

Tin Allotropic Transformation ~ Tin Pest

Chris Hunt, Ph.D.

National Physical Laboratory Division of Engineering and Process Control

+44 208 943 7027

+44 208 614 0428

chris.hunt@npl.co.uk

EXECUTIVE SUMMARY

It is known that pure tin will undergo an allotropic transformation below 13°C where it becomes a semiconductor with a 26% 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.

An analysis based on the lattice parameter of α tin to find similar materials was substantiated and was used to select inoculators to minimize the incubation period. Following which a number of experiments were conducted using CdTe. To further the study the transformation process was videoed using time lapse photography with the sample held at -35°C in vacuum system. The transformation progressed radically 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 sample would completely transform in just over 24 hours.

Further work is now looking at the effect of cubic ice, temperature on the transformation and the effect of alloying additions in influencing the transformation process.

The roll of this particular lattice form of ice is a worrying aspect, since it can commonly occur under the relevant temperatures. Experiments have shown that ice can act as the inoculators, seeding the transformation, particularly when other inoculators are in the vicinity.

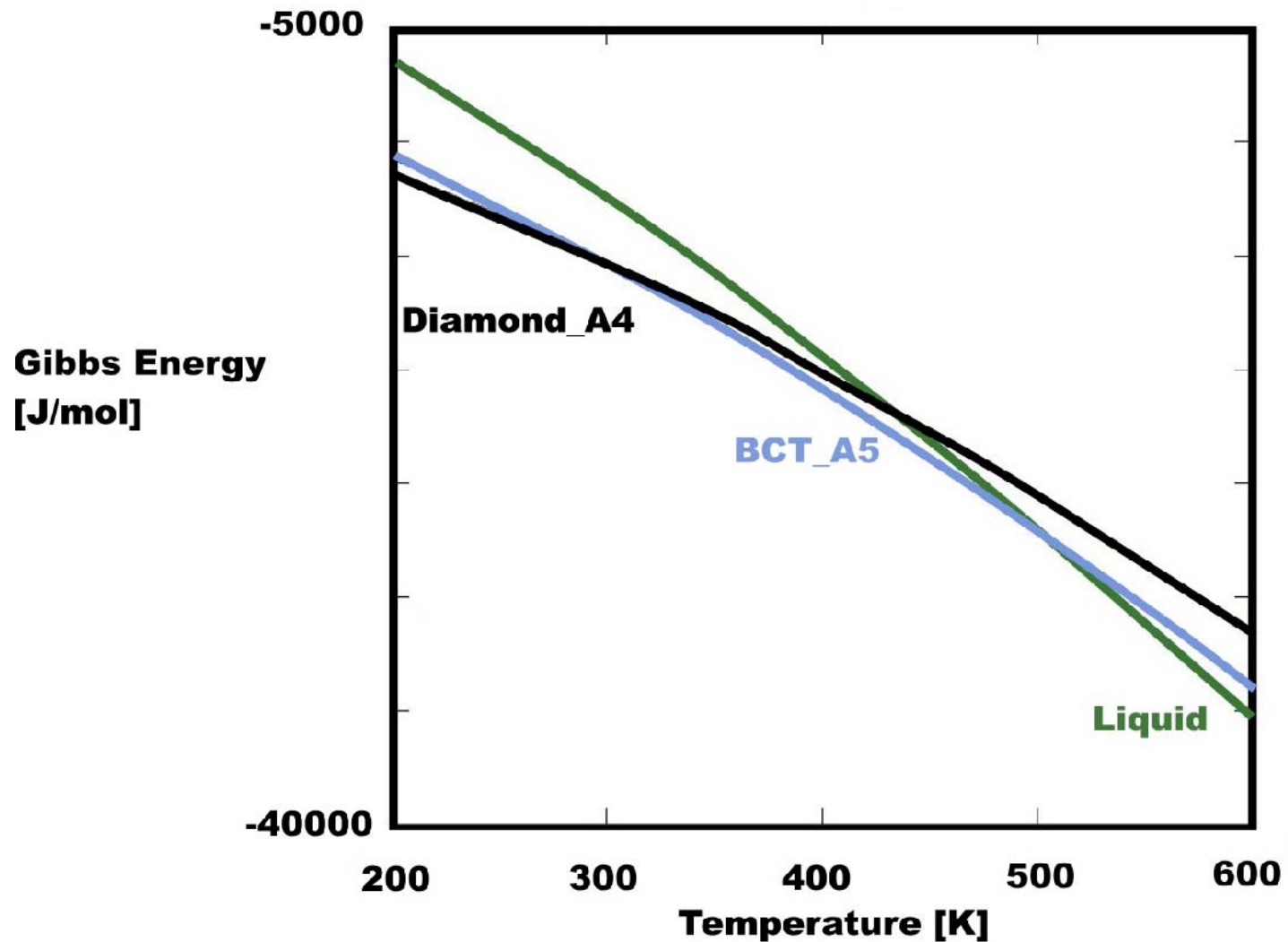
Time-Lapse Photography of the β -Sn/ α -Sn Allotropic Transformation

