

**LOW TEMPERATURE INVESTIGATIONS OF PHASE TRANSFORMATION IN PURE TIN**

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**Abstract**

The better understanding of mechanism of phase transformation of white tin to grey tin will help to protect the historical tin artifacts. The goal of this study is to explain some of the low temperature phenomena by isothermal measurement of phase transformation in the range 180 – 300 K by X-ray powder diffraction (XRD) and Mössbauer spectroscopy. The phase analysis was focused on the transition of the  $\beta$ -tin (bct) phase to the  $\alpha$ -tin (fcc) phase. Avrami equation was applied to the data for the time dependences of this transition for the constant temperatures, and its parameters were used for the Arrhenius plot. Results derived from data from Mössbauer spectroscopy show a maximum transformation rate at ~200 K. Similarly, XRD data shows the maximum at ~210 K. The difference can be ascribed to changes in the cooling conditions in cryostats in the Mössbauer spectrometer and XRD equipment.

**Keywords:** Tin, grey tin, XRD, Mössbauer spectroscopy, phase transformation

**1. INTRODUCTION**

The phase transformation of white tin to grey tin is a well known phenomenon in the fields of materials science and solid-state physics. Although it is mentioned from medieval times the mechanism was not explained sufficiently yet. The better understanding of this phenomenon is going to have an essential impact to protect historical and cultural heritage and economic impact.

When white tin, also known as  $\beta$ -tin, is cooled below 13.2 °C [1], it undergoes a phase transformation to grey tin, also known as  $\alpha$ -tin. This information is common knowledge and as such is not cross-referenced to the source. The other information about the maximal rate of phase transformation and healing process of tin are incorrect.

The  $\alpha$ - $\beta$  transition in tin is explained [2] as the simplest and prototypical case of an entropy-driven structural transformation which is determined by the harmonic vibrational properties of the two phases of the material. The body-centered cubic phase of metals at high temperature and the description of martensitic transformations in transition-metal alloys [3].

The key features of the allotropic transition in Sn are examined [4], and the processes of  $\alpha$ -tin nucleation are identified. It is shown that  $\alpha$ -tin nuclei may only form on substances close in chemical bonding and lattice parameter to  $\alpha$ -tin. Such substances, stable or metastable, grow epitaxially on similar structures in amounts undetectable analytically but sufficient for initiating the phase transition of Sn.

The organ pipe material from Sn with a very small amount of Cu was observed in study [5]. After 2.5 h of exposure to -50 °C, first traces of phase transformation were observed in the form of cracks in the  $\alpha$ -Sn inoculated

part of the sample. After 5 h exposure to -50 °C, increased number of cracks was observed in different direction. It seems that the phase transformation is not orientation dependent.

## 2. EXPERIMENTAL

### 2.1 Material

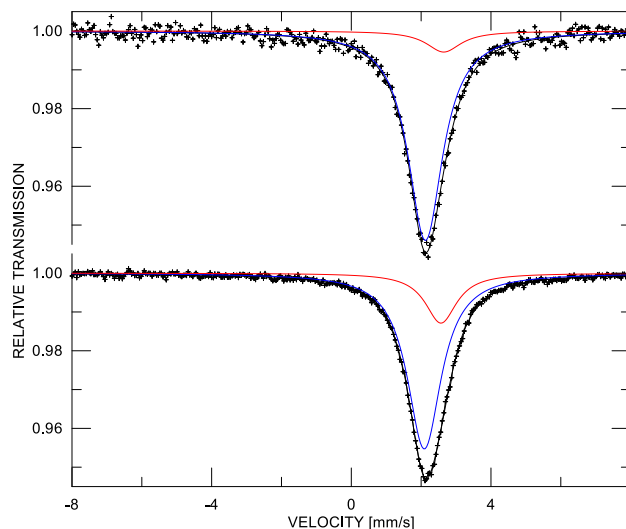
The pure beta-tin thin sheet (5N, AlfaAesar) was infected by pressing alpha-tin particle, it was measured at first. Further it was left to transform in a common kitchen freezer into alpha-tin at 256 K for about 14 days. After that was annealed at 60 °C for about 3 days and transformed back to the beta-tin. This process was repeated three times. The phase composition due the all steps of the cycles was verified by XRD at RT.

