THE Zn INFLUENCE ON DEGRADATION BEHAVIOUR OF Sn-BASED MATERIALS

[1]Alena MICHALCOVÁ, [1]Dominika FINK, [1]Šárka MSALLAMOVÁ, [1]Jáchym PALEČEK, [2]Martin FRIÁK

[1] University of Chemistry and Technology, Prague, Department of Metals and Corrosion Engineering, Prague, Czech Republic, EU, michalca@vscht.cz

[2] Institute of Physics of Materials, v.v.i., Czech Academy of Sciences, Brno, Czech Republic, EU, friak@ipm.cz

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Abstract

The influence of Zn presence on degradation mechanism of Sn-based alloys was studied on naturally aged historical material. Special attention was paid to low temperature phase transformation of Sn also known as tin pest. The Zn addition to Sn-based alloys may be used in soldering materials to improve mechanical properties of the join. By means of optical and scanning electron microscopy and XRD, we have proven that it also accelerates the phase transformation. Even a low content of Pb (0.1 wt%) suppress the phase transformation of Sn. The effect of addition of both Pb and Zn was also described.

Keywords: Metallurgy, tin, zinc, tin pest, organ pipes

1. INTRODUCTION

Modern soldering materials are designed to be environmentally friendly and because of this the reason they are lead free. This awakes the ancient problem of low temperature phase transformation in Sn, also known as tin pest. It was suppressed by using Sn-Pb alloy system. Even very low concentration of Pb protects material against tin pest [1-5]. On the other hand, in some studies [6, 7] the material of eutectic Sn37Pb composition underwent the phase transformation.

The composition of soldering material is usually chosen based on its mechanical properties and the possible tin pest affection is neglected. The Sn-Zn based soldering materials are used [8, 9] although it was already observed that Zn is the tin pest accelerator [1-7,10,11].

In this work, we will describe the effect of Zn on tin pest in Sn-Pb historical material.

2. EXPERIMENTAL

The material from organ pipe approximately 200 years old, which was labelled as “Zn containing organ pipe” was used in this study. The SEM sample was prepared from the cross-section of the organ pipe by cutting and grinding up to paper P4000 and polishing by D2 and D0.7 diamond paste. The sample for measuring chemical composition was grinded on both sides up to paper P2500. The chemical composition was measured by X-ray florescence using Axios spectrometer by PANanalytical. The same sample was used for low temperature exposure at -50 °C. The SEM analysis was performed using TESCAN VEGA 3 LMU equipped by EDS analyser by Oxford Instruments. The overview micrographs of samples after low temperature exposure were performed by stereomicroscope SZX10 IE Power Kit.

3. RESULTS AND DISCUSSION

Historical organ pipe material was studied in this work. It was extremely brittle (as illustrated in **Figure 1**) and partially pulverized so as it underwent phase transformation (tin pest). Chemical composition of this material was analyzed on both sides and the results are given in **Table 1**.

Table 1 XRF analysis of chemical composition (wt%)

Element	Inner side	Outer side
Sn	86.810 ± 0.3	85.149 ± 0.3
Pb	11.265 ± 0.09	13.046 ± 0.1
Cu	0.918 ± 0.03	0.885 ± 0.03
Zn	0.242 ± 0.01	0.247 ± 0.01
Bi	0.228 ± 0.01	0.267 ± 0.02
Fe	0.049 ± 0.009	0.070 ± 0.01
As	0.095 ± 0.009	0.098 ± 0.009
Rb	not detected	0.019 ± 0.004
Na	0.190 ± 0.01	0.098 ± 0.01
Al	0.015 ± 0.004	0.025 ± 0.005
Si	0.040 ± 0.006	0.064 ± 0.008
P	0.005 ± 0.002	0.007 ± 0.003
S	0.016 ± 0.004	0.013 ± 0.003
Cl	0.092 ± 0.009	0.011 ± 0.003
K	0.035 ± 0.006	not detected

