

REPORT

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**Measuring the effect of the
allotropic transformation in
tin and lead free solder alloys
and their implications for
industry**

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Measuring the effect of the allotropic transformation in tin and lead free solder alloys: Measuring the effect and their implications for industry

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ABSTRACT

This jointly funded industry and UK government project, addressed concerns with the allotropic transformation in tin. β -Sn is stable between 232°C and 13°C. Below this temperature, α -Sn becomes the equilibrium phase. This transformation has catastrophic consequences on the material, mainly because of a 26% volume expansion that accompanies the change from the BCT (body-centred tetragonal) to the diamond cubic structure. This phenomenon has recently become of interest in the field of electronic interconnections, due to the high tin content of the soldering alloys used for the assembly of printed circuit boards.

Previous studies have shown that this transformation can occur in soldering alloys, if the right conditions are met. There are many variables that can influence the formation or suppression of the α -Sn and this study has investigated four of these. In particular, this work has determined the effect of one thermal cycle to room temperature, of cubic ice as a transformation seed, of thermal-cycling on the transformation rate to α -Sn, and of the propensity for commercial Sn alloys to transform.

Cubic ice is a naturally occurring allotropic form of ice that can enhance the nucleation speed of α -Sn in pure tin. When a seed promotes the transformation, the nucleation time is greatly reduced. The work reported here shows that this nucleation process can propagate from tin, such as in a tin plated component termination, into a tin alloy.

This study also determined the propensity of 3 commercial Sn alloys SnCuNi, SAC305 and Sn Ag Cu Bi (SACX) to transform.

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CONTENTS

1	EFFECT OF EXPOSURE TO ROOM TEMPERATURE DURING NUCLEATION (PACKAGE 1).....	1
1.1	INTRODUCTION	1
1.2	EXPERIMENTAL PROCEDURE	1
1.3	RESULTS	2
1.4	DISCUSSION	3
2	EFFECT OF STRESS ON TIN PEST NUCLEATION (PACKAGE 2)	4
2.1	INTRODUCTION	4
2.2	EXPERIMENTAL PROCEDURE	5
2.3	EXPERIMENTAL RESULTS	5
2.4	DISCUSSION	6
3	EFFECT OF CUBIC ICE AS A NUCLEATION AGENT (PACKAGE 3)	7
3.1	INTRODUCTION	7
3.2	EXPERIMENTAL PROCEDURE	7
3.3	EXPERIMENTAL RESULTS	8
3.4	DISCUSSION	9
4	STUDY ON NUCLEATION TIME AND TRANSFORMATION SPEED OF COMMERCIAL ALLOYS (PACKAGE 4)	9
4.1	INTRODUCTION	9
4.2	EXPERIMENTAL PROCEDURE	9
4.3	EXPERIMENTAL RESULTS	10
4.4	DISCUSSION	12
5	CONCLUSIONS	12
6	REFERENCES.....	13

1 EFFECT OF EXPOSURE TO ROOM TEMPERATURE DURING NUCLEATION (PACKAGE 1)

1.1 INTRODUCTION

β Sn is thermodynamically stable above 13°C. Below this temperature α Sn is the Sn phase predicted by the phase diagram. The β/α transformation, however, tends to occur at much lower temperatures. The maximum transformation rate has been reported to be at -40 °C (Raynor & Smith, 1958). The transformation is also very slow, in particular in its nucleation phase. Depending on the conditions and on the material, this can take from several hours to years. What physical changes occur in the material during this time is still an open question. Atom movement occurring at non-equilibrium defect sites is predicted to be the main mechanism. However, it is not known if these changes occur immediately after the tin matrix is in the right conditions or if there is an “incubation” time, before which no nucleation occurs. The α phase growth follows immediately from nucleation.

The effect of thermal transients to room temperature on the nucleation time is unknown. There are two possible scenarios. The first one implies that the incubation and nucleation process could potentially be reset, and the whole process restarted from when the sample is reintroduced in to the cold environment. The second hypothesis is that the nucleation continues when samples are returned to low temperature, implying there is a memory effect, and hysteresis.

The aim of this work is determining if the nucleation time for the tin transformation is reset if a sample is taken from cold to room temperature, before the growth phase has started.

1.2 EXPERIMENTAL PROCEDURE

Twelve tin samples were prepared by melting 3 g of tin in a 40 mm long mould. To promote the transformation, 5 mg of CdTe powder were inserted in the middle of the sample. This was achieved by locally melting the tin (using a small blowtorch) and pushing the powder under the surface of the molten tin. CdTe has the same crystal structure as α -Sn and a very similar lattice parameter. This material provides a nucleation site for α -Sn to grow and therefore the nucleation time is greatly reduced².