Chris Hunt and Davide Di Maio
National Physical Laboratory

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

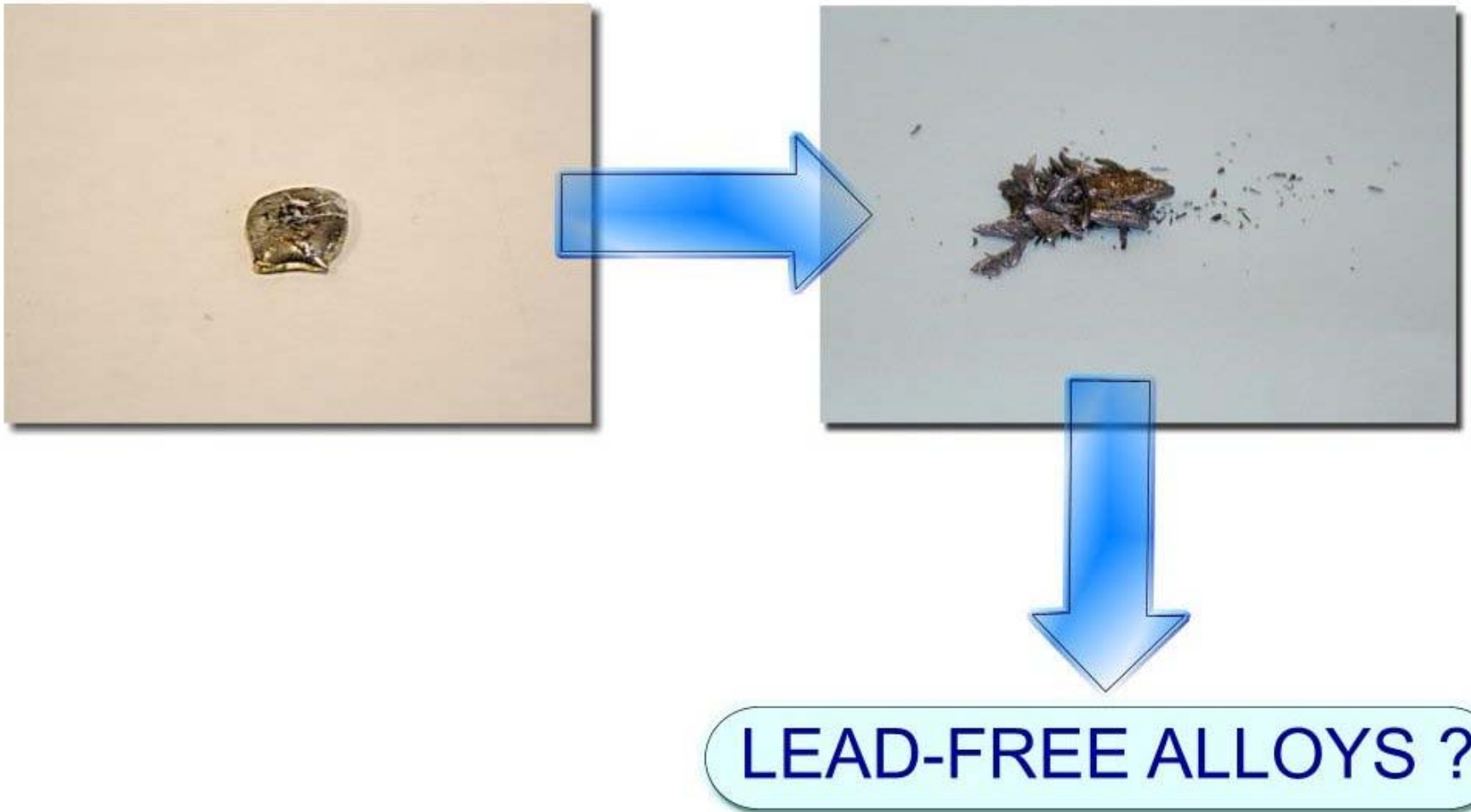
Introduction: the Tin Phase Diagram



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

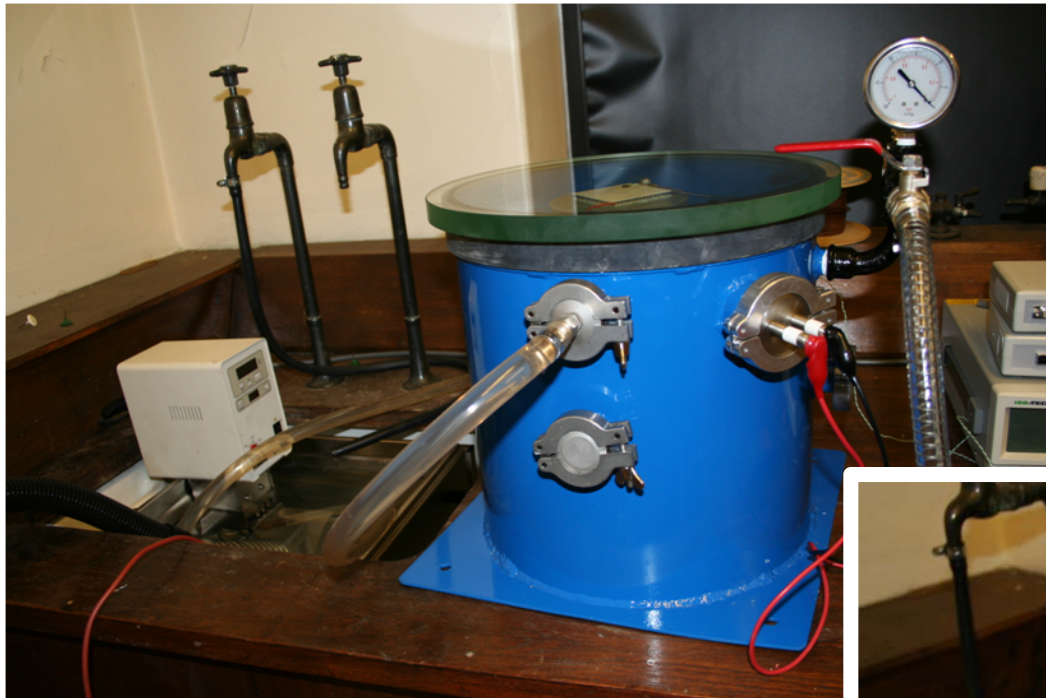


Ways for "Inducing" the Transformation

