phase diagrams. Solidification theory suggests that an objective of the addition should be to promote the rapid development of a constitutionally undercooled zone ahead of the advancing solid/liquid interface since this is known to favour the repeated nucleation required to achieve a fine grain structure. The results contribute to the growing body of knowledge on the development of microstructure in lead-free solder alloys.

Key Words: Lead-free solders, grain structure, nucleation, solidification

### Introduction

Most of the significant differences between the commonly used lead-free solders, those based on additions of copper and/or silver to tin, and the eutectic tin-lead solder that they are replacing can be related to the microstructure. The microstructure of the tin-lead eutectic is made up of interleaved layers of a lead-rich tin metallic phase and a tin-rich lead metallic phase while that of the lead-free solders is essentially a pure tin matrix in which are dispersed particles of one or both of the intermetallics  $\text{Cu}_6\text{Sn}_5$  and  $\text{Ag}_3\text{Sn}$ .

While the equilibrium phase diagrams for the lead-free solders with 3-4% silver and 0.5-1% copper predict a microstructure dominated by eutectics with a fine dispersion of the intermetallics, the conditions during solidification in production soldering processes are usually very far from thermodynamic equilibrium. The situation is further complicated by interactions with substrates with much of the  $\text{Cu}_6\text{Sn}_5$  ending up at the interface. The consequence is that the microstructure is predominantly tin with a dispersion of intermetallics that often have a morphology more typical of a primary phase than that formed by the coupled growth of a eutectic.

A further factor with implications for joint reliability is that there are typically very few individual tin grains in a solder joint. In the very small joints to the area array packages that account for an increasing proportion of the connections in modern electronic assemblies there are typically only two or three grains and sometimes only one. The reliability consequences of having so few grains are particularly severe in tin because of the extreme anisotropy of its physical properties. Given that anisotropy the time to failure for a particular joint under the conditions to which it is exposed when it is subjected to thermal cycling can be very dependent on the orientation of those few grains [1].

While grain boundaries can themselves contribute to failure the reduction in the anisotropy of a solder joint by increasing the number of randomly oriented grains would be an advantage and the observation has been made that joints with a finer effective grain size last longer in thermal cycling than otherwise expected [2].

Given the continuing need to increase the reliability of solder joints an avenue that warrants exploration is reducing the grain size of the tin matrix.

### Factors that Affect Grain Size

It has been found to be difficult to reduce the grain size of as-solidified tin because tin has been found to be particularly difficult to nucleate [3]. For a grain to form from the molten alloy the first requirement is a solid particle to which tin atoms from the liquid can attach in the ordered arrangement of the body-centred tetragonal crystal of the beta allotrope that is the stable form of tin at temperatures above 13.2°C. The grain size of the solder joint is inversely related to the number of nuclei activated in each joint during solidification. In pursuing this possible avenue of solder joint reliability improvement, therefore, the challenge is increasing the number of active nuclei in each joint.

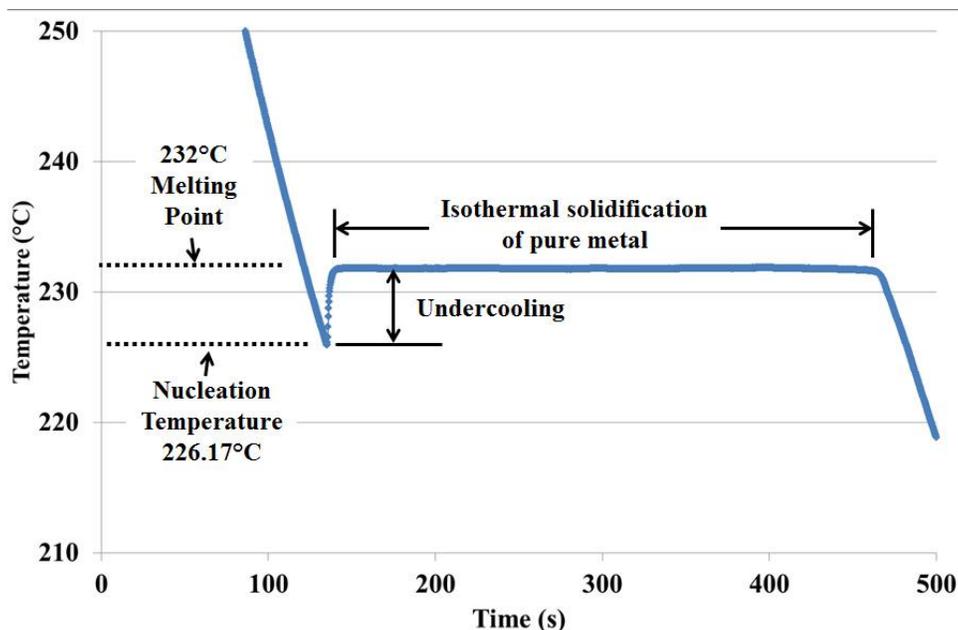
Two methods of increasing the number of active nuclei are to:

- Introduce foreign particles that can act as nuclei for tin (heterogenous nucleation)
- Create conditions during solidification that favour homogeneous nucleation

Attempts at tin grain refinement with heterogenous nuclei have not been successful in significantly increasing the number of grains in a solder joint [3] and in the study reported in this paper the focus has been on the promotion of homogeneous nucleation. Homogeneous nucleation occurs when atoms from the liquid organise into a particle of the crystal lattice large enough to provide a stable base to which other atoms can attach. Measures that promote homogeneous nucleation also have the effect of increasing the likelihood that any heterogenous nuclei that are present will be activated.

Because of the need to create a new high energy solid/liquid interface homogeneous nucleation requires the driving force of a large free energy reduction so that it does not occur at the equilibrium melting point. Cooling has to continue to temperatures below the melting point before there is sufficient free energy available to initiate nucleation. This is the phenomenon known as undercooling. As molten tin cools the plot of temperature versus time (Figure 1) initially follows Newton's Law of Cooling. Because of the difficulty of nucleation the cooling continues past the theoretical melting point until a temperature is reached at which there is sufficient driving force (Gibbs free energy) to create the high energy solid/liquid interface required for a stable nuclei to form. In Figure 1 the undercooling is only 6 degrees but undercooling as large as 187°C has been measured in extremely high purity tin [4].

Once solid tin has been nucleated and growth begins the latent heat released by the solidifying tin results in the temperature climbing to the equilibrium freezing temperature (the melting point) and in a pure metal or eutectic solidification proceeds at that temperature until all liquid has solidified, after which Newton cooling continues.



**Figure 1. Cooling curve for pure tin showing the undercooling required to trigger nucleation of solid.**

It has been demonstrated that tin dendrites grow very quickly once solidification has commenced [1] so that particularly in a small joint there is little time for further nuclei to activate. For this reason nucleation of more grains should be favoured by slowing down solidification.

The rate of solidification can be reduced by lowering the melting point of the liquid at the interface. The liquid then has to cool further before solidification can proceed. The resulting delay provides additional time and the extra cooling additional driving force for the activation of other nuclei. Such a reduction in the melting point of the liquid at the interface can be achieved by adding to the tin an element that lowers the melting point of tin and that has relatively low solubility in solid tin. As the solid tin interface advances the concentration of the rejected additive in the liquid adjoining the interface is increased and its freezing temperature reduced. This is the effect known as constitutional undercooling.

The greater the reduction in the melting point per unit of additive the more effective the additive should be in promoting constitutional undercooling. And the lower the solubility of the addition in solid tin the faster its concentration will build up. These two factors therefore provide a basis for selecting candidate grain refining additives.

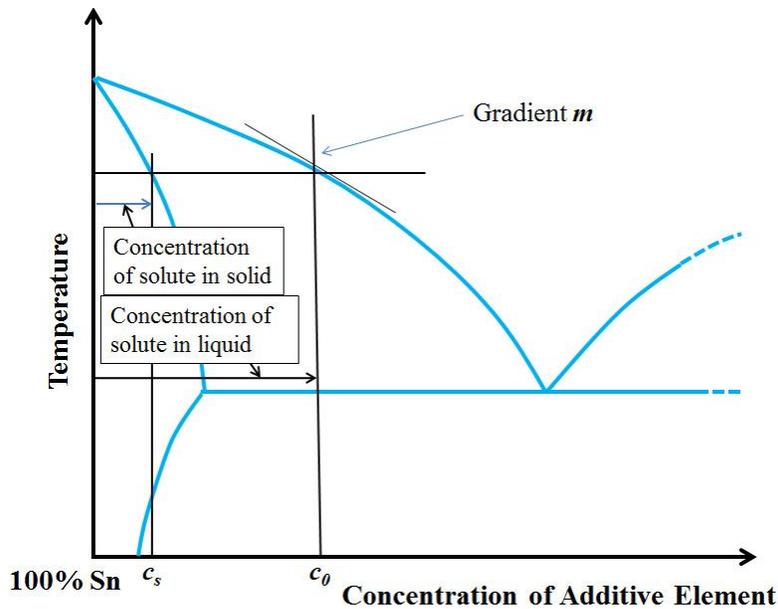
The effect can be quantified by the use of what is known as the Growth Restriction Factor (GRF) which is a measure of the extent to which the advance of the solid interface into the adjoining liquid under the influence of a temperature gradient is limited by the increase in solute concentration in the area adjacent to the interface. This in turn is determined by the rate at which the solute atoms diffuse through the region of liquid ahead of the interface,  $Q$ , which is defined [5] as