The samples were then connected to a 4 probe electrical resistance measurement system. The electrical resistance in the samples was periodically measured. This indicates the real-time status of the transformation (Di Maio & Hunt, 2009b)

Three samples were first placed in a freezer at a constant temperature of -40°C. These were used to calculate the average nucleation time of Sn, without taking it to room temperature.

Further samples were subjected to varying periods (T_1) at -40°C. The samples were then subjected to a 60 minute “recovery” at room temperature (T_R), after which they were reintroduced into the freezer until the transformation was completed. The elapsed time from T_R to the end of the nucleation will be designated as T_2 . Therefore, the total

time for nucleation can be considered to be $T_1 + T_2$. Four types of samples were prepared, and these are listed in Table 1.

Table 1: Type of samples prepared for package 1.

	T_1 – initial time at -40°C	T_R – Recovery time at RT
Type 1	0 mins	0 mins
Type 2	140 mins	60 mins
Type 3	210 mins	60 mins
Type 4	370 mins	60 mins

1.3 RESULTS

During the test, the electrical resistance of the samples was monitored. Typical data for two samples are shown in Figure 1. As expected, the electrical resistance is higher at room temperature. After growth starts, the electrical resistance increases rapidly by several orders of magnitude, as the material transforms into the grey α tin, which is a semiconductor.

The nucleation time was arbitrarily considered to conclude when the electrical resistance increased by 400% from the initial value. At that point, nucleation is replaced by growth of the second phase. The nucleation time was measured before and after recovery for all samples for a total time of $T_1 + T_2$. Results are shown in Figure 2.

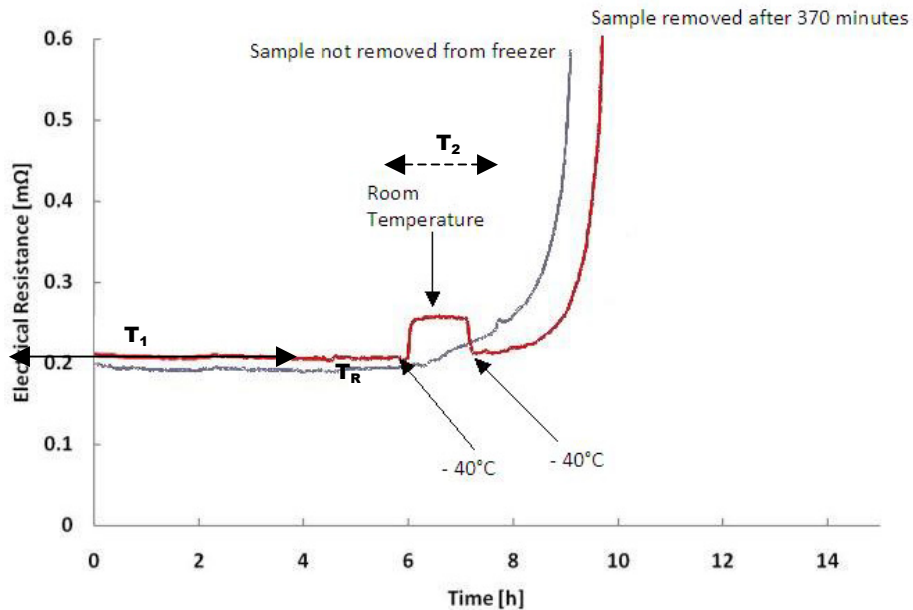


Figure 1. Electrical resistance change during the monitoring of the allotropic transformation for a sample that was left in the freezer and a sample that was taken out after 370 min for 1 hour and put back in.

