Tin Allotropic Transformation ~ Tin Pest

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Abstract
It is known that pure tin will undergo an allotropic transformation below 13°C where it becomes a semiconductor with a 26% [1,2] volume increase, and in appearance turns from a bright shiny metallic material, white β tin, to a dark blue/grey dust, α tin. Such a transformation for an electrical interconnect is disastrous, if it were to occur in any of the high tin lead-free alloys it would be a catastrophe. The elimination of lead, one of the best elements to arrest the transformation process, has resulted in a number of high tin content alloys about which the potential to transform is unknown. Environmental factors that may enhance or arrest the rate and the incubation period of the transformation processes are also unknown.

Due to the optimal transformation temperature of approximately –35°C and the long time required for the transformation, a direct observation of the phenomenon has not been possible. This study proposes a new method for observing the β/α transformation *in situ* using a time-lapse photographic technique. This study concentrates on pure tin, but the applicability of the method opens new possibilities for studying the phenomenon for other tin alloys, such as the two commonly encountered eutectics of SnCu and SnAgCu. The transformation progressed radially from the inoculation point, starting at the surface. Propagation into the bulk occurred by peeling; with the external layers tending to "roll out" due to the volume expansion of the internal layers. In the meantime, cracks parallel to the propagation direction formed. Typically a pure tin sample would completely transform in just over 24 hours.

Introduction
If pure β-Sn is kept at temperatures below 13°C for a sufficient amount of time it could potentially undergo an allotropic transformation and become α-Sn. The two phases are very different; β-Sn is a ductile metal, whilst α-Sn is a brittle semiconductor. β-Sn has a tetragonal crystal structure; α-Sn has a diamond cubic crystal structure. Most of all α-Sn has a volume of approximately 26% higher than β-Sn [1]. This normally has a catastrophic effect on the transformed material, which tends to crack and fall apart due to the volume expansion.

Whilst this could potentially be devastating if it happened on an electronic assembly in service, studies have shown so far that it can happen on pure tin, and in rare occasions on alloys, such as Sn-0.5Cu [3]. There is a possible risk that this phenomenon could occur in current electronic assemblies since all the SnPb replacement alloys have a high tin content, such as the SAC (Sn-Ag-Cu) alloy family. For this reasons more studies are required to make sure that these alloys are really risk-free so that they can reliably be used in low-temperature applications.

The transformation is normally quite slow, and could require months or even years before showing the first signs of occurrence. However, it is possible to "artificially" accelerate this phase by introducing a seed in contact with the tin. This is a material with a similar crystal structure and lattice parameter to that of α-Sn [4].

So far it has been possible to observe the transformation only by removing the sample from the freezer and hence altering its progress. This research aims to find a method for obtaining a sequence of images of the "tin pest" transformation in order to clarify what happens to the material during this transformation.

Experimental Procedure
Equipment
The equipment used to produce time-lapse photography of tin pest consisted of: a vacuum chamber with a transparent top, a liquid cooling system, a microscope and an imaging system. The vacuum chamber was used in order to avoid ice formation on the tin samples. The model used for this study was produced by Island Scientific^{TM} and consisted of a steel cylindrical container with a toughened glass top, as shown in Figure 1. An external pump was connected to the chamber system to achieve a vacuum level of 1 bar.

In order to reach the low temperatures required for the allotropic transformation, a peltier element was used (SuperCool^{TM} PE-127-20-15). This device had 62 *mm* sides and a thickness of 4.6 *mm*. By setting suitable values of voltage and current, the peltier element can achieve a high level of cooling on the top side, provided that the heat produced at the bottom side can be removed promptly. For this reason, the peltier was placed on a fully enclosed aluminum tank, connected in series with a liquid cooling system. A water and glycol mixture was pumped into the aluminum tank from a reservoir were it was stored and kept at a temperature of approximately –5°C. This temperature was obtained by using a Haake DC30 chiller. A thermocouple was placed on the peltier surface in order to obtain real-time temperature measurements.

A thermistor (an NTC 2 kΩ at 25°C), part of a power divider circuit, was also placed on the surface of the peltier. The electrical resistance of this component was related to the temperature value by using a calibration curve. This was calculated using the thermocouple described before. These temperature readings were transmitted to a PC using a data logger PICO ACD-11. They were stored by a Visual Basic software package and used to control the power supply connected to the peltier element in order to set the desired temperature.