$$Q = mc_o(k-1)$$

where  $m$  is the gradient of the liquidus at the composition of the alloy and  $k$  is the Partition Coefficient defined as

$$k = c_s/c_o$$

where  $c_o$  is the concentration of the additive in the liquid and  $c_s$  is the concentration of the additive in the solid that forms from that liquid. These features are indicated on the schematic eutectic phase diagram in Figure 2.



**Figure 2. Parameters used in the calculation of the Growth Restriction factor in non-equilibrium solidification.**

It has been proposed [ ] that when the constitutional undercooling is small this equation could be used to predict the grain size. When the constitutional undercooling is large a plot of grain size against  $Q$  makes it possible to determine whether the additive is functioning as a nucleant or a promoter of constitutional undercooling. For elements that function as a promoter of constitutional undercooling there should be a linear increase in grain size with  $1/Q$ . If the additive is acting simply as a heterogeneous nucleant the grain size will simply decrease with increasing concentration up to the saturation limit [7].

### Selection of Grain Refiners

The elements listed in Table 1 were selected for evaluation as grain refiners on the basis that they met the criteria for promoting significant constitutional undercooling in tin. The values for the liquidus slope,  $m$ , and partition coefficient  $k$ , were estimated from published phase diagrams. Except for Ag and Cu the decision to select these elements was reinforced by reports in the literature of grain refining effects in tin and high tin alloys. Ag and Cu were included not only because of their significant growth restriction factors but because they are the most common alloying additions in lead-free solder.

### Experimental Procedure

#### Alloying

The elemental additions were made to 99.9% tin via master alloys prepared by heating mixtures of the elements to temperatures up to 800°C for 2 hours.

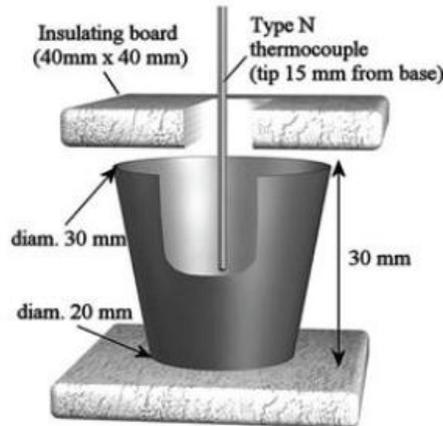
**Table 1. Elements Selected as Potential Grain Refiners**

Element	Liquidus Slope m	Partition Coefficient k	Growth Restriction Factor		
			0.3Wt%	0.5% Wt%	1.0 Wt%
Al	-6.6	0	1.98	3.3	-
Ag	-3.20	0	-	-	- 3.2
Bi	-1.63	0.63	0.18	0.30	-
Co	-2.96	0	0.88	1.48	-
Cu	-7.14	0	2.14	3.57	-
Mg	-13.36	0	4.00	6.68	-
Zn	-3.8	0	1.14	1.90	-

Thermal Analysis

1kg for the alloy was melted in graphite crucibles coated with boron nitride, which is inert to these alloys and not expected to play any role in nucleation. The crucible was stabilized at 332°C (100°C above the melting point of tin) for two hours, the dross removed from the surface and the alloy stirred thoroughly to ensure uniformity. A 30ml sample was poured into a non-wetting stainless steel cup and a thermocouple inserted. The crucible was located between insulating boards as in the set up illustrated schematically in Figure 3. In this arrangement heat is lost mainly in the radial direction.