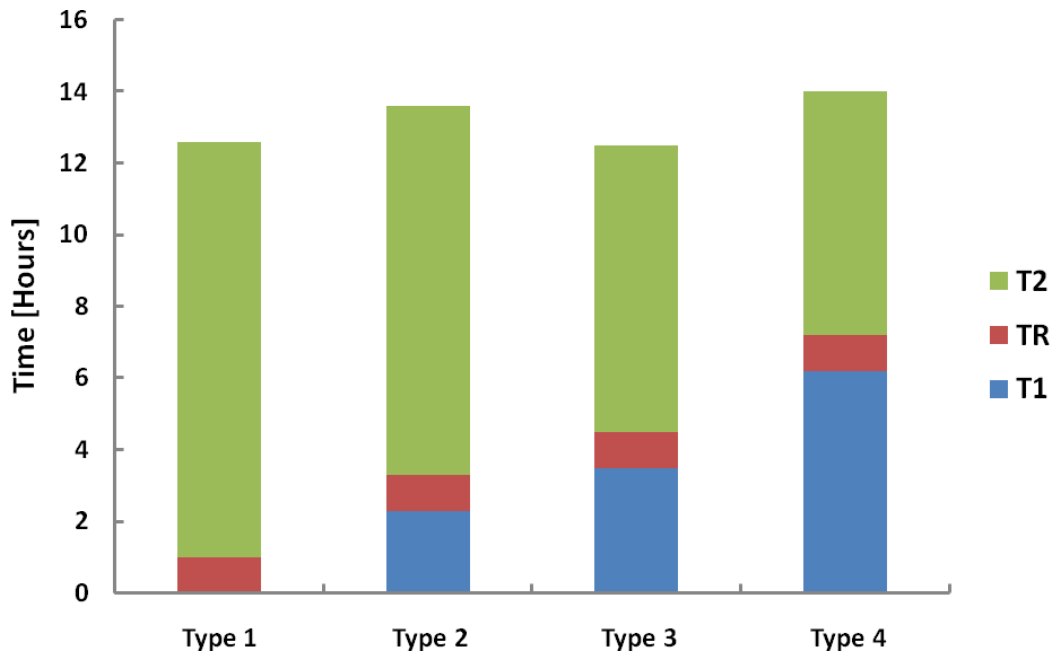


Figure 2. T1, TR, and T2 times for different sample types prepared in this experiment.

From the graph in Figure 2 it can be observed that the transformation time T_2 after the recovery decreases linearly with increasing T_1 . More importantly it can be observed that the total time to the end of “nucleation” is approximately constant.

1.4 DISCUSSION

This experiment shows that when a sample is seeded, the recovery of the sample at room temperature does not influence the total transformation time. This can be interpreted in at least three ways.

1. One hypothesis is that the effects of nucleation are not reversible and room temperature annealing does not produce any change to the incipient transformation at low temperature. In this case, nucleation produces a metastable transformation that is retained at room temperature. This would be consistent with the “memory” effect in tin reported by Styrkas (Styrkas, 2003).
2. A second hypothesis is that the recovery time at room temperature was too short for reversing the transformation. Further research is needed to verify this finding. For example longer annealing times or higher annealing temperatures could be used.
3. Finally, a third hypothesis is that the nucleation stage is much shorter than expected, and immediately after cooling to $-40\text{ }^{\circ}\text{C}$, growth starts with effects that are too small to be detected by the method used here. If this is the case, the samples were taken out of the freezer after growth had already started.

The cases are summarised in Figure 3.

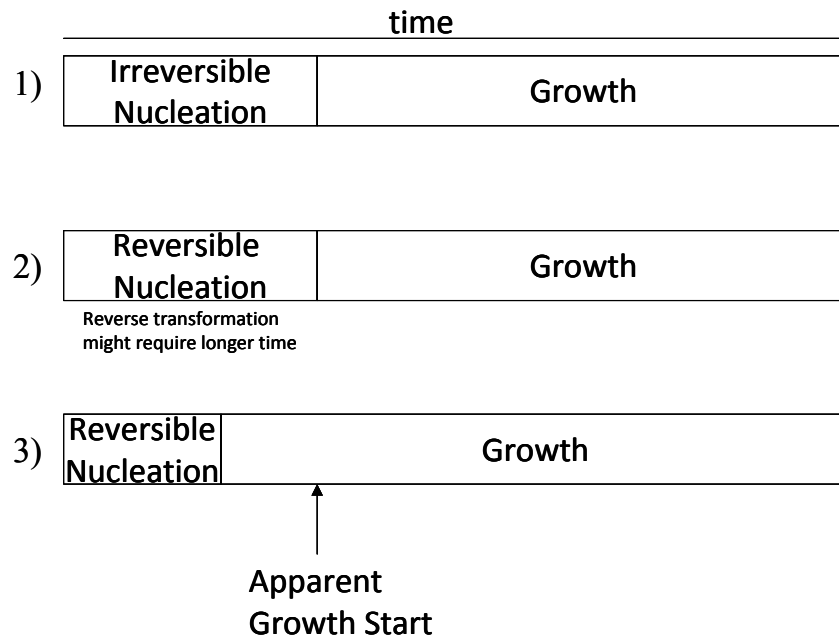


Figure 3: Hypotheses on the nucleation of α tin, and the impact of a temperature cycle above the equilibrium phase transformation temperature. (1) Irreversible nucleation. (2) Reverse transformation (α to β) requires long time. (3) Growth of the α phase has already occurred before the room temperature excursion, and hence nucleation is no longer an issue.