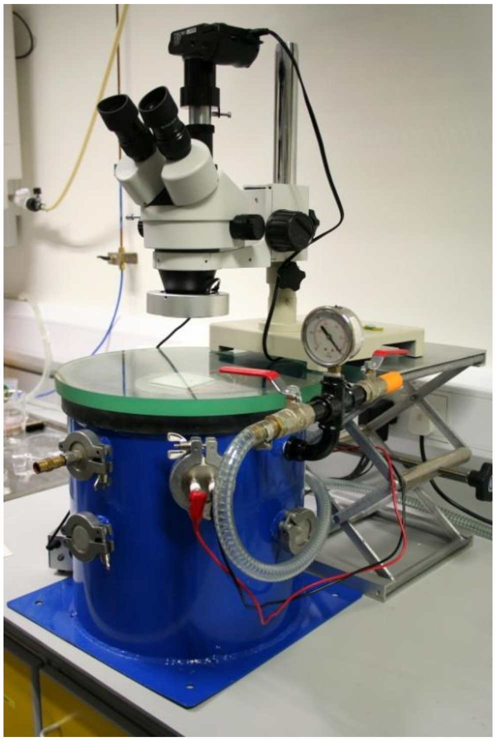

Figure 1. Vacuum chamber used for the time-lapse photography experiment.

A digital camera (Olympus SP-350), attached to an optical stereo microscope (Brunel Microscope IMXTZ) was used to take the time-lapse photos. The sample was illuminated by an LED ring attached to the microscope objective. The camera was controlled by the software InPhoto Capture (www.akond.net), which could take photos at pre-defined time intervals and transfer them directly to the computer's hard disk. The same images were also used with the imaging system LaVision Davis Strainmaster System to study the movement of the surface more accurately.

Materials and Samples

The β-Sn/α-Sn allotropic transformation was studied on very pure tin (99.99% Sn). As reported by Williams [4], the incubation time for this allotropic transformation can be greatly reduced by introducing in the tin a material with the same crystal structure of α-Sn. The samples were prepared by melting a small amount of tin in a mould (50 *mm* long, 2 *mm* thick and 2 *mm* wide). On some parts of the surface 3-5 grams of CdTe powder were placed, and the area was brought briefly to melting temperature, to facilitate the "molecular contact" of the inoculator to the tin [5]. Afterwards the sample surface was manually polished with SiC paper until the surface was reasonably flat for optical microscopy observation.

Experimental Procedure

The tin samples prepared with the above procedure were placed on top of the peltier, in the vacuum chamber. Plasticine was used attach the sample to the surface. When the cooling liquid reached –5°C the software activated the power supply controlling the peltier. The set temperature for the peltier element was –35°C . At the same time the time-lapse photography software was started. The time interval between each photo was set to two minutes. At the end of the transformation the photos were edited by adding a scale bar and joined together to produce a motion video.

Experimental results

Each of the tested samples completed the transformation in less than 48 hours. Several samples were tested, in order to observe the transformation at different magnification. Two samples were inoculated in several areas on the surface; two samples were inoculated only at one extremity.

Some of the frames obtained from 3 different samples are shown in Figure 2: a and b. The arrow in the first frame depicts where the seed was placed. It can be observed that the transformation starts from the region where the inoculator was placed and then propagates in the surrounding areas. Frames 2 and 3 of Figure 2b show that the expansion is radial from the starting point. The average speed at which the interface moves was measured from the sequence of images and was found to be 9 ± 1 $\mu m/mm$ and 5 ± 0.8 $\mu m/min$ for the two samples shown in Figure 2.