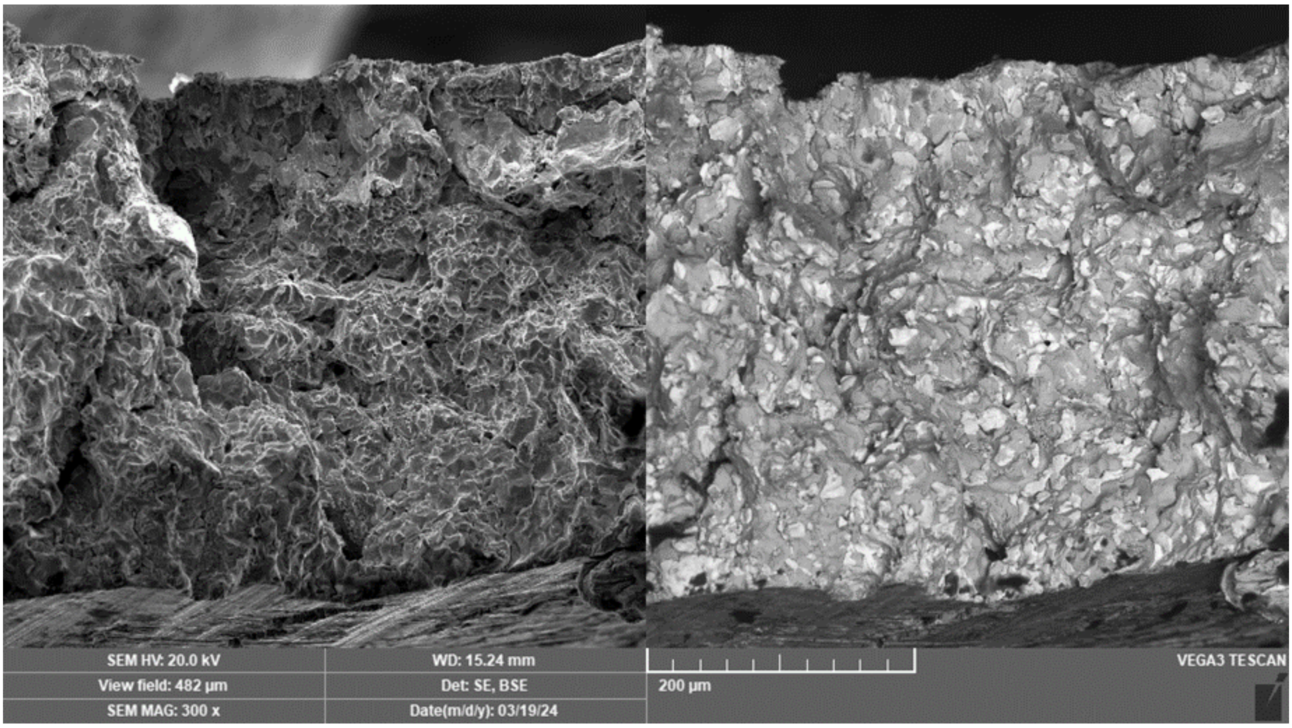

Figure 1 Fracture surface of the organ pipe material

The fracture surface in **Figure 1** exhibited brittle morphology. The material was formed Sn matrix and minor Pb containing particles. The exact elemental distribution mapping is not possible to perform on fracture surface as the majority of signal is reabsorbed.

Based on the results shown in **Table 1**, the occurrence of the tin pest is highly improbable. The Pb content of approx. 12 wt% should protect the material. In contradiction to this hypothesis, after 3 weeks of exposure at -50 °C the degradation was observed. The crack was surrounded by dark material (α-Sn) and the typical blisters caused by volume changes occurred, as shown in **Figure 2**.

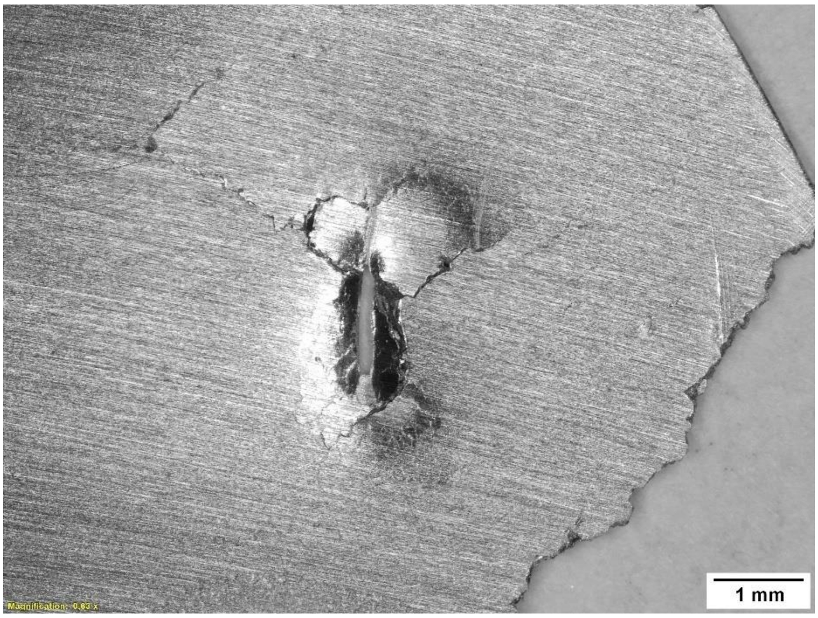

Figure 2 The degradation caused by tin pest

The overview micrograph and EDS elemental mappings of the original material are presented in **Figure 3**. It is shown that the microstructure was composted of Sn matrix and Pb particles and minor Cu containing phases, most probably formed by Cu_6Sn_5 phase.