It can be concluded that to prevent the transformation to occur it is important to prevent the onset of nucleation. If this has started, an annealing at room temperature is not enough to prevent the α -Sn growth.

2 EFFECT OF STRESS ON TIN PEST NUCLEATION (PACKAGE 2)

2.1 INTRODUCTION

The presence of defects in Sn can accelerate the β/α allotropic transformation. In particular, it has been observed that cold working reduced the nucleation time by increasing the number of reacting sites (Becker 1958). Lead-free electronics is at risk of this allotropic transformation, due to the high tin content in the alloys used in interconnection. Furthermore solder joints are subjected to high plastic deformation during use, mainly because of the stresses induced by the different thermal expansion of the heterogeneous materials in the electronic assembly during thermal-cycling.

This study aims to investigate the effect of the thermal stresses on the β/α transformation speed. Tin samples were constrained in a rig and thermally cycled in a chamber for 500 cycles. The different thermal expansion rates of the tin and the rig generated stresses in the tin samples. After cycling the samples were placed in a freezer at -40°C and monitored electrically. The incubation time was compared to a non-cycled sample with the same geometry.

2.2 EXPERIMENTAL PROCEDURE.

A rig to constrain and thermally stress the samples has been built of an Invar Sn/Ni alloy. This has a thermal expansion of $1.7\text{--}2.0 \times 10^{-6} \text{ K}^{-1}$ between 20 and 90°C and is much lower than that of Sn ($22 \times 10^{-6} \text{ K}^{-1}$). Twelve pure Sn samples were prepared, with the same method described in Package 1. Six of them were seeded with CdTe, six were not seeded. Three seeded and three un-seeded samples were mechanically clamped to the rig (see Figure 4). These were thermally cycled for 500 cycles between -55 and 100°C, with a cycle time of 70 minutes. The thermal cycling was undertaken to generate plastic deformation in the tin, in a similar manner to solder on a PCB in field service. The cycle time chosen was too short to generate a transformation during the low temperature part of the cycle, even for the seeded samples. Cycled and un-cycled samples were then introduced into a freezer and kept at -40°C, whilst being electrically monitored.

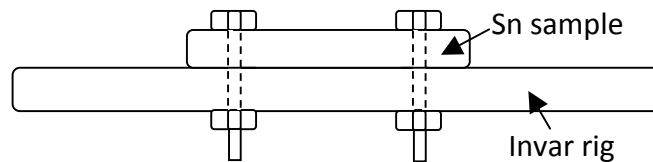


Figure 4: Experimental setup for thermal cycling tin samples.

2.3 EXPERIMENTAL RESULTS

A typical curve obtained from the electrical monitoring of the samples is shown in Figure 5, in this case from a seeded and thermally cycled sample. Similar curves were obtained from unseeded/thermal-cycled, seeded/un-cycled and unseeded/un-cycled samples.

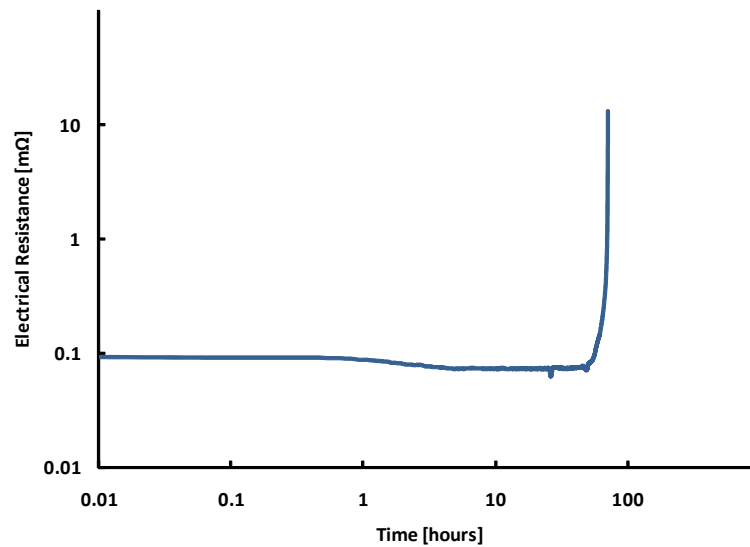


Figure 5: Curve obtained from the seeded, thermal-cycled Sn sample, held at -40°C .

2.4 DISCUSSION

From results typical of those shown in Figure 5 the initial point of the transformation was extracted, according to the method described in (Di Maio & Hunt, 2009b). Three samples per condition were tested and the statistical mean was calculated and is shown in Figure 6 together with the standard error.