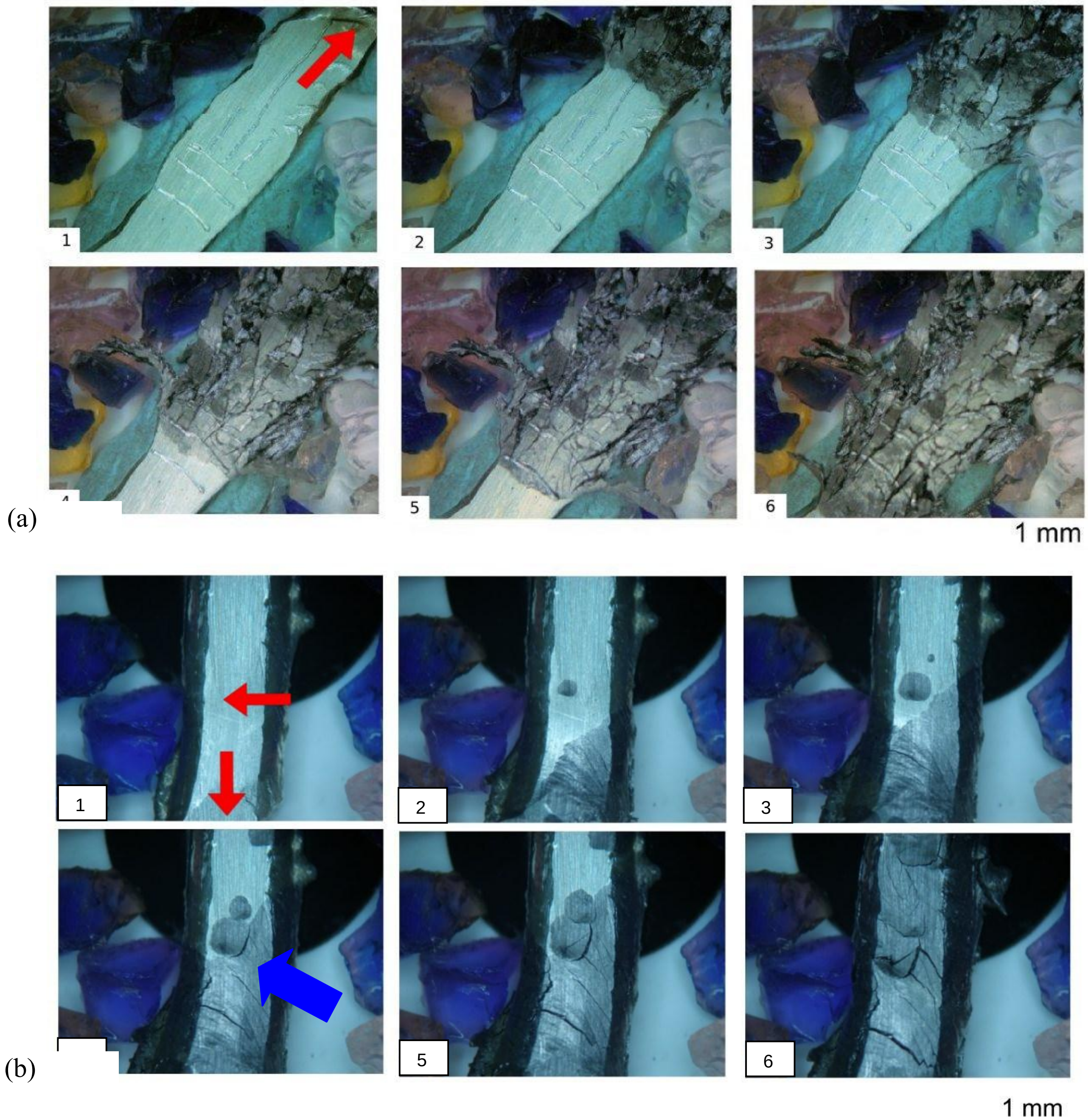

Figure 2. Time lapse shots of tin transformation.
(a) Tin sample with seed on one extremity. (b) Tin sample with multiple seeding.

It was also possible to observe that the transformation rate was not constant in the whole sample, as it can be inferred from Figure 3.

The volume growth associated with the transformation can also be easily observed from the same images. The percent increase in area from frame 1 in Figure 2c to frame 6 was calculated to be around 18±1% which is compatible with the theoretical volume increase of α-Sn of 26%. In fact if a unite cube increases uniformly its volume by 26%, its area should increase by 17%.