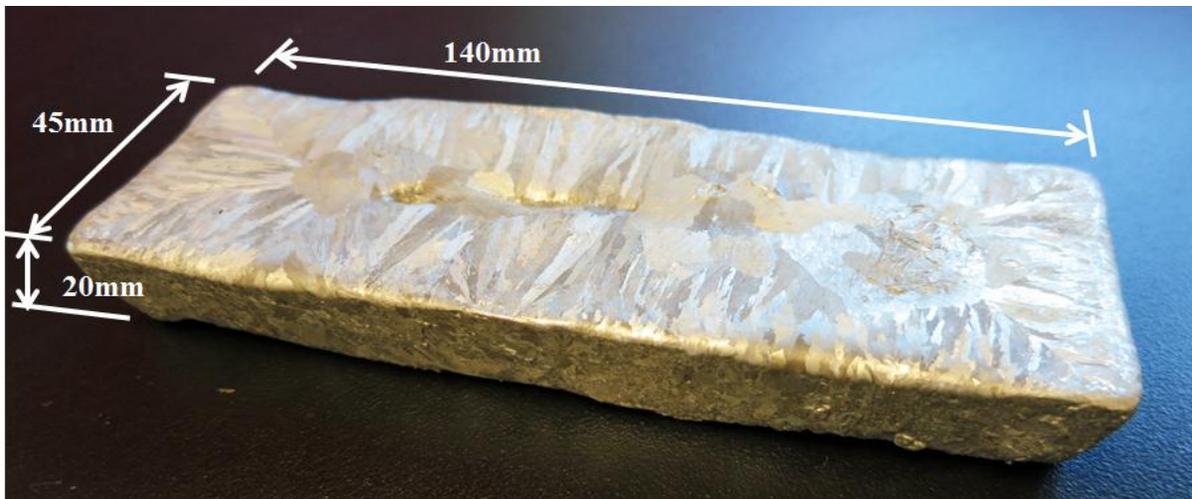
Data was sampled from the thermocouple every 0.2 seconds and written into an ASCII file via a DOS program. The derivative calculated to permit more accurate determination of the liquidus and solidus temperatures. These files were then transferred to Excel worksheets for analysis and plotting.



**Figure 3. Thermal analysis set up [ ]**

Grain Size Measurement

The alloys were cast into ingots (Figure 4) for macro examination and cross-sectioning.



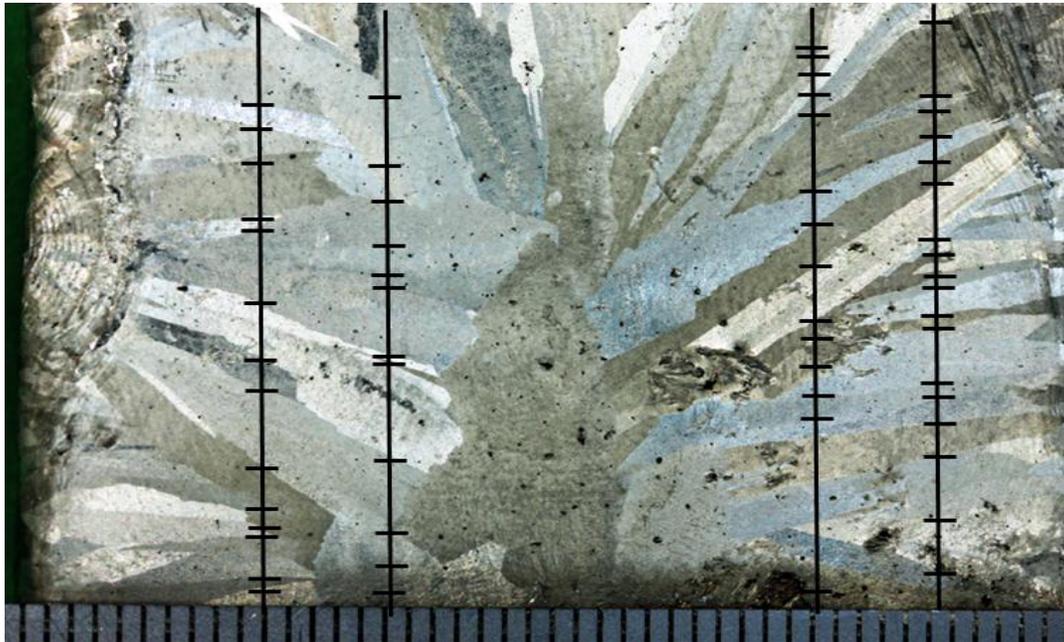
**Figure 4. Ingots cast for grain size determination.**

It was found that mechanical damage caused by cross-sectioning triggered recrystallization, something that is not unexpected in tin, which is very soft and so vulnerable to deformation and at normal room temperatures is at a relatively high homologous temperature- about  $0.6T_m$ , which is equivalent to, for example, copper at about  $530^{\circ}\text{C}$ .

