KINETICS OF THE TIN PHASE TRANSFORMATION

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Abstract

The most common allotropic modification of tin is white tin (β tin), which is thermodynamically stable from 13.2 to 232 °C. The allotropic modification of the grey tin (α tin) is thermodynamically stable below 13.2 °C. When pure white tin is structurally transformed to pure grey tin, it results in the total disintegration of pure tin objects and pure tin solders. We investigated the relationship between the temperature and the kinetics of both the phase transformation of β→α tin and the reverse transformation α→β tin. To accelerate the rate of the phase transformation of β→α tin, the particles of the pure α tin were used. The samples were stored at -60 °C, -40 °C and -20 °C. Particles of the pure α tin were stored at +60 °C, +40 °C and +20 °C to study the kinetics of the reverse transformation of α→β tin. The rates of phase transformation and reverse transformation were determined by XRD analysis using a PAN analytical X'pert Pro diffractometer and by image analysis using Image J software. Our results suggest that temperature plays the main role in both types of transformation. Interestingly, whereas the literature often suggests that the phase transformation of β→α tin occurs most quickly from -40 °C to -50 °C, we found that it was quickest at -60 °C. The rate of α→β tin reverse transformation accelerates with increasing temperature.

Keywords: grey tin, white tin, phase transformation, kinetics

1. INTRODUCTION

Today the tin represents an important material the food and telecommunication industry [1].

Two main types of degradation of tin are known:
- The atmospheric corrosion of tin (the main corrosion products are SnO and SnO_2 [2]).
- The phase transformation of tin which is connected with the low temperature.

The pure tin has two common allotropic modifications. The first one is metallic white tin (β tin) which is thermodynamically stable from 13.2 °C to the melting point with a tetragonal body centered crystal system (bct). The second allotropic modification is semiconducting grey tin (α tin) which is thermodynamically stable below 13.2 °C according to the theoretical calculation. The grey tin has a cubic diamond structure [3] and is practically observed during a long time storage of pure tin object at the temperature below 0 °C.

The phase transformation of β tin with a density of 7.29 g/cm^3 to α tin with a density 5.77 g/cm^3 is accompanied by a change of volume. The volume of cubic diamond structure of α tin increases about 27 % [3, 4] and the parameters *a*, *b*, *c* in the cubic lattice expands about 8.3 % at a same rate [4] (**Fig. 1**). The result of this phase transformation is total disintegration of pure tin objects which is well known as a tin pest.

The phase transformation β→α tin is affected by several factors:
- The rate of phase transformation β→α tin is accelerated by cold drawing and tensile stress [4, 5].
- The presence impurities such as Sb, Ag eventually Cd slow down the rate of phase transformation, while Pb and Bi (> 0.1 wt.%) completely block it up. On the other hand, Zn, Al, Ge, Cu or Mg accelerates it [6].

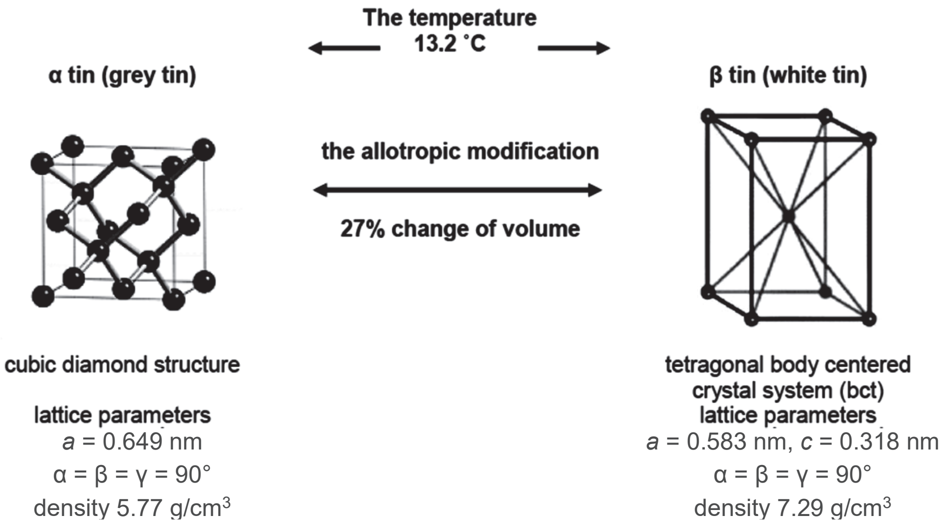


Fig. 1 The scheme of the phase transformation β→α tin

The temperature has a key role at the phase transformation of pure β→α tin. As mentioned above, the grey tin is thermodynamically stable below 13.2 °C. But the process of tin phase transformation is too slow at the temperatures higher than 0 °C. The grey tin is practically observed at the temperature below 0 °C. The literature suggests that the rate of β→α tin phase transformation reaches the maximum value between -40 and -50 °C [3, 6, 7]. On the other hand, any β→α tin phase transformation wasn´t observed at -196 °C [3]. The lower temperature reduces the mobility of tin atoms in the structural lattice and therefore the rate of β→α tin phase transformations reduces too [6].