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

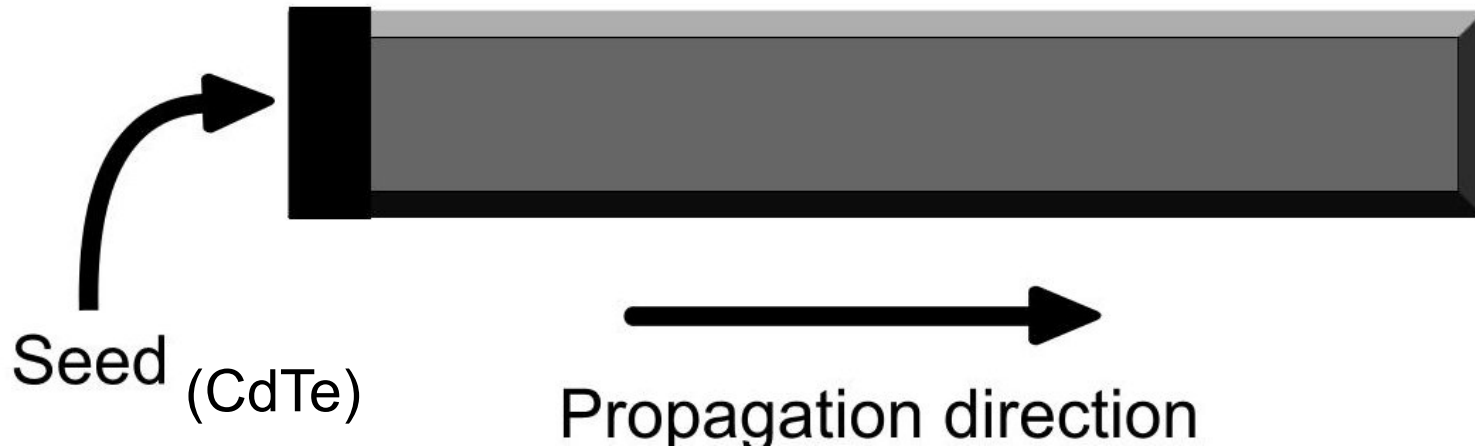
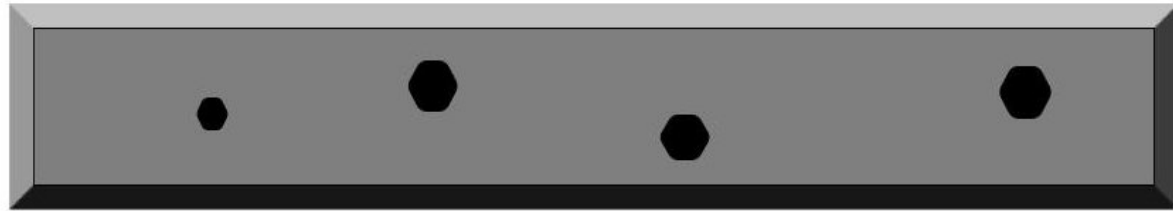
Substance	System	Lattice Parameter
α - Sn	Diamond	a=6.489
Si	Diamond	a=5.43
Ge	Diamond	a=5.65
InSb	Diamond	a=6.489
CdTe	Diamond	a=6.41
Metastable Ice	Diamond	a=6.36
Hg	Rhombohedral	a=3.005
SnO	Tetragonal	a=3.80,c=4.84