The opportunity was thus taken of extending the study to include the effect of the selected alloying additions on the recrystallized grain structure as well as the as-cast grain structure. Because of this recrystallization, with the techniques available the as-cast grain size could be determined only by examination of the exterior surface.

#### Measurement of As-Cast Grain Size

To reveal the grain structure the as-cast approximately 1kg ingots were etched in a bath of 2% HCl + 5%  $\text{HNO}_3$  in ethanol. Macrographs of the etched surface were taken with a 16Mp SLR camera. Because of the cooling direction in the ingot mould the grain structure was predominantly columnar and the dimension measured was the width (Figure 5). Sufficient measurements were taken to get a statistically significant result.

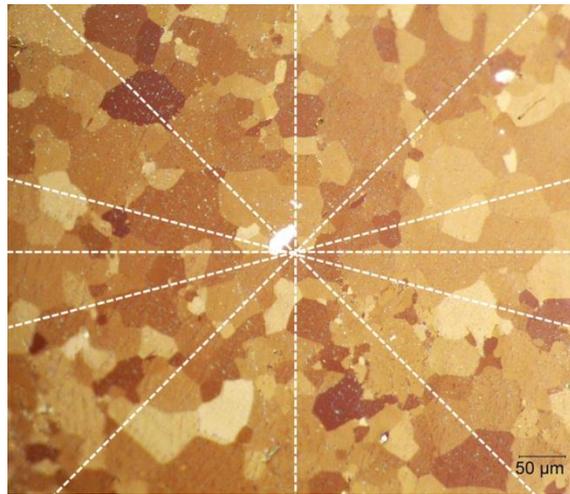


**Figure 5. Intercept counting method used to characterize the size of as-cast grains.**

#### Measurement of Recrystallized Grain Size

Thermal analysis samples were cut in half and mounted in epoxy resin, ground on silicon carbide paper and polished with  $0.5\mu\text{m}$  diamond with a final finish with SiC. If necessary to reveal the grain structure samples were etched in with 5%  $\text{HNO}_3$  in ethanol.

The grain size was measured using the linear intercept method. Because of the directional character of the grain structure in some alloys intercepts were measured along lines at right angles and at  $45^{\circ}$  as well as lines  $\pm 15^{\circ}$  from the transverse (Figure 6). From the number of grains intercepted the Grain Size Number was calculated. The Grain Size Number was averaged over the samples measure and converted to a grain size in microns with a standard deviation being calculated.



**Figure 6. Intercepts along which the recrystallized tin grain were counted in cross sections.**

## Results

### Thermal Analysis

The results of thermal analysis are summarized in Table 2

**Table 2. Data from Thermal Analysis**

Sample Composition	Nucleation Temperature [°C]	Undercooling [°C]	Observations
99.9Sn	226.17	5.63	-
Sn-1.0Ag	225.16	2.42	Low temperature eutectic phase present
Sn-0.3Al	228.40	1.05	-
Sn-0.5Al	228.72	0.64	-
Sn-0.3Bi	227.65	3.35	-
Sn-0.5Bi	228.87	2.33	-
Sn-0.3Co	230.30	1.22	-
Sn-0.5Co	231.12	0.61	-
Sn-0.3Cu	219.86	10.25	Large undercooling possible experimental error
Sn-0.5Cu	225.80	2.78	Clearly defined primary and eutectic phases
Sn-0.3Mg	224.85	3.22	Evidence of a low melting point phase
Sn-0.5Mg	225.52	3.16	Evidence of low melting point phase
Sn-0.3Zn	228.47	1.29	Evidence of two low temperature phases
Sn-0.5Zn	227.63	1.04	Two low temperature phases clearly defined.

The results in Table 2 sorted by undercooling are presented in Figure 7 in which the relationship between undercooling and nucleation temperature is apparent.