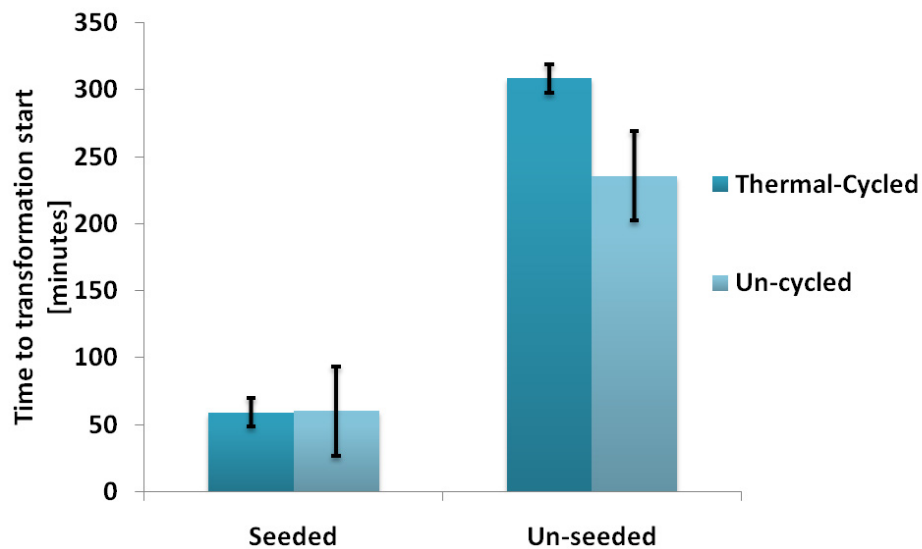


Figure 6: Mean time to transformation start point for seeded/un-seeded, thermally-cycled and un-cycled samples.

As expected, the seeded samples transformed earlier than the un-seeded. However the effect of the thermal cycling in accelerating the transformation was not observed. For the seeded samples the initial point of the transformation was very similar for both

cycled and un-cycled samples. Surprisingly, of the un-seeded samples, the thermally cycled samples transformed slower than the un-cycled samples. However, the differences are small and not statistically significant. It is believed that no effect on the growth rate was observed because the thermal-cycling did not induce any surface damage. The growth phase of the allotropic transformation is known to occur first on the surface (Di Maio & Hunt, 2009b), especially in the presence of surface defects and damage produced by plastic deformation.

In conclusion, the thermal-cycling experiment described here did not initiate any earlier the transformation in pure Sn. A caveat to this is that no surface damage was observed in the samples after thermal cycling. Future experiments should target cases in which surface damage is produced by thermal-cycling.

3 EFFECT OF CUBIC ICE AS A NUCLEATION AGENT (PACKAGE 3)

3.1 INTRODUCTION

The nucleation stage of the β/α allotropic transformation of Sn can be greatly accelerated by introducing into the Sn matrix a seed with the same crystal structure and similar lattice parameter as α Sn. This reduces the energy required for the transformation and facilitates the neighbouring atoms to move to the thermodynamically preferred configuration. Elements that were shown to have these effects include: α -Sn (self-inoculation), InSb, CdTe, SnO and metastable cubic ice. The first four types are not normally found on a printed circuit board in service. Cubic ice, however, could naturally form from small droplets of water in the atmosphere (Murray, Knopf, & Bertram, 2005). This form of ice could potentially be the initiation point for the allotropic transformation, in particular if in contact with pure Sn finished components. It was shown in previous studies (Di Maio & Hunt, 2009b) that the transformation could progress from pure tin to an alloy if they are in intimate contact and there is not an interfacial zone separating them.

The aim of this study is to determine if cubic ice can act as seed and propagate the transformation first to pure tin and then to a tin alloy. This emulates the situation of a component with tin finish and soldered with a lead free alloy, where the tin finish near to the component body has not reached a sufficient temperature to reflow.

3.2 EXPERIMENTAL PROCEDURE

Three tin hybrid samples were prepared in similar way as described in (Di Maio & Hunt, 2009b). These were made partly of pure Sn and partly of a Sn3.5Cu alloy. In this case, a CdTe seed was not introduced in to the sample, but the sample and seed were placed in same container but without direct contact. Electrical connections were attached on the alloy side of the samples as shown in Figure 7.

The pure Sn side of the hybrid sample was facing the CdTe seed. These were put at a distance of 1 mm apart. The container was filled with deionised water and placed in a freezer at -40°C and monitored electrically. The same procedure was repeated with three un-seeded samples.