The reverse transformation of pure α→β tin is thermodynamically stable above 13.2 °C. During the reverse transformation the semiconductor grey tin changes to metallic white tin. The mechanism of α→β tin reverse transformation shows that the process has only partially diffusional character [7]. The reverse transformed white tin is very porous and the remelted white tin alloy is cracking [8]. The presence of higher concentration of impurities such as Zn or Al could reduce the transition temperature of α→β tin reverse transformation to 10 - 11 °C [6, 8].

In the present paper, the influence of temperature on the kinetics of phase transformation and reverse transformation of tin were studied.

2. EXPERIMENTAL PROCEDURE

In this experiment, the metallic plate of high-purity β tin was used. The purity of tin plate was 99.99 wt.% and content of main impurities is shown in the **Table 1**. The thickness of the tin plate was 0.07 mm. The square samples with dimensions 20 x 20 mm were prepared.

Table 1 Chemical composition of pure tin plate

Element	content (wt.ppm)	Element	content (wt.ppm)
Sn	matrix	In	5
Sb	10	Fe	1
Bi	10	Pb	20
Cd	3	Mg	0.3
Cu	10	Ag	0.2
Ni	0.5	Tl	1

To accelerate the phase transformation of β→α tin, particles of the pure α tin were used. In the first case, the particles of α tin were sprinkled (without press) on the surface of β tin samples. In the second case, the particles of α tin were pressed by electromechanical machine LabTest 5.250SP1-VM (load 3200 N for 10 s) into the surface β tin samples. The samples were stored at -60 °C, -40 °C and -20 °C in the deeply freezing box TENAK for 70 days. The kinetics of β→α tin phase transformation was measured and determined by image analysis using Image J software. The interval between measurements was 24 hours during the first week of exposure and several days in the following weeks.

Particles of the pure α tin were stored at +60 °C, +40 °C and +20 °C in the drying oven Binder for 70 days. The kinetics of the reverse transformation of α→β tin was measured and determined by XRD diffractometer PANanalytical X´Pert PRO + High Score Plus. The interval between measurements was the same with the above mentioned.

For observation of β→α tin phase transformation the scanning electron microscope TESCAN VEGA 3 LM4 and optical microscope EMZ-13TR were used.

3. RESULTS AND DISCUSSION

3.1 Kinetics of the β→α tin phase transformation

Fig. 2 shows the experimental temperature dependencies of the phase transformation rate of β→α tin. In this case, the particles of α tin were sprinkled on the surface of the β tin samples. It is obvious that the phase transformation of β→α tin accelerates with decreasing temperature. The highest rate was observed at -60 °C. The time required for the 100 % transformation β→α tin was 7 days at -60 °C and 35 days at -40 °C. Only 15 % of β tin was transformed to α tin after 70 days of exposure at -20 °C.

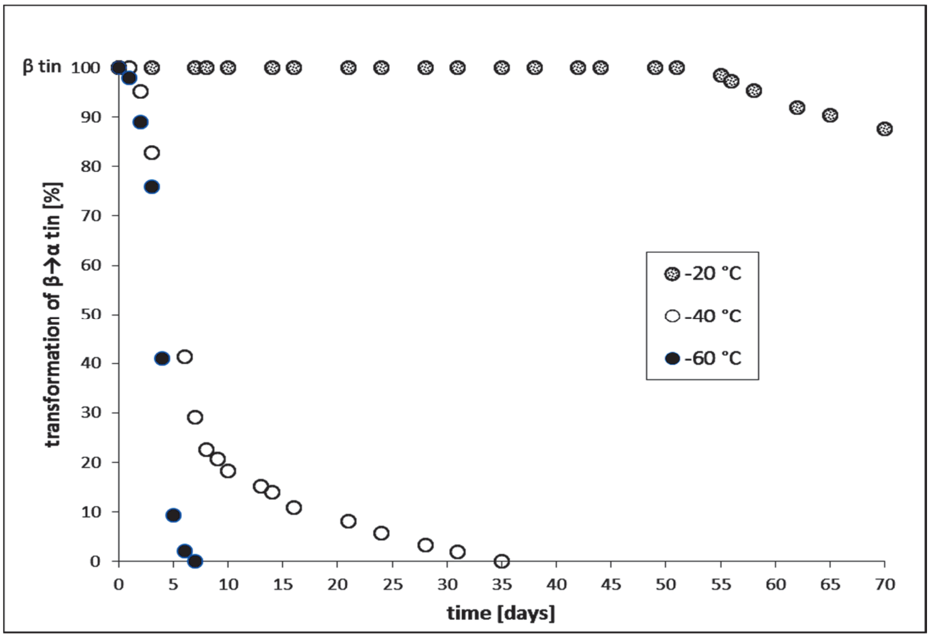


Fig. 2 Kinetics of the phase transformation β→α tin (without press)