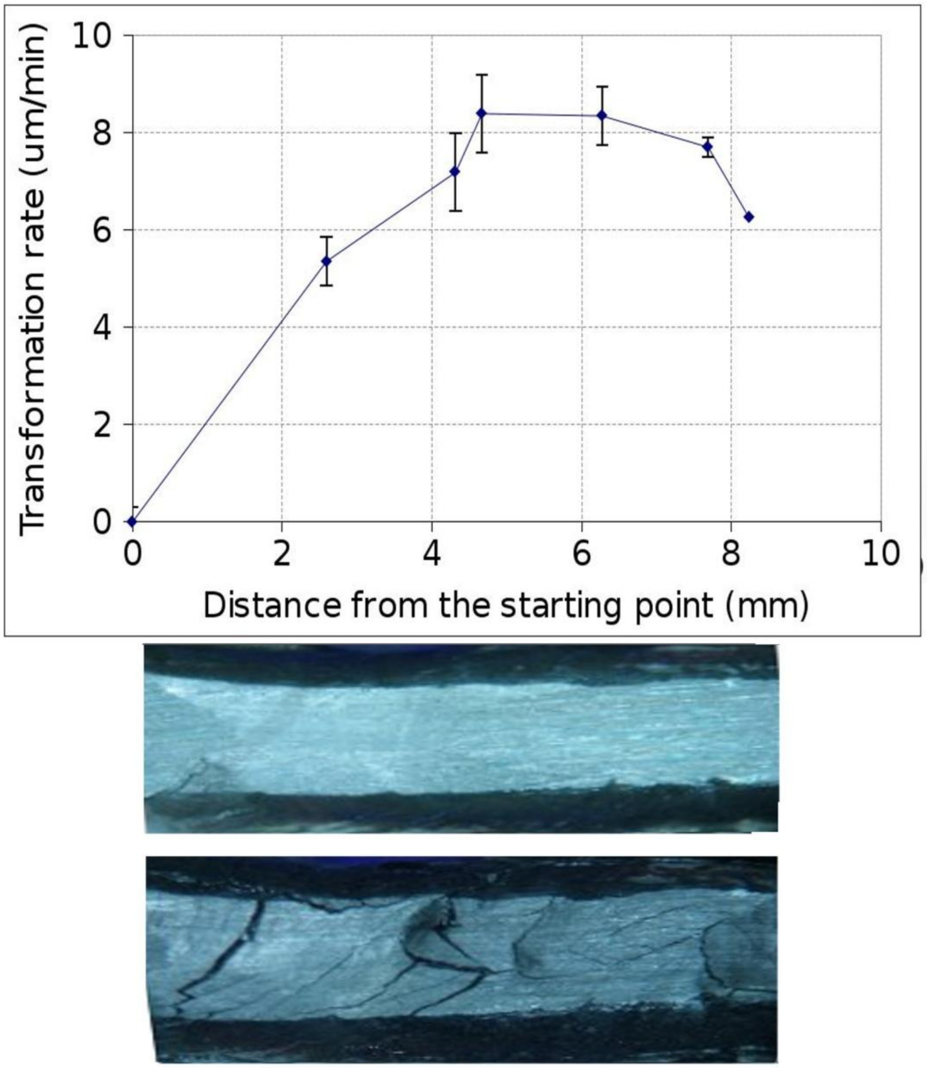

**Figure 3. Variation of the transformation rate on the sample surface in µm/min.
The corresponding sample at the beginning and at the end of the transformation is shown.**

It was also observed that cracks form on the surface, and they tend to be perpendicular to the direction of the moving interface (or parallel to the propagation direction), as shown in Figure 2.

Discussion

The formation of α-Sn requires an incubation time [6], defined as the time before the transformation commences. This incubation time ceases when the nucleation of the first few atomic layers of the new phase. The long incubation (compared to the transformation rate) is probably due to the time required for few a β-Sn atoms to "align" to the inoculator crystal. Despite this is a thermodynamically favorable (lower energy) state, the low temperature reduces the kinetics of the transformation. This incubation time is a function of the temperature in two concurrent ways. Firstly a lower temperature increases the driving force of the transformation, while at the same time however, the low temperature decreases the probability that the atoms will transform to the α lattice [7]. The length of the incubation time depends on which of these two factors prevails. Once the first energy barrier is overcome and the first α-Sn is nucleated, the transformation proceeds faster, as the neighboring atoms have the same orientation of the tin that has already transformed.

The higher magnification test showed that the propagation seems to follow scratches on the surface parallel to the propagation direction. The initially transformed material on the surface creates a compressive stress at the internal α/β interface, as shown in Figure 4. This stress will produce cracks between the two phases, parallel to the propagation direction of the transformed material. These newly created free surfaces are now available for further transformation (see Figure 4). A similar transformation mechanism was reported also by Plumbridge [3].

The peeled surfaces will tend to "roll" out of the surface, due to the expansion of the next inner layer of α tin that is still attached to the sample and has started to transform (see Figure 4). At the same time, the volume expansion will tend to create cracks that are parallel to the propagation direction. These type of cracks were also described in [8,9]. Similar images from a SEM of a partially transformed sample can be seen in Figure 5. Here, multiple layers of transformed material can be observed, consistent with the proposed model of propagation of the transformation.

Cracks can also appear when two isolated areas that are transforming interfere with each other. At the boundary the mismatch in the transformed α-tin will lead to a crack. This can be seen in Figure 2(c) frames 3 and 4 (blue arrow).

Figure 4. Peeling process

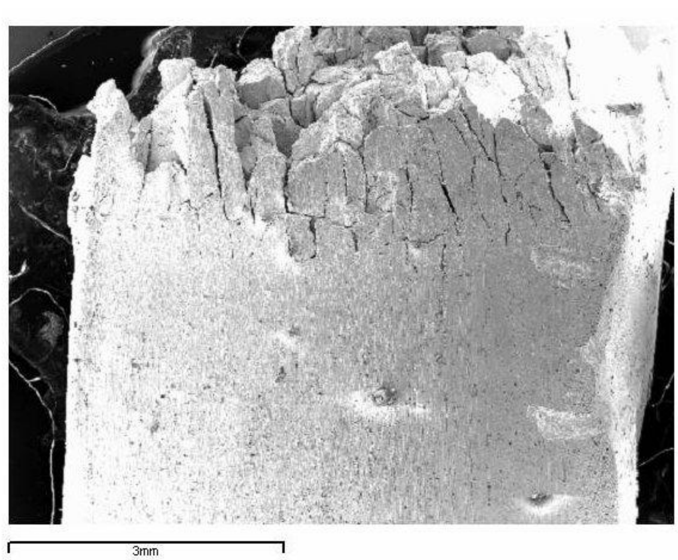

Figure 5. SEM Image

Conclusions

This research has established a method for observing *in situ* the allotropic transformation from β-Sn to α-Sn. A model for the macroscopic transformation of tin has been suggested, based on these observations. It is deduced that the transformation starts on the surface and gradually proceeds in the bulk by small layers of materials transforming sequentially. This creates the disintegration of the upper layer material, which peels away. Two types of cracks are formed. One type is parallel to the propagation direction. These cracks are formed by the stress generated between transformed and untransformed regions. Another type of crack is perpendicular to the propagation direction. These are formed when two transforming regions meet.