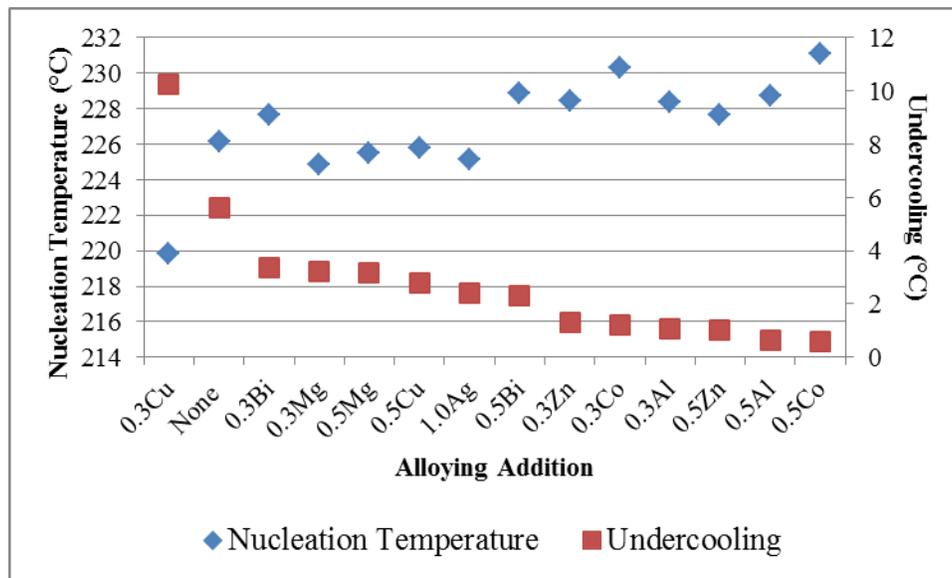


Figure 7. The effect of composition on nucleation temperature and undercooling with the results presented in order of decreasing undercooling

### As-Cast Grain Size

The results of the measurements of the as-cast tin grain size are summarized in Table 3.

Table 3. As-cast grain size.

Composition	Average Grain Size [mm]
99.9Sn	1.53 ± 0.39
Sn-1.0Ag	1.89 ± 0.46
Sn-0.3Al	0.45 ± 0.17
Sn-0.5Al	0.54 ± 0.20
Sn-0.3Bi	2.01 ± 0.59
Sn-0.5Bi	1.56 ± 0.37
Sn-0.3Co	2.55 ± 0.60
Sn-0.5Co	Larger than 0.3Co
Sn-0.3Cu	2.04 ± 0.46
Sn-0.5Cu	4.09 ± 1.39
Sn-0.3Mg	1.15 ± 0.38
Sn-0.5Mg	1.04 ± 0.21
Sn-0.3Zn	1.26 ± 0.34
Sn-0.5Zn	1.19 ± 0.33

In Figure 8 the data in Table 3 has been ranked in order of decreasing grain size for the alloys with the 0.3Wt% additions with the results for pure tin and the 1%Ag addition interpolated. It is interesting to note that the two most common alloying constituents of lead-free solder, copper and silver, both appear to have the effect of increasing grain size. Bismuth and cobalt, which are also included in some lead-free solder formulations also appear to increase the as cast grain size. Even allowing for the error bars it is clear that aluminium has a strong effect, reducing the grain size as measured by more than a factor of three.

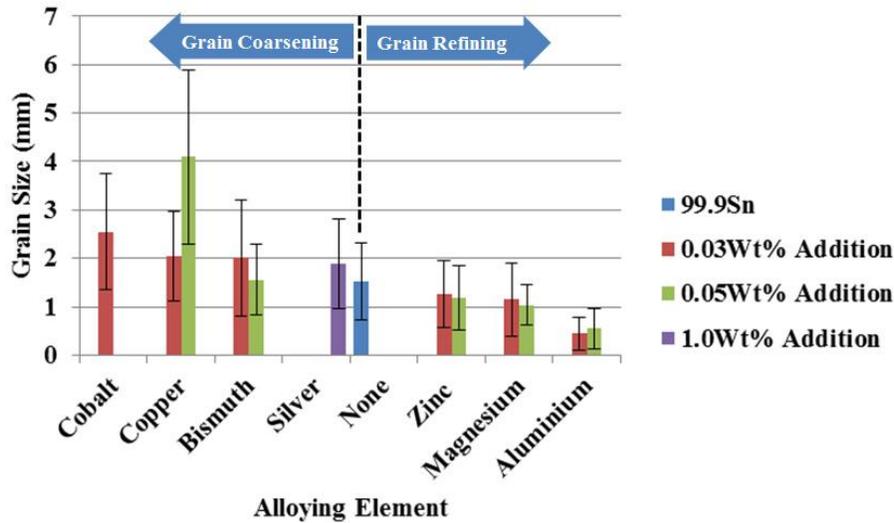


Figure 8. Effect of alloying addition on as-cast tin grain size.

### Recrystallized Grain Size

The results of measurement of the recrystallized grain size are summarized in Table 4. At an average of about  $30\mu\text{m}$  the recrystallized grains of tin are only one fiftieth of the measured size of the as cast grains which averaged  $1.5\text{mm}$ .