Experimental set-up



Sample Geometry

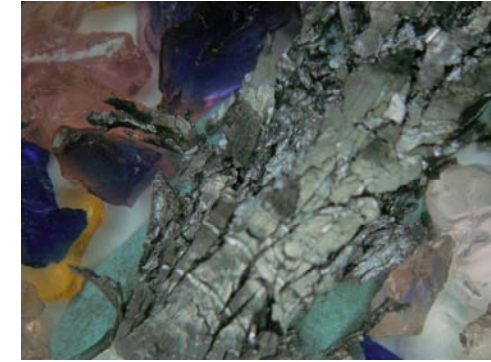
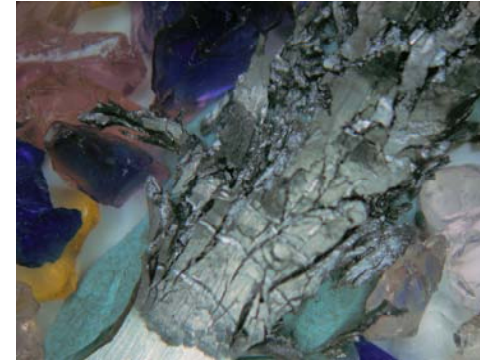
Seeds on the surface



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

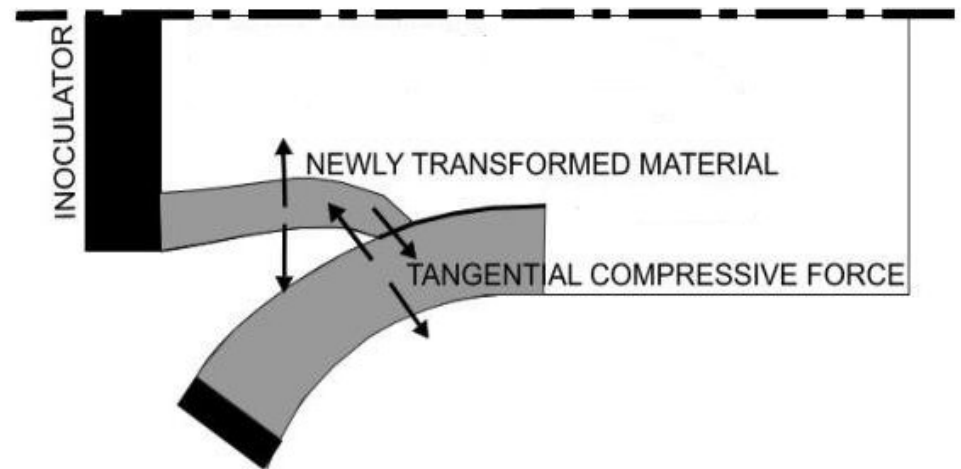
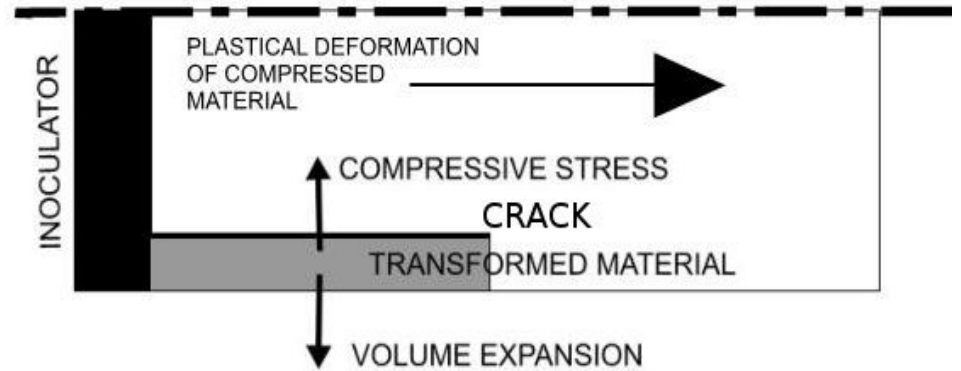
Experimental Results



1 mm

Discussion

- The incubation time (15-20h)
- The transformation mechanism
- The cracks geometry
- The transformation speed ($0.15\mu\text{m/s}$)



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