The time-lapse photography method developed here was used to study the case of β to α transformation, but with only small changes could be used for studying the reverse transformation. Other future research fields where this method could be applied include the effect of temperature variations on the transformation rate and the study of the transformation in alloys, in particular lead-free alloys that are of interest to the electronics industry.

Acknowledgments
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References
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Time-Lapse Photography of the β-Sn/α-Sn Allotropic Transformation

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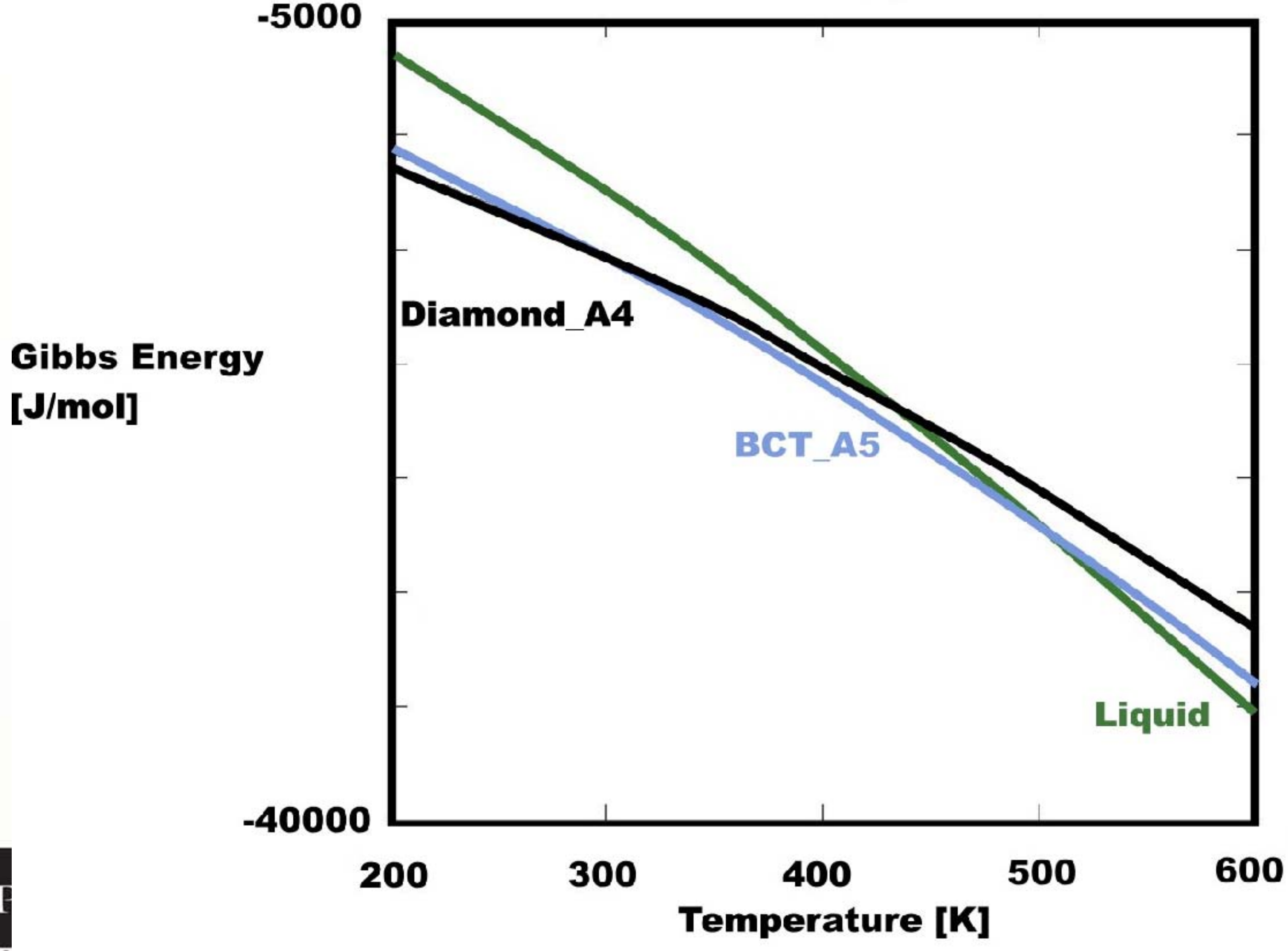
Summary

- Introduction: the Tin Phase Diagram
- The Potential Problem of ”Tin Pest” in a LF Electronics World
- Ways for Inducing the Transformation
- Experimental Procedure
- Experimental Results: Time Lapse Photography of the transformation
- Discussion
- Present and Future Work