### 2.2 Methodology

<sup>119</sup>Sn Mössbauer spectra of the powder sample were measured using <sup>119m</sup>Sn in CaSnO<sub>4</sub> matrix source in standard transmission geometry in temperature range 5 – 350 K in closed cycle He cryostat. The velocity scale of the spectrometer was calibrated using measurement of  $\alpha$ -Fe at room temperature with <sup>57</sup>Co in Rh source. The fitted position of the single line of the BaSnO<sub>4</sub> measured at room temperature 293 K was  $0.099 \pm 0.006$  mm. The computer processing of the spectra was carried out by CONFIT program package [6]. The fitted function yielded intensities *I* of the components (atomic fraction of Fe atoms), their hyperfine inductions *B*<sub>hf</sub>, isomer shifts *IS*, quadrupole splittings  $\Delta E_Q$ , and quadrupole shifts  $\epsilon_Q$ .

All the spectra are reported according to alpha Fe calibration. The spectrum of the beta Sn was fitted by single line with isomer shift  $2.646 \pm 0.005$  mm/s and the spectrum of the alpha Sn sample after 30 days measurement at 293 K was fitted by single line with isomer shift  $2.079 \pm 0.031$  mm/s (both relative to the velocity scale calibrated against alpha Fe). The alpha Sn powder was encapsulated in an aluminum foil to get good temperature contact in cryostat.

The content of beta Sn phase slowly increased during the measurement at 293 K. Comparison of the spectra after 3 days and 30 days measurements is shown in **Figure 1**.



**Figure 1** Spectra of the originally alpha Sn sample after 3 days (above) and 30 days measurement at 293 K (below). The blue line represents the alpha phase component, the red line beta phase component. The crosses correspond to the measured points.

The original alpha-tin sample was measured at room temperature heated up to 320 K in cryostat where alpha to beta phase transition occurred and sample with beta phase was obtained for the starting point. Subsequently

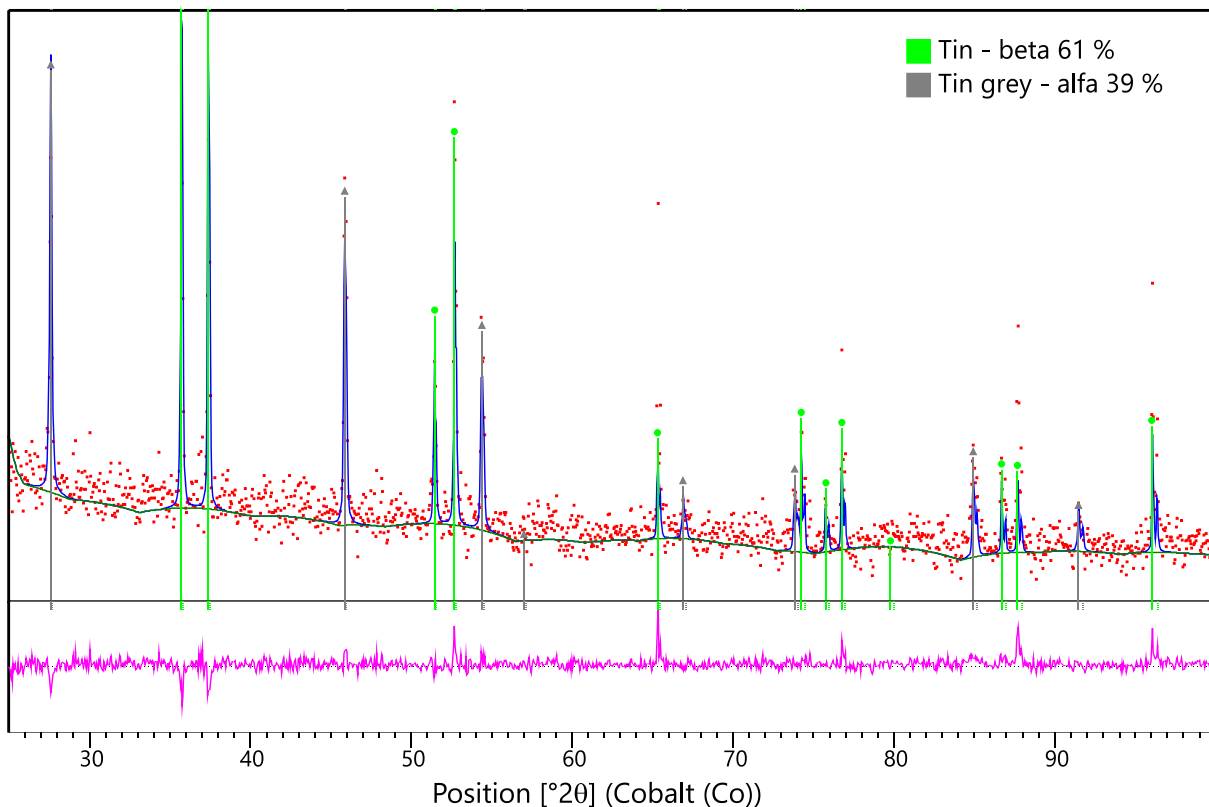
the sample was fast cooled down to the requested temperature, where the beta to alpha time dependent transition was followed.

