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The Microscopic Study of the Evolution of the Phase Transformation in the Tin after the Indentation of an Inoculator

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This paper describes β-Sn to α-Sn transformation in its initial phase. This process is also known as a tin pest and currently it causes problems mainly in the field of soldering materials. To avoid misrepresentation of the results of artificial ageing of the samples; we have decided to use historical materials for our study. A sample from historical organ pipes was indented by naturally formed α-Sn polycrystalline particles by the load of 1 kg. The sample in the initial state was observed by SEM and analysed by EBSD mapping. The position of inoculator particles was documented again by SEM observation. Subseqently, the sample was freezed at -50 °C. The evolution of cracks started after 2.5h in the vicinity of indented α-Sn particle. After 5 h of freezing, new cracks were observed also in the untouched parts of the sample. The crystallografical interconnectedness was not proven for polycrystalline samples.

Keywords: Tin Pest, Microscopy, Pictures, Inoculator

1 Introduction

The tin-based materials are often used mainly as soldering material. Nowadays, the main attention is focused to the lead-free solders from ecological reasons [1]. Materials in general are influenced by environment temperature changes. Usually, the microstructure evolutions are studied at elevated temperatures, but low temperatures can also lead to microstructural changes [2]. In case of tin, the situation is complicated by presence of low temperature allotropic modification α-Sn with the volume significantly larger than the higher-temperature β-Sn, see e.g. our recent theoretical study [3]. The phase transformation from metallic β-Sn to covalent, powder α-Sn is called the tin pest [4]. This phenomenon is usually studied on artificialy aged samples, which can misrepresent the results. This problem can be elegantly solved by analysing historical materials with the same composition as have the soldering materials. These materials can be found e.g. organ pipes.

The orientation dependence between α-Sn inoculator and transforming β-Sn matrix was already described. In the real situation, that could be described as "infection by tin pest" the α-Sn particle is not necessary monocrystalline. In the following paper, the initial phase of β-Sn to α-Sn transformation is shown attempting to be as close to the real situation as possible. The sample from historical organ pipes was indented by α-Sn particles created naturaly in the church environment.

2 Experimental

The sample taken form original organ pipe material was observed in this study. The chemical composition of the material was inhomogenous. The sample observed in this study was taken in the central part composed mainly of Sn with Cu content under the detection limit of EDS analyzer. The sample was prepared by ion polishing using Gatan PIPs system that is original dedicated for the TEM sample preparation. It explains the shape of the sample (3 mm disc) and the hole in the middle of the sample. The ion polished sample was observed by TESCAN VEGA 3 SEM equipped by EBSD analyzer by Oxford Instruments. The sample was indented using FUTURE TECH FM-700 testing machine with a 15 s dwell time and 1 kg load. Two positions were inoculated by α- Sn particle and one position was only indented by diamond.

3 Results and Discussion

The orientation mapping performed on the initial sample by EBSD technique is shown in Fig. 1. The sample quality was sufficient in places exposed to ion. The places located under the sample holder had low surface quality and did not exhibit Kikuchi patterns. This explained the unindexed places in left bottom and right top corner of Fig. 1. The grains of initial samples were uniaxial with predominantly [111] and [101] crystallographic orientations (see the blue and green colored grains in the right-side sub-figure in Fig. 1) and size of sereval tenth of micrometers. The preferential orientation of the β-Sn grains is important because the crystallographic orientation dependence of forming α-Sn to initial β-Sn was described in literature [5,6,7].

After observing of the initial sample shown in Fig. 1 and Fig 2a, the sample was indented. The positions of indents are shown in Fig 2b and labelled with red arrows. The positions "1" and "2" were inoculated by α-Sn, while position "3" was indented just by diamond indentor. After 2.5 h of exposure to -50 °C temperature, first cracks occurred, as shown in Fig. 2c and labelled with yellow arrow. When compared with the EBSD map in Fig. 1, the crack was not located in one specifically oriented grain.

