MINOR PHASES IN TIN-RICH HISTORICAL MATERIALS

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Abstract

The historical organ pipes used to be manufactured from tin and tin-lead alloys. The tin-rich organ pipes usually contained copper as alloying elements, which make them similar to modern lead free soldering materials. The historical organ pipe materials can be used as model materials for natural ageing of soldering materials. Tin pest is a term for modification from white tin to grey tin, which leads to degradation of tin or tin-rich alloys. The influence of individual alloying elements has not been reliably described, yet. Not only on the concentration of the alloying element, but also the distribution may play the important role. In dependence on heat-treatment, the Cu can be in the Sn matrix present in these forms: i) as large intermetallic particles after casting (Cu_6Sn_5), ii) as solid solution after homogenization annealing and iii) as fine precipitates after ageing. The microstructure of the real historical organ-pipes material was studied and it was proven that contradictionary to the equilibrium phase diagram the Cu enriched was observed.

Keywords: Metallurgy, tin, copper, tin pest, TEM

1. INTRODUCTION

Tin has been a common material since early history and has been used for various applications. Nowadays, its usage is more or less limited to the several fields where it has irreplaceable function e.g. food industry (due to its non-toxicity) and soldering (due to its low melting temperature). The traditional solders were composed of eutectic Sn-Pb (39 wt% Pb) alloy. For ecological reasons, the content of Pb in solders is undesirable and Sn-based materials with low content of alloying elements (Cu, Ag, Zn, Bi, Ni and traces of Pb) are used as a replacement [1,2]. Utilization of almost pure or low alloyed Sn causes serious problems during its application in areas with persistently low temperatures leading to gradual disintegration of soldered joint [3]. The effect of alloying elements on the degradation caused by a tin pest, which is the historical name for $\beta(Sn) \rightarrow \alpha(Sn)$ phase transformation, was described [4-7] but information in each source is very divergent and sometimes even contradictory. When the most important ones are picked up: Pb should suppress the transformation [4,7], Au and Ag should suppress it [6,7], Zn should enhance it [6, 7], Ge could inhibit it [4] or slow it down [7] or promote it [5], Cu could inhibited it [4] or promote it [5, 7] or have negligible influence [8]. In case of Cu is the situation even more complicated by formation of Cu_6Sn_5 whiskers during soldering e.g. solar cell parts [9].

The eutectic occurs in the Sn-Cu system at 0.7 wt% of Cu and temperature of 227 °C [9]. When the cooling rate is slow, the material is formed by Sn matrix and Cu_6Sn_5 intermetallic phase. By rapid quenching, the cooling rate might be fast enough to freeze the supersaturated solid solution. By consequent ageing, the Cu_6Sn_5 whiskers may precipitate, as it was mentioned above. The real microstructure of material and the real distribution of alloying elements are usually neglected by tin pest studies. In this paper, the microstructure of real organ pipe is described to ensure the influence of Cu distribution.

2. EXPERIMENTAL

The material from organ pipe approximately 200 years old was used in this study. The TEM sample was prepared from the cross-section of the organ pipe by cutting and grinding up to paper P2500. Consequently, 3 mm disc were cut and the final step was ion polishing using Gatan PIPs machine. The samples were observed by JEOL 2200 FS transmission electron microscope (TEM) equipped with EDS detector by Oxford Instruments. The STEM observation was performed with spot size of 1 nm.

3. RESULTS AND DISCUSSION

In the microstructure of organ pipe material, Cu_6Sn_5 intermetallic particle was found, as shown in **Figure 1**.

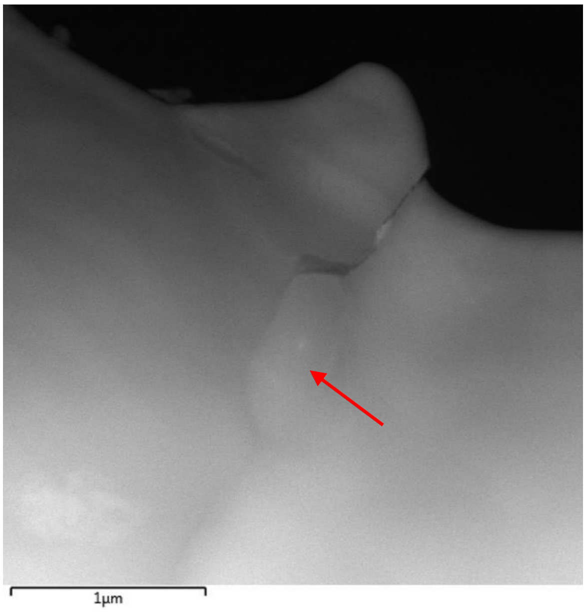

Figure 1 Intermetallic Cu_6Sn_5 particle (STEM/HAADF)

Chemical composition of the particle, its vicinity and matrix were determined by point EDS analysis, the results are given in **Table 1**. For each position at least 3 measurements were performed.