Two methods were applied by Mössbauer spectra analysis as function of time. The first approach was based on analysis of partial spectra in which alpha and beta phases were analyzed. The partial spectra were yielded by subtraction of the spectrum after time interval usually 1 day.

In the second methods the isomer shifts of the sum spectrum of the overlapped single lines, formed by singlet of both alpha and beta phases were calculated.

The X-ray powder diffractometer (XRD) was used to determine the phase composition of every sample at RT and in situ at low temperatures measurements. The automatic diffractometer Empyrean Pananalytical (Nederland) with  $\text{CoK}\alpha_{1,2}$  radiation was equipped by Oxford Instruments PheniX closed cycle He cryostat (United Kingdom). The qualitative analysis of data was performed by HighScore 4+ (Pananalytical) program using ICSD Database FIZ Karlsruhe (PAN ICSD, Germany). The quantity analyses were computed by the same program using Rietveld model with external Si standard and based on the same databases model and BGMN [7].

The beta-tin powder was inserted into the cryostat in a diffractometer and the chamber was evacuated and cooled to the designed temperature. The cooling rate was chosen in agreement with the same experiment performed during the MS measurements to 6 K/min. Contrary to MS analyses the measured steps provided by XRD were very quick. Each loop takes only 10 min and is measured in the range  $25\text{-}100^\circ$  (Cobalt) which contains at least 7 significant peaks from each phase - see **Figure 2**. Final comparison of both methods showed very similar results. With decreasing activity of the source during long time measurements the second one was more effective due to lower pulse statistic in the spectra.



**Figure 2** Example of XRD sheet obtain during LT measurement. The gray line represented the  $\alpha$ -tin, the green  $\beta$ -tin, red dots measured data, blue line computed results and the pink line difference plot.

### 3. RESULTS

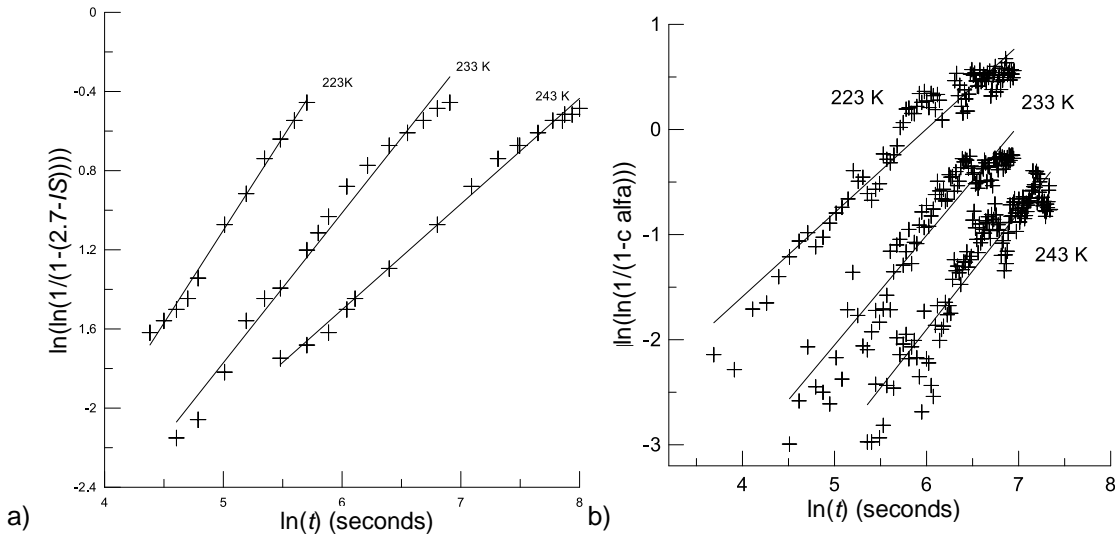
According to the Kolmogorov-Johnson-Mehl-Avrami equation [8], the transformation kinetics under isothermal heating can be described by

$$f = 1 - e^{-(kt)^n} \quad (1)$$

where:

- $f$  represents the volume fraction of the transformed phase,
- $k$  is the kinetic rate constant,
- $n$  is the Avrami exponent.

This Avrami exponent depends on the crystal growth morphology where  $1 \leq n \leq 2$  for one dimensional growth,  $2 \leq n \leq 3$  for two dimensional growth, and  $3 \leq n \leq 4$  for three dimensional growth. We have used  $IS$  as the measure of the transformed phase see in the **Figure 3**.