Introduction: the Tin Phase Diagram



β-Sn/α-Sn Comparison

- *β-Sn (white tin)*
  - Metal
  - Ductile
  - Tetragonal crystal
  - Shiny

- *α-Sn (grey tin)*
- *"Tin Pest"*
  - Semiconductor
  - Brittle
  - Diamond cubic cell
  - Dull grey
  - Volume 27% higher than β-Sn

The Potential Problem of ”Tin Pest” in a LF Electronics World

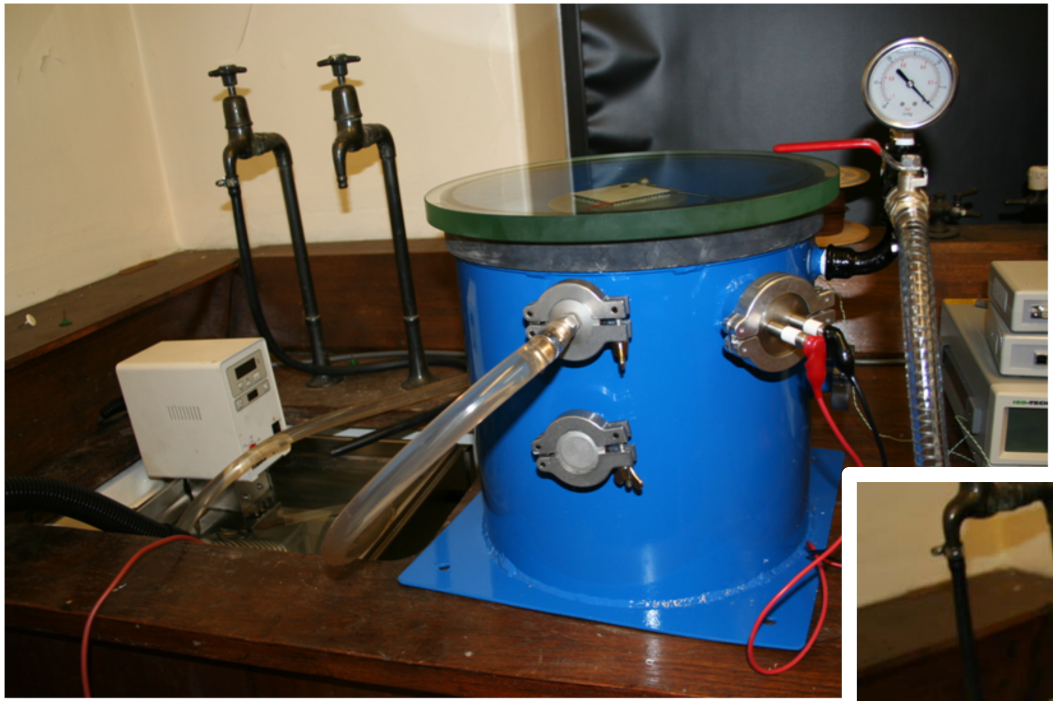
LEAD-FREE ALLOYS ?