In the second case, the particles of α tin were pressed into the surface of β tin samples. The pressed particles of α tin lead to the increase of the internal stress in the β tin matrix. The internal stress and deformation of β tin lattice significantly accelerate the rate of β→α tin phase transformation as shown in the **Fig. 3**. The highest rate was observed at -60 °C. The time required for the 100 % transformation β→α tin was 3 days at -60 °C and 15 days at -40 °C. The 96 % of β tin was transformed to α tin after 70 days of exposure at -20 °C. The internal stress and deformation of β tin lattice lead to approximately twofold increase in the rate of β→α tin phase transformation (**Fig. 2**, **Fig. 3**). **Fig. 4** shows the visual change of the tin surface during the β→α tin phase transformation at -60 °C.

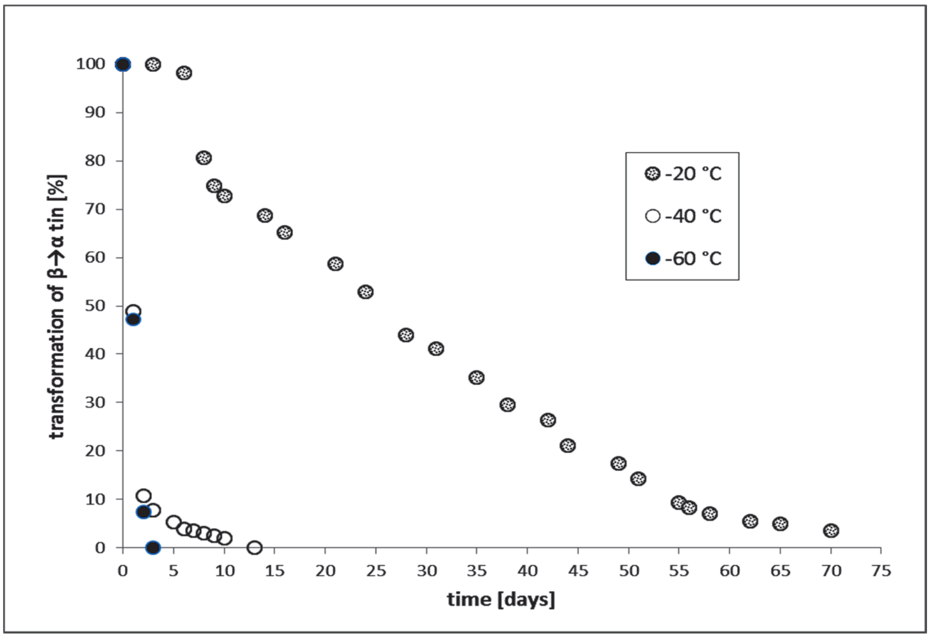


Fig. 3 Kinetics of the phase transformation β→α tin (pressed)

3.2 Kinetics of the α→β tin reverse transformation

Fig. 5 shows the experimental temperature dependencies of the reverse transformation rate of α→β tin. The reverse transformation of α→β tin is partially diffusion process and the rate of it obviously accelerates with the increasing temperature. The highest rate of α→β tin reverse transformation was observed at 60 °C. The time required for the 100 % reverse transformation of α→β tin was 3 days at 60 °C, 51 days at 40 °C and 70 days at 20 °C.