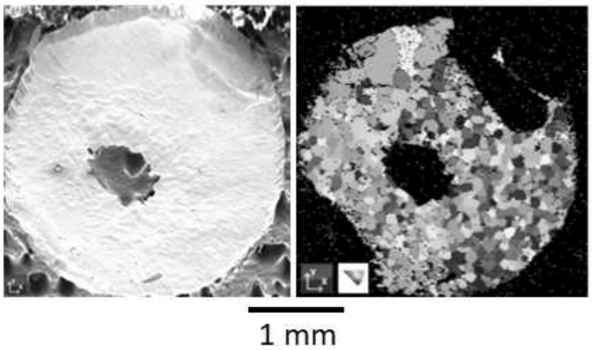

Fig. 1 *Orientation mapping of initial sample (EBSD)*

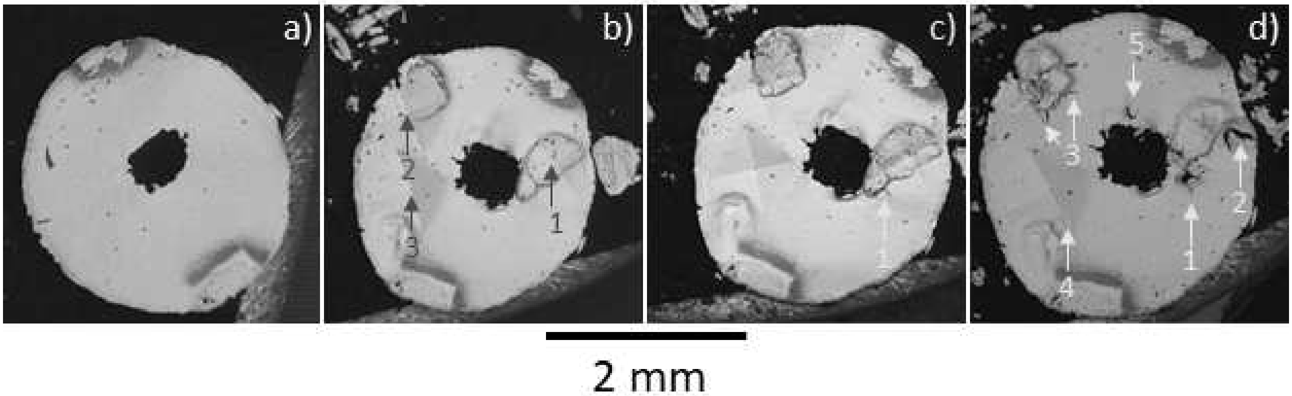

Fig. 2 *Sample stages overview – a) initial state, b) after indentation with red labelled indentations, c) sample after 2.5 h at -50 °C with yellow labelled cracks, d)) sample after 5 h at -50 °C with yellow labelled cracks*

To prove the orientation of crack, EBSD map was performed on the sample exposed to – 50 °C. Unfortunately, the indentation and crack formation led to deformation of the sample that shifted the sample out of the diffraction plane. Only extremely poor EBSD map was obtained, as illustrated in Fig. 3.

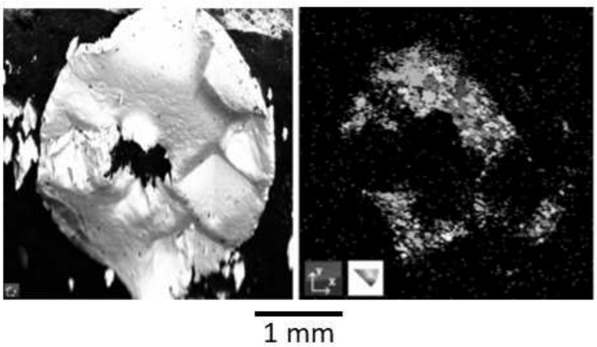

Fig. 3 *Orientation mapping of indented sample after 2.5 h at -50 °C (EBSD)*

Interestingly the main changes were observed in the morphology of the inoculator. That proved the recrystallization of deformed α-Sn particles.