Table 4. Recrystallized grain size

Composition	Grain Size Number	Average grain size [ $\mu\text{m}$ ]
99.9Sn	7.11	$29.98 \pm 13.95$
Sn-1.0Ag	8.84	$16.41 \pm 3.57$
Sn-0.3Al	10.47	$8.42 \pm 0.79$
Sn-0.5Al	10.89	$7.22 \pm 0.65$
Sn-0.3Bi	9.39	$13.79 \pm 2.81$
Sn-0.5Bi	9.32	$14.11 \pm 2.92$
Sn-0.3Co	5.67	$48.01 \pm 10.15$
Sn-0.5Co	5.63	$48.53 \pm 10.33$
Sn-0.3Cu	7.80	$23.46 \pm 5.48$
Sn-0.5Cu	8.07	$21.61 \pm 4.85$
Sn-0.3Mg	8.16	$20.79 \pm 4.95$
Sn-0.5Mg	8.38	$19.05 \pm 4.39$
Sn-0.3Zn	7.46	$25.94 \pm 5.54$
Sn-0.5Zn	8.24	$19.37 \pm 3.80$

In Figure 9, the data in Table 4 has been ranked in order of decreasing grain size for the alloys with the 0.3Wt% additions with the results for pure tin and silver interpolated. While the largest and smallest grain sizes occur in the alloys with cobalt and aluminium respectively as was the case with as-cast grain size the ranking between those two is quite different

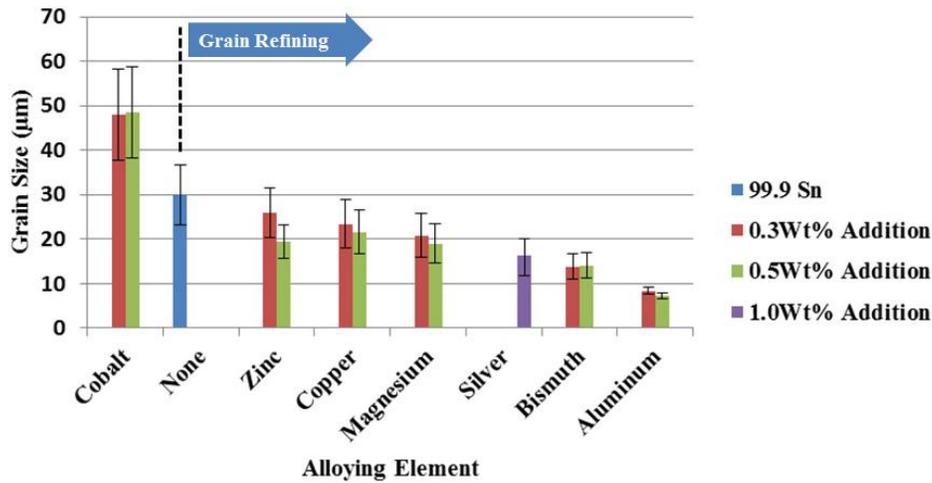


Figure 9. Effect of alloying addition on the recrystallized tin grain size. Results ranked by grain size with 0.3Wt% addition with results for pure tin and silver interpolated.

### Discussion

The results presented in Figure 8 indicate that zinc, magnesium and aluminium reduce the grain size of that as-cast alloy with aluminium having the greatest effect. When the results are analysed in terms of the growth restriction factor there is evidence of a trend that suggests that aluminium is having a strong growth restriction effect (Figure 10). Copper and cobalt appear to be promoting grain coarsening rather than refinement.