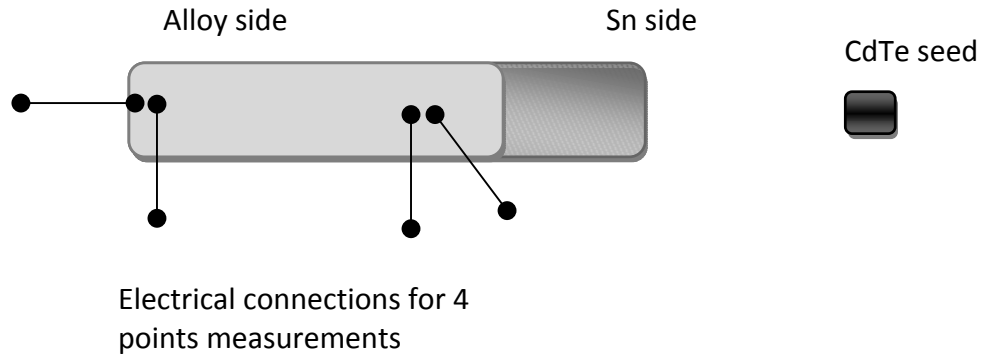


Figure 7: Experimental setup for package 3.

3.3 EXPERIMENTAL RESULTS

Resistance changes for the three un-seeded and the three “seeded” samples are shown in Figure 8. “Seeded” here means that the sample is 1 mm away from a CdTe crystal, and the two are separated by water (ice). The three “seeded” samples transform earlier than the un-seeded samples. Some scatter is observed in the test results. In all samples the transformation had reached the SnCu side and transformed the whole sample.

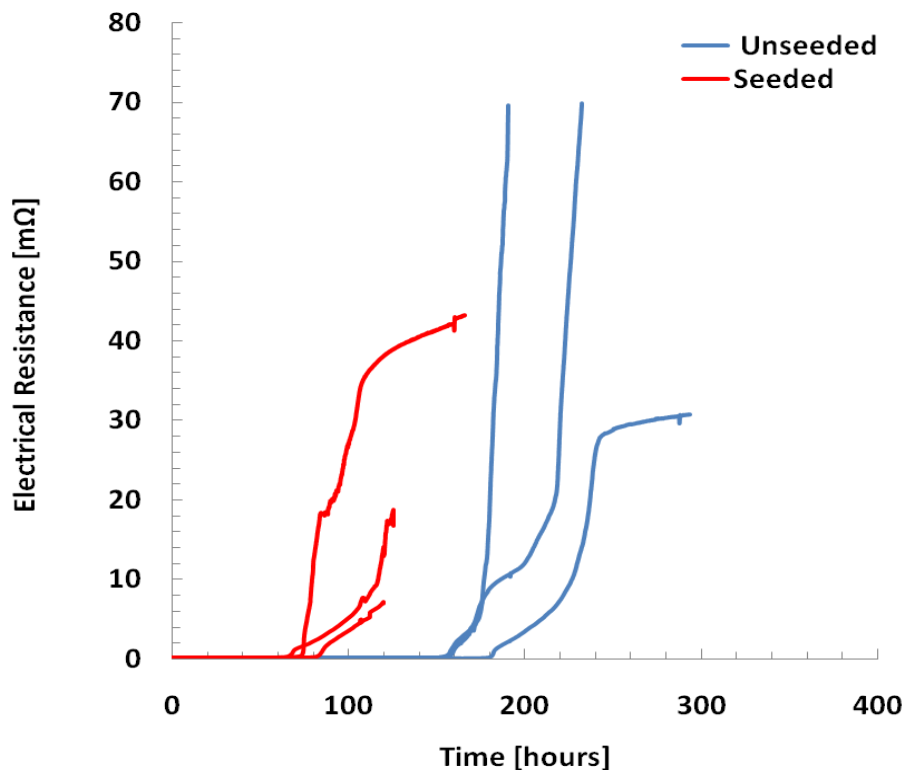


Figure 8: Electrical resistance change during the experiment of package 3 (for graphical clarity not all curves are shown to completion).

3.4 DISCUSSION

The fact that the “seeded” samples transform earlier than the unseeded samples, shows that the seed is effective in accelerating the transformation, even though it is separated from the sample. The ice forming between the surfaces of Sn and the CdTe seed is likely to grow with the diamond cubic crystal structure, due to the presence of the CdTe seed, transferring the lattice information from the seed to the tin. The cubic ice itself then can act as seed for the tin, which starts transforming faster. It is surprising however, to see that the samples that were not seeded, transform relatively quickly. It is expected that a pure tin sample would start transforming several weeks in air, whilst here it takes about 1 week only. The general effect of ice on the transformation remains unclear and requires further investigation. It is possible that sufficient cubic ice forms naturally to promote the seeding action on the tin.