Ways for ”Inducing” the Transformation

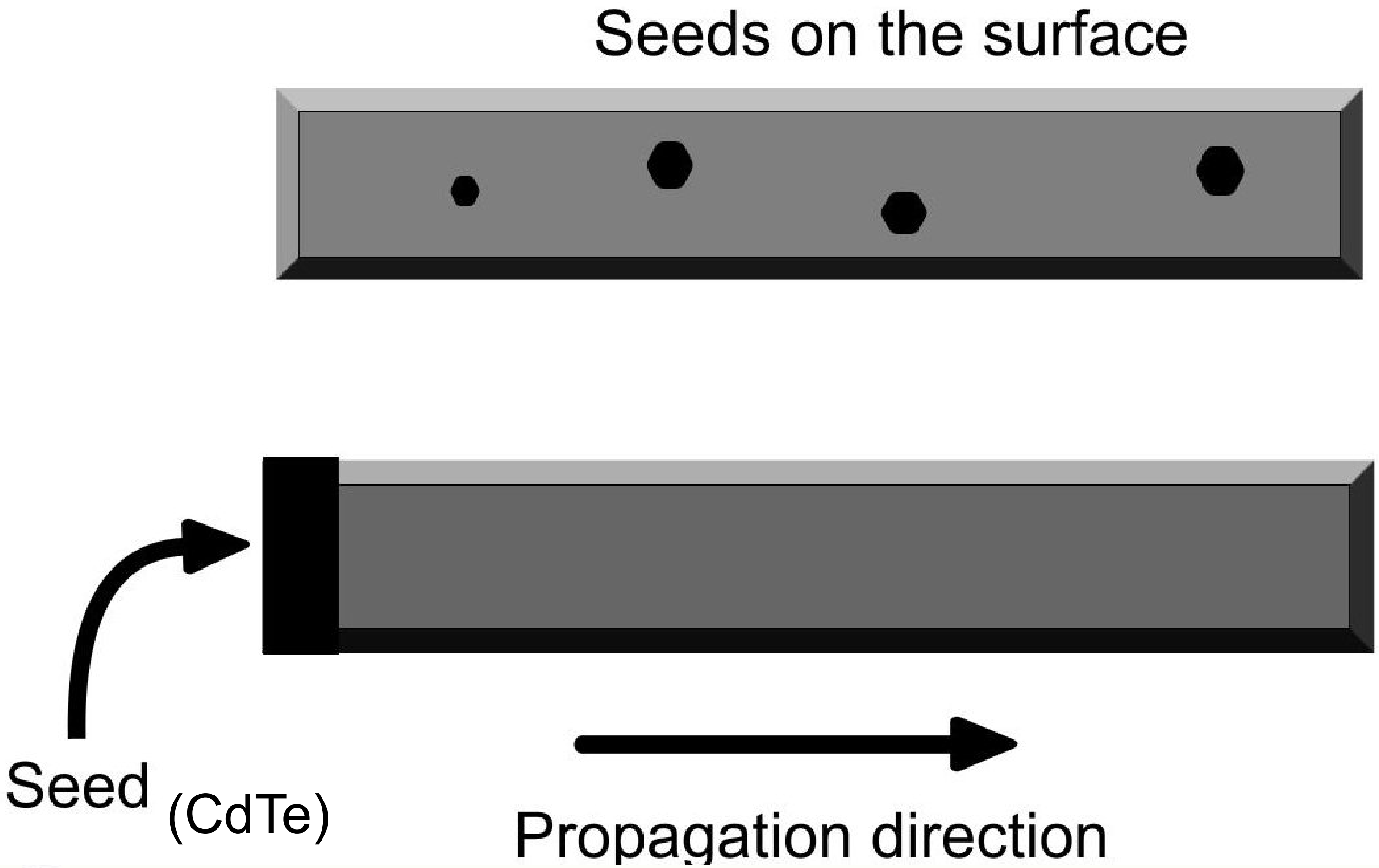
- Pressed-in seeds (”molecular” contact)
- Seeds without molecular contact
- Infection from SnO

Substance	System	Lattice Parameter
α – Sn	Diamond	a=6.489
Si	Diamond	a=5.43
Ge	Diamond	a=5.65
InSb	Diamond	a=6.489
CdTe	Diamond	a=6.41
Metastable Ice	Diamond	a=6.36
Hg	Rhombohedral	a=3.005
SnO	Tetragonal	a=3.80,c=4.84