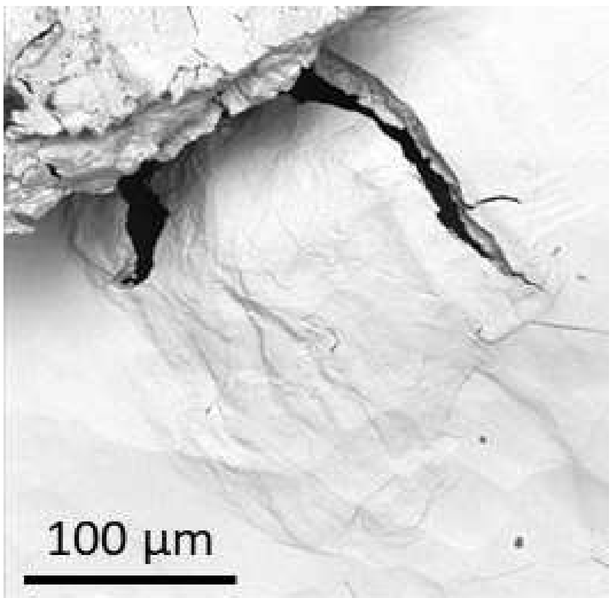

Fig. 4 *Detailed micrograph of sample after 2.5 h at -50 °C in position labelled with yellow "1" in Fig. 2c*

Fig. 4 shows the detail of the very first cracks formed after 2.5 h of sample freezing. The cracks were probably formed by change of volume during the phase transformation. The material in the vicinity of the cracks is deformed in a form of blisters that are typical sign of the tin pest.

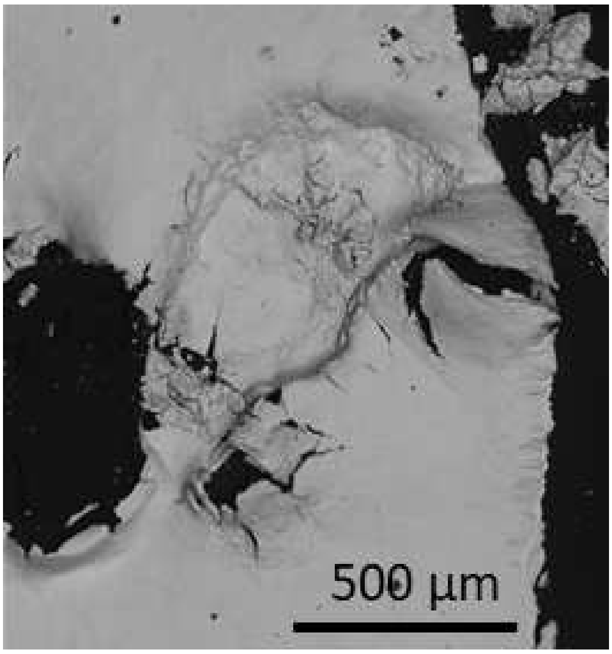

Fig. 5 *Detailed micrograph of sample after 5 h at -50 °C in positions labelled with yellow "1" and "2" in Fig. 2d*

After freezing for another 2.5 h (5 h in total), the evolution of cracks can be observed in Fig. 2d. When compared Fig. 4 and Fig. 5, the inoculator cannot be distinquished after longer time of freezing. Due to the branching of the cracks, it is not possible to calculate the rate of transformation. Interestingly, the newly formed crack "2" is even longer than the first observed crack, see Fig. 5.

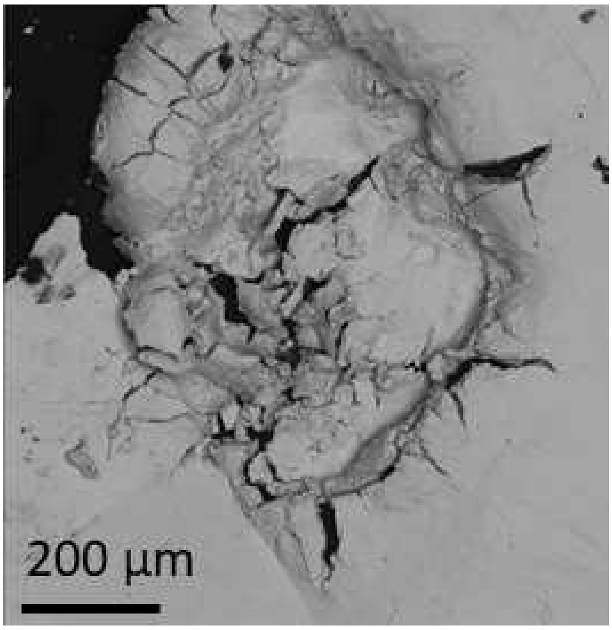

Fig. 6 *Detailed micrograph of sample after 5 h at -50 °C in position labelled with yellow "3" in Fig. 2d*

Fig. 6 shows the crack evolution that occurred radialy around the inoculating α-Sn particle. The length of the cracks is comparable independently on the direction of the crack.