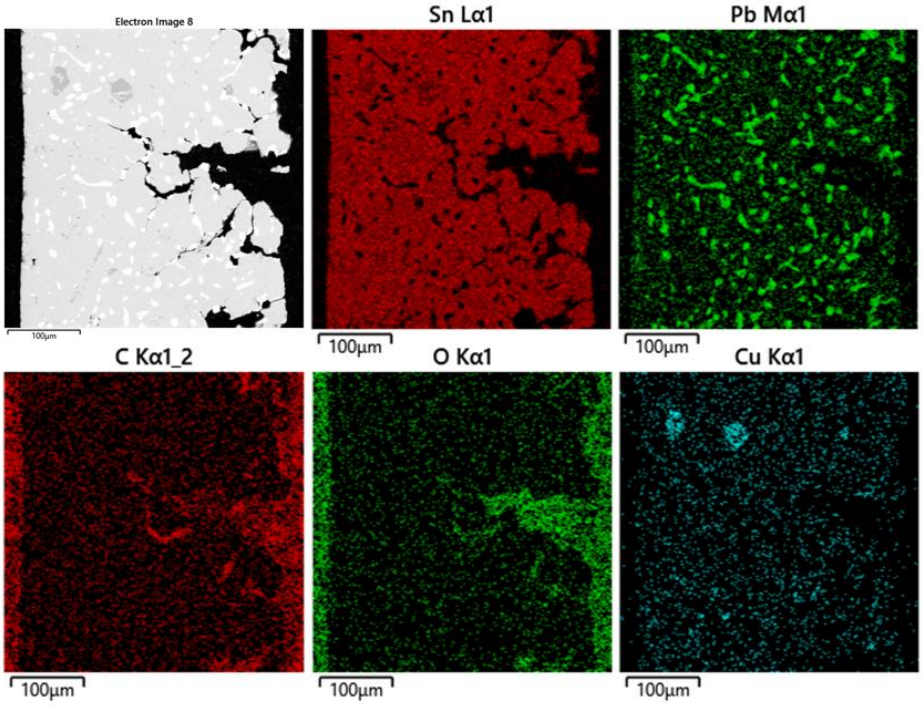

Figure 3 SEM micrograph of cross-sectioned material

The Zn presence was proven in seldom places in the cross-sectioned material, see **Figure 4**. The Zn containing particle is in the vicinity of the materials surface.

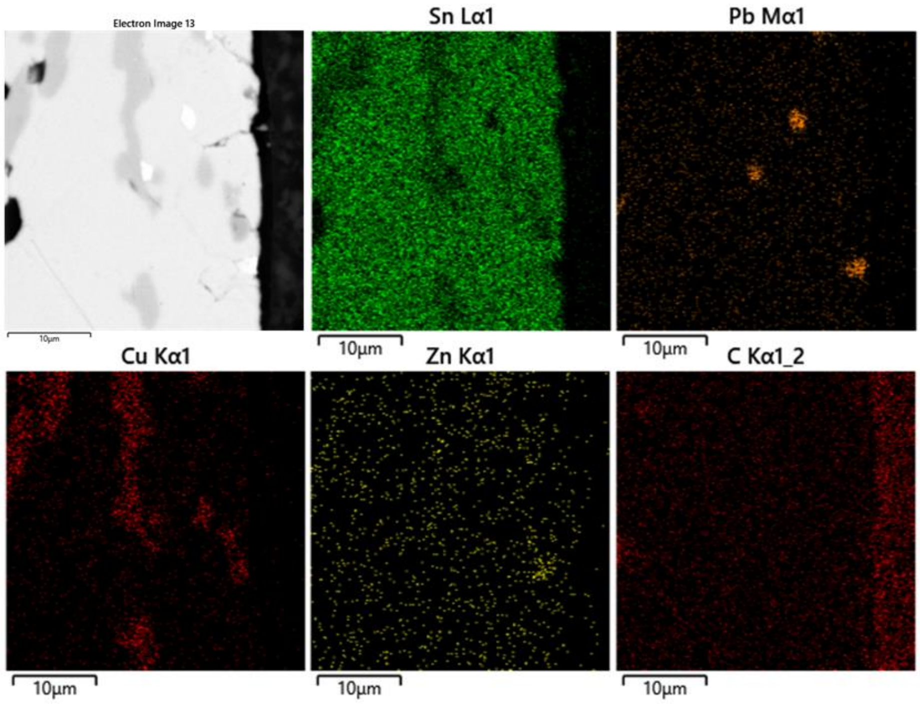

Figure 4 Detailed SEM micrograph of cross-sectioned material

There are two possible explanations of not detecting higher amounts of Zn. The detection limits for EDS analysis are higher than for XRF-WDS analysis presented in **Table 1**. In this case, Zn would be dissolved in the Sn matrix. The other explanation is that the Zn is distributed unevenly and preferentially on the surface. Even the particle in **Figure 4** is located very close to the surface. Taking in account that the interaction volume of Sn with X-rays is about 1 μm, this particle would be detected during XRF measurements. Phase diagrams are usually used to distinguish the form in which Zn will be present in the alloy. In our case, the situation is complicated, as the phase diagram differs in literature. The Sn-Zn phase diagram presented e.g. in [12] exhibits no solubility of Zn in Sn solid solution. On the other hand, in the [13] the solubility is approx. 1 at%, which is above the Zn content