**Figure 3** Avrami dependences for denotes temperatures obtain from a) Mössbauer spectra and b) XRD. The crosses denote experimental points and the lines the fitted linear functions.

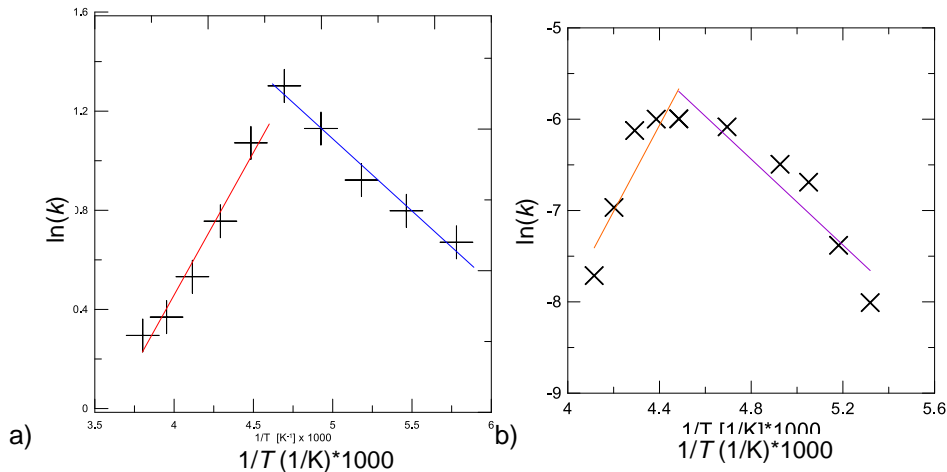
According to Arrhenius relation [9] the activation energy is related to rate constant by:

$$k = Ae^{-(Ea/RT)} \quad (2)$$

where:

- $R$  is the gas constant,
- $Ea$  is the activation energy of the transition,
- $A$  is constant called the pre-exponential factor or, more commonly, the frequency factor.

Using the data from the Avrami calculations Arrhenius plot can be drawn in **Figure 4**. From that the critical temperature  $T_0$  [10] can be estimated from Mössbauer spectra to  $218 \pm 3$  K. The fitted linear functions are  $\ln(k) = 1150.007*(1/T) - 4.142$  for high temperature part above  $T_0$  and  $\ln(k) = -582.742*(1/T) + 4.002$  for the temperatures below  $T_0$ . This corresponds to  $Ea/R = -1150.007$  K and  $Ea = -9561.0$  J/mol for  $T > T_0$ , and  $Ea/R = 582.742$  K and  $Ea = 4844.9$  J/mol for  $T < T_0$ . From the XRD experiments the critical temperature was estimated to  $223 \pm 3$  K. The fitted linear functions are  $\ln(k) = 1270.73*(1/T) - 26.816$  for the temperatures higher than  $T_0$ , and  $\ln(k) = -459.84*(1/T) - 4.84$  in temperatures lower than  $T_0$ . This match to  $Ea/R = -1270.73$  K and  $Ea = -10565$  J/mol for  $T > T_0$ , and  $Ea/R = 459.8$  K and  $Ea = 3823$  J/mol for  $T < T_0$ .



**Figure 3** Arrhenius plot derivate from Avrami dependence from a) Mössbauer spectra and b) XRD.

#### 4. DISCUSSION

Transitions between different phases of the same compound can be characterized by the temperature  $T_0$ , at which two phases can coexist in equilibrium [10].

The solid-solid transitions of the first order occur by the nucleation mechanism. It implies that the process rate increases with the supercooling on cooling as well as with the superheating on heating. This means that the transition rate is zero at  $T_0$ , but increases as temperature deviates from  $T_0$ . Because of the phenomena of supercooling and superheating, there is a significant gap between the temperatures, at which the transition on heating and on cooling becomes detectable. This makes it rather difficult to pinpoint the exact position of  $T_0$  [10].

Fitting the temperature dependence of this process rate to the Arrhenius equation yields positive activation energy for the temperatures above  $T_0$ , and, on the other hand, below  $T_0$  due to its negative temperature dependence fitting the rate of this process to the Arrhenius equation yields negative activation energy.

The same approach can be applied to the transition between two different mechanisms during the temperature dependence of the transition. Above  $T_0$  nucleation of the  $\alpha$ -tin is dominating process but with decreasing temperature effect of structure defects prevails in a further growth of  $\alpha$ -tin content.

#### 5. CONCLUSION

The paper presents the different temperature of maximal rate of phase transformation  $T_0$  between  $\alpha$ -tin and  $\beta$ -tin from the common knowledge which is confirmed by two independent methods.

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