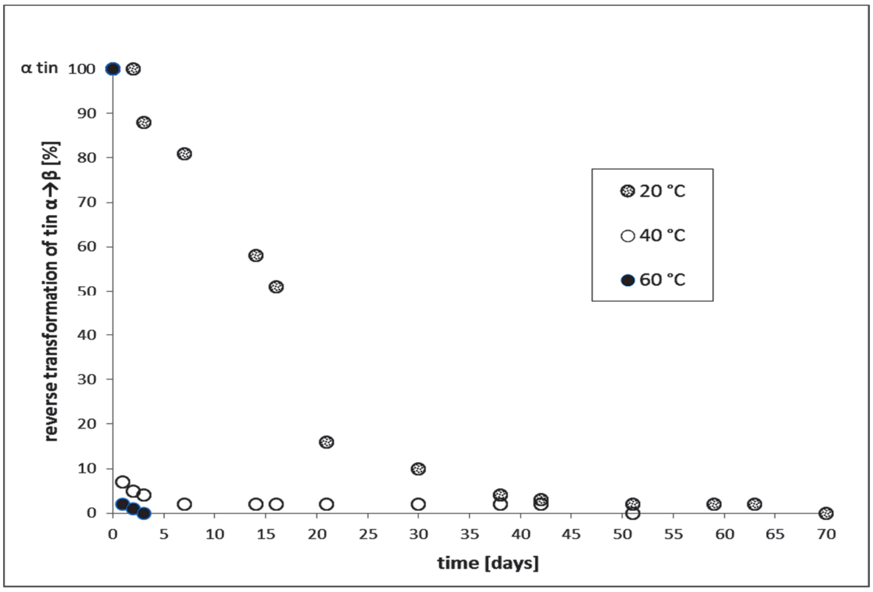
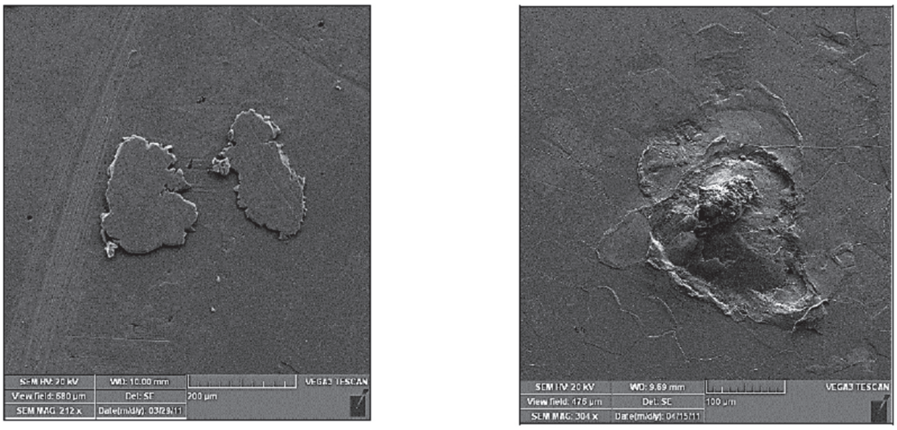
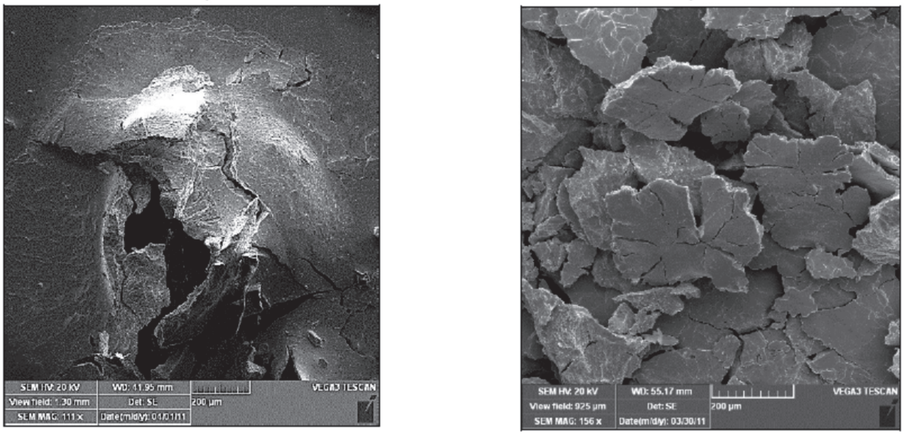


Fig. 5 Kinetics of the α→β tin reverse transformation



the pressed particles of α tin to β tin surface before exposure

the pure β → α tin structure transformation after one hour exposure at -60 °C



the pure β → α tin structure transformation after four hour exposure at -60 °C

the pure β → α tin structure transformation after 24 hour exposure at -60 °C

Fig. 4 Disintegration of tin during the phase transformation of pure β→α tin at -60 °C

CONCLUSION

On the basis of our results, the rate of β→α tin phase transformation reaches the maximum value at -60 °C. It is 10 °C less in comparing with the maximum values mentioned in the literature. The internal stress and deformation of β tin lattice produced by pressed particles of α tin accelerate the rate of β→α tin phase transformation. The rate of α→β tin reverse transformation accelerates with increasing temperature. The grey tin (α tin) can´t be possible to determine by XRD diffractometer after several months of its exposure at room temperature.

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