After 5 h at -50 °C, the crack occurred even in the not inoculated part of the sample. One crack was observed close to diamon indent and was labelled "4" in Fig. 2d and its detail is presented in Fig. 7.

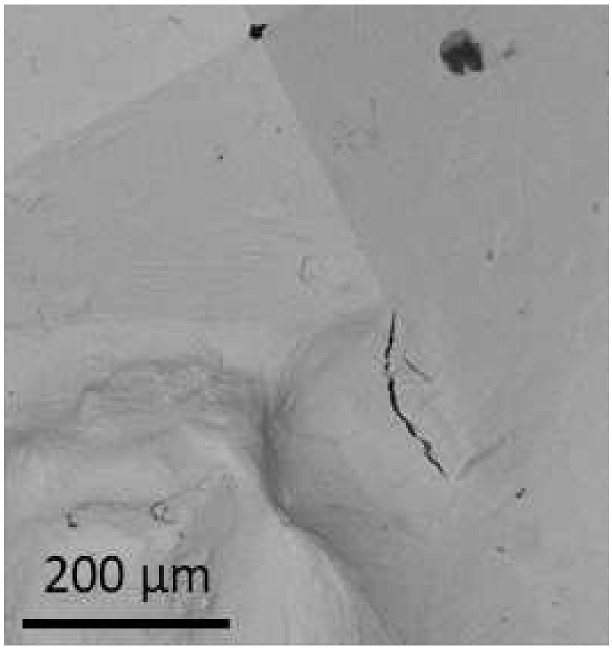

Fig. 7 *Detailed micrograph of sample after 5 h at -50 °C in position labelled with yellow "4" in Fig. 2d*

Interestingly, the crack labelled by "5" in Fig. 2d is located in the non-inoculed and non-indented part of the sample, detailed micrograph is given in Fig. 8.

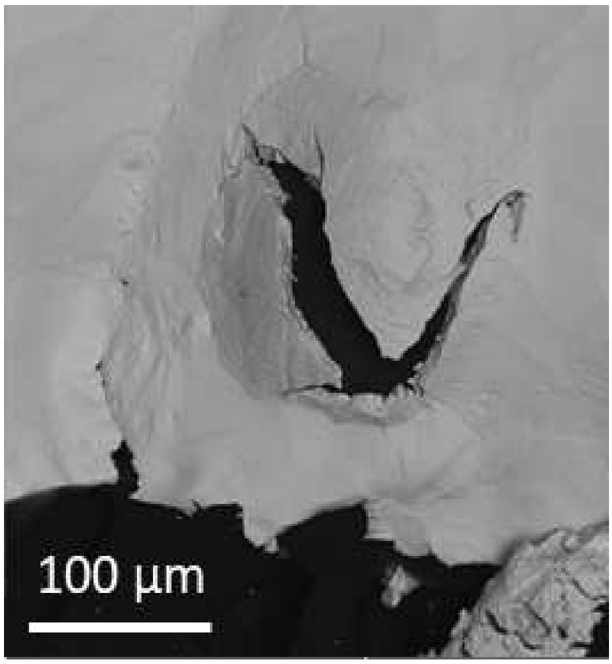

Fig. 8 *Detailed micrograph of sample after 5 h at -50 °C in position labelled with yellow "5" in Fig. 2d*

Original historical material was used for this study that was stored at room temperature for several year. Still, it is possible that the material contained very small amount of non-transformed α-Sn that served as internal inoculator. Unfortunately, its amount is low to be detected by XRD and by overview EBSD that is presented in Fig. 1. Performing EBSD map in sufficient resolution on the whole surface of the sample would be extremely time consuming with a chance of sample drift as it is glued by carbon tape to the sample holder. In future, observation of the ion polished samples is planned that could solve the above-mentioned problems.

4 Conclusion

The organ pipe material from Sn with very small amount of Cu was observed in this study. After 2.5 h of exposure to -50 °C, first traces of phase transformation were observed in form of cracks in the α-Sn inoculated part of the sample. After 5 h exposure to -50 °C, increased number of cracks was observed in different direction. It seams that the phase transformation is not orientation dependent.

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