Experimental set-up



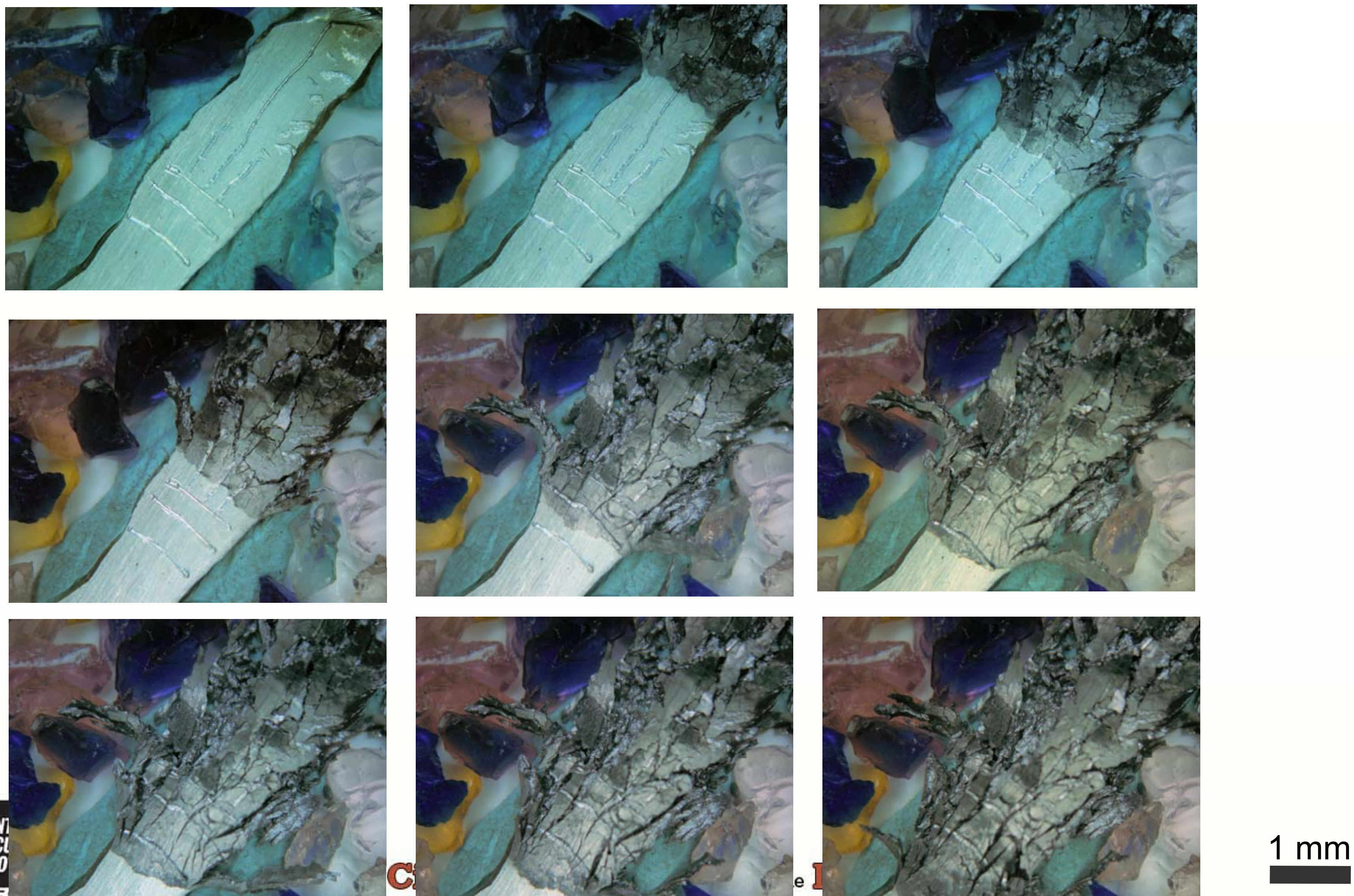
Sample Geometry



Experimental Conditions

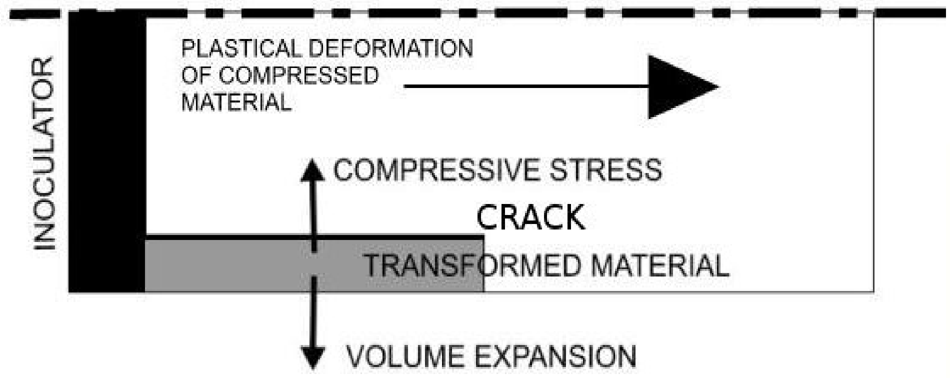
- Material: ”Pure” (4N) Sn, inoculated with CdTe
- Temperature: -32 ° C
- Time: 35h
- A photo was taken every 2 minutes
- Silica gel was used to absorb residual humidity in the chamber

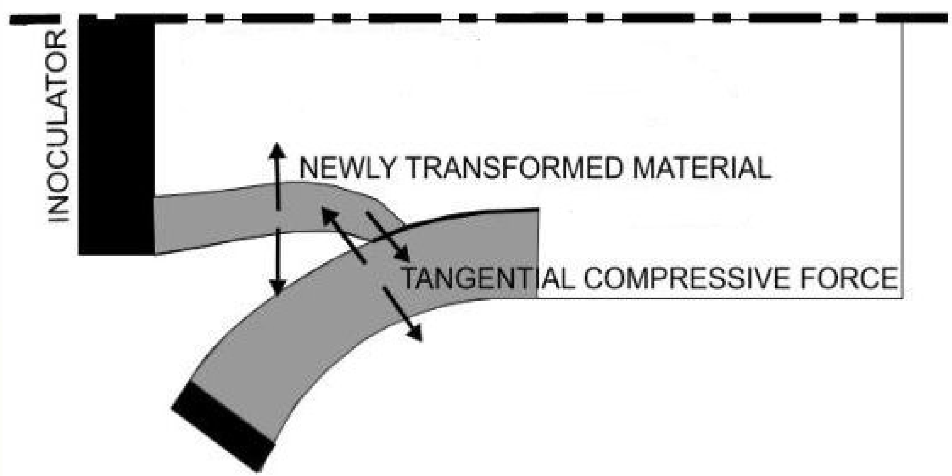
Experimental Results



Discussion

- The incubation time (15-20h)
- The transformation mechanism
- The cracks geometry
- The transformation speed (0.15μm/s)





Present and Future Work

- Monitoring the transformation by measuring the change in electrical resistance
- Transformation in Sn binary alloys: Sn-Ag, Sn-Cu, Sn-Bi, Sn-Ni, Sn-Zn, Sn-In, Sn-Pb
- Transformation in commercial SAC(305), Sn100C alloys
- Temperature history, cycling
- Transformation on solder joints