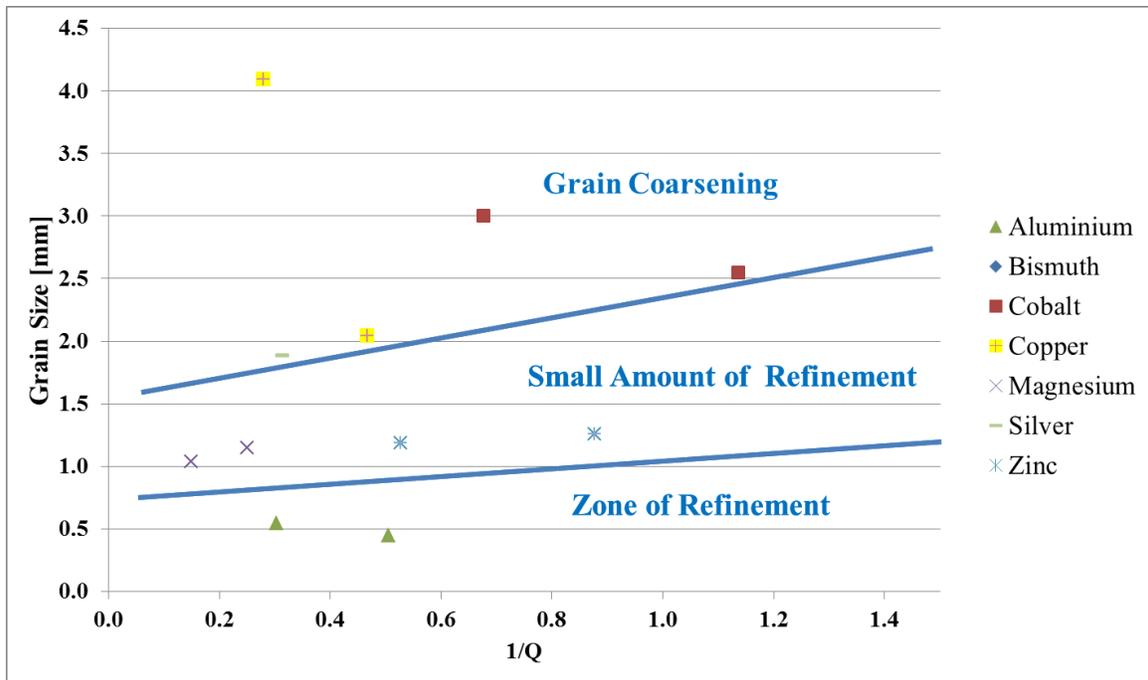
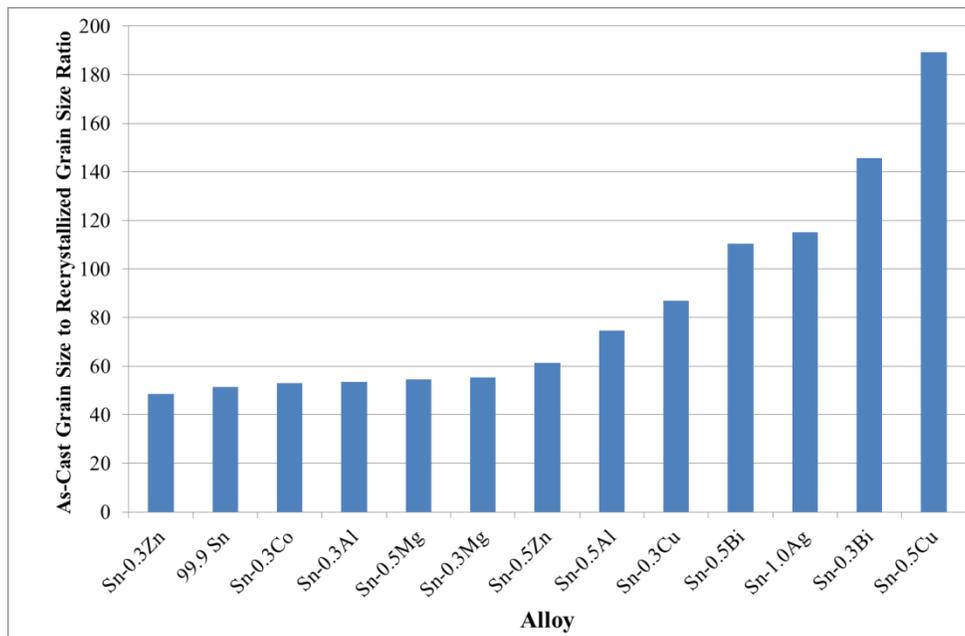


Figure 10. Relationship between the grain and the reciprocal of diffusion rate of solute atoms in the liquid at the solid liquid interface (the growth restriction factor).

While copper seems to promote a coarse grain size even after recrystallization the other additions all have some effect in reducing the recrystallized grain size. However, aluminium appears to have the strongest effect in promoting a fine recrystallized grain size.

As a matter of interest the ratio of the as-cast to recrystallized grains sizes was calculated and plotted in Figure 11. There is a clear trend with additions of copper, bismuth and aluminium and zinc at the 0.5Wt% levels significantly increasing the extent of grain refinement on recrystallization.



**Figure 11. Ratio of as-cast to recrystallized grain size as a function of alloy.**

### Conclusions

The addition that has emerged from this study with the greatest potential for refining the as-cast and recrystallized grain structure is aluminium. With this candidate identified future work will focus on the effectiveness of the this addition in solder joints

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