4 STUDY ON NUCLEATION TIME AND TRANSFORMATION SPEED OF COMMERCIAL ALLOYS (PACKAGE 4)

4.1 INTRODUCTION

The β/α allotropic transformation of Sn has been observed in Sn-alloys and a previous study (Di Maio & Hunt, 2009b) has confirmed that the transformation can occur even in SnPb and SnBi alloys (containing at least 0.4% of the alloying element). Not all alloys, however, present the same growth rate. Elements such as Pb, Bi and Sb tend to suppress the β/α transition (Plumbridge 2008). The Sn solder alloys commercially available have different compositions, and therefore their propensity to the β/α growth will be different.

The aim of this study is investigating the nucleation time and growth rate of available commercial Sn alloys.

4.2 EXPERIMENTAL PROCEDURE

Three alloys were chosen for this study, the Sn / 0.5-0.7 Cu / < 0.1 Ni (Sn100C), the Sn / 3.0 Ag / 0.5 Cu (SAC305) and the Sn 0.3 Ag 0.7 Cu 0.1 Bi (SACX). Three samples were prepared for each alloy. The alloys and the pure Sn were cut in small pieces, each weighing 1 g. Each sample was prepared by joining a piece of alloy on either side of a piece of pure Sn to form a small bar as described in (Di Maio & Hunt, 2009b). The resultant sample was approximately 3 cm long with a 1 cm central portion of pure Sn. The joining procedure was achieved by melting the interface with a torch and pushing the pieces together (see Figure 9). This created a composition gradient that extended 2.5mm either side of the original interface (from EDX measurements).

During the joining operation, the central Sn part of the sample was seeded with CdTe. The extremities of all samples were connected to a 4 point probe measurement system so that the electrical resistance could be monitored during the transformation. The samples were then placed in a freezer at -40°C . The electrical resistance of the samples was recorded every 2 minutes. All samples were left in the freezer for a period of 4 months.

4.3 EXPERIMENTAL RESULTS

The allotropic transformation starts in the proximity of the seed, in the pure tin centre of the sample and then spreads towards the alloy at either end of the sample. The initial transformation point of the alloy was taken to be 7.5 mm from the centre of the sample. Table 2 shows transformation distance for each of the alloys from the centre of the sample, the % increase of electrical resistance during the test, and the time required for a 15% resistance increase, which in ³ was defined as the incubation time. Optical images of the transformed samples are shown in Figure 10 (3 for each condition).

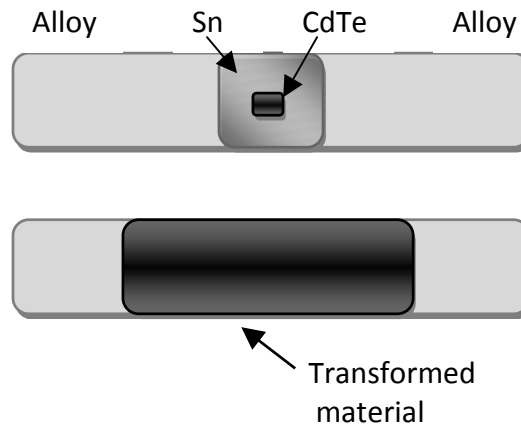


Figure 9: Sample configuration before and after the test

Table 2: Transformation progress in the commercial alloys at the end of the test. The distance is measured from the centre of the sample. The composition gradient Sn/Alloy terminates after $\approx 7.5\text{mm}$.

	Extension from the centre of the sample of $\alpha\text{-Sn}$ [mm]	% Electrical Resistance Increase at the end of the test	Incubation time [hours]
Sn100C	9.0 ± 0.8	$52\% \pm 15$	1350 ± 200
SAC305	10.8 ± 1.6	$170\% \pm 50$	313 ± 20
SACX	3.3 ± 1.6	$24\% \pm 10$	3000 ± 800