Table 1 STEM/EDS point analysis results

Position	Sn (at%)	Cu (at%)
Cu_6Sn_5 particle	49 ± 5	51± 5
Cu_6Sn_5 vicinity	99.5± 0.1	0.5± 0.1
matrix	100	0

The composition of particle is in good agreement with theoretical stoichiometry that contains 45 at% of Sn. The content of Cu in the vicinity of the particle is surprising, because according to equilibrium phase diagram, there should not be any solubility of Cu in Sn solid solution [9]. To disprove the influence of spot size (overlap of beam with intermetallic particle), the contamination spots are shown in **Figure 2**.

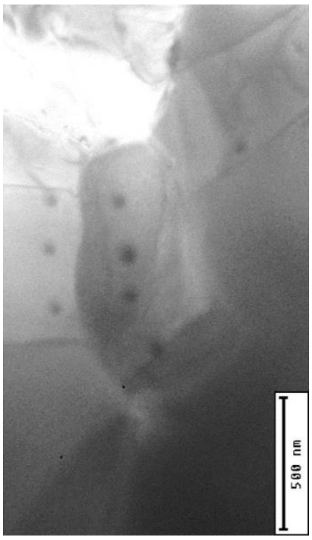

Figure 2 Dark contamination spots after measurement of EDS point analysis (TEM)

To describe the phase composition of intermetallic particle, selected area electron diffraction (SAED) was performed. It was proven, that the Cu_6Sn_5 intermetallic particle is hexagonal, which is the high temperature modification of this phase.

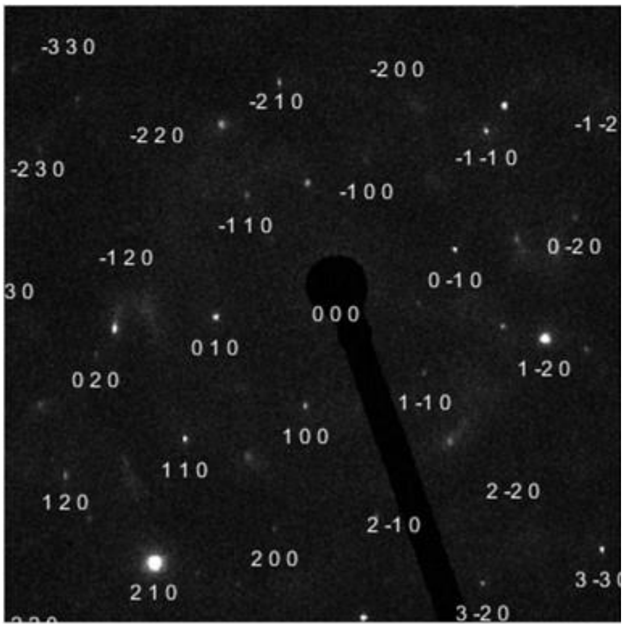

Figure 3 SAED pattern of hexagonal Cu_6Sn_5 with zone axe [0 0 1]

In **Figure 4** is shown scheme of Cu distribution in the organ pipe material showing Cu_6Sn_5 particle (red) and supersaturated solid solution (green) in its vicinity.

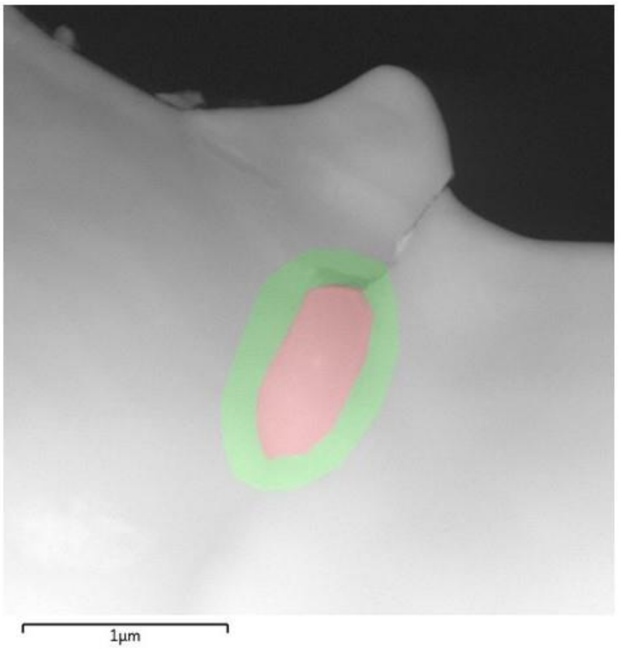

Figure 4 Scheme of Cu distribution in Cu_6Sn_5 particle (red) and supersaturated solid solution (green)

The presented results shows that the distribution of Cu in the real system does not follow the equilibrium phase composition although the material has naturally aged over 200 years. In the following research, the influence of real Cu distribution on the tin pest phenomenon will be studied.

4. CONCLUSION

It was proven that the phase composition of historical organ pipe material is not in equilibrium. It consists of high temperature hexagonal modification of the Cu_6Sn_5 intermetallic phase. In the vicinity of the particle, area enriched by Cu was observed. These results show that it is not possible to study tin pest phenomenon only in dependence of alloy composition but also the elemental distribution should be described.

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