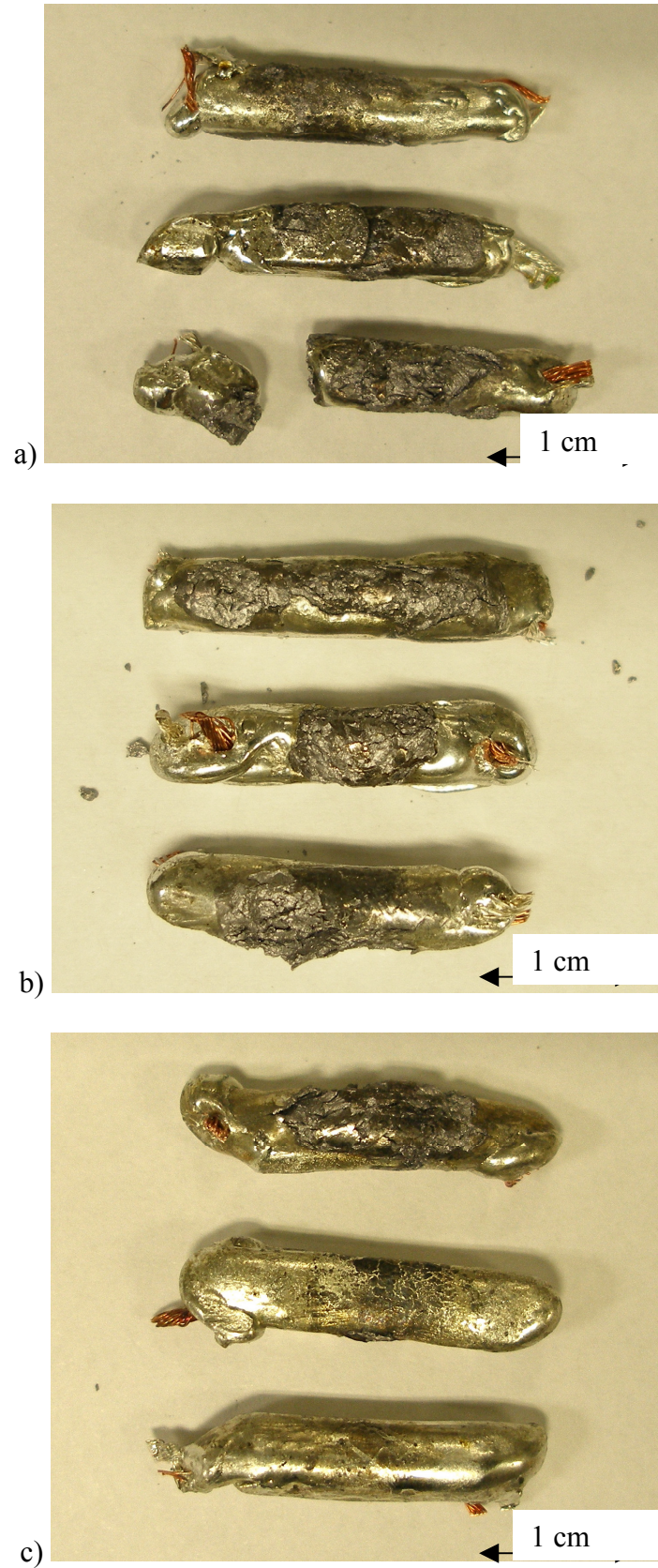


**Figure 10: Optical image of the samples made of commercial solder:
a) Sn100C; b) SAC305; c) SACX**

4.4 DISCUSSION

Results in Table 2 show that all the three commercial alloys have a very slow transformation compared to the binary alloys studied in (Di Maio & Hunt, 2009a). Only the alloy SAC305 reached the 400% increase in electrical resistance taken as a reference point for the “propensity to transformation” and only in one of the repeats. This result demonstrates that minor alloying elements and a number of impurities slow down considerably the transformation. The phase disruption at the Sn grain boundaries caused by the secondary phases in the alloy represent an obstacle to the rearrangement of the atoms in the α crystal structure. Amongst the commercial alloys tested here, SAC305 was shown to have the shortest incubation time and the highest amount of material transformed at the end of the experiment.

In (Di Maio & Hunt, 2009b) it was shown that the binary alloys SnAg and SnCu are amongst those that more readily transform, however their combination in a ternary alloy clearly slows the transformation down considerably.

The most resilient to the transformation was found to be the SACX alloy. The Bi contained in the alloy has caused this, reflecting the well-known effect of stopping the allotropic transformation (Bornemann, 1956).

5 CONCLUSIONS

Experiments looking at different factors affecting the growth phase of the β/α allotropic transformation were carried out. In particular, the effect of temperature changes, of thermal stresses, cubic ice as nucleation agent and of multi-component alloying elements were studied. The main findings of this research are summarised below:

- In the presence of a seed, the time to transformation is not reset if the sample is taken temporarily to room temperature, even if there is no evident initial sign of transformation.
- Thermal stresses that do not produce surface damage, do not accelerate the growth of the α phase.
- Ice has an accelerating effect on the growth of the α phase. If ice grows in its diamond cubic structure, it can induce the transformation in pure Sn. Potentially this can then propagate in an alloy such as the case of a tin coated termination soldered with a lead-free alloy.
- The α phase growth in multi-component alloys is slower than in binary alloys. It is likely that this is due to the disruption formed by the secondary phase at the Sn grain boundary. Alloys containing small amounts of Bi (such as the SACX alloy) are the most resistant to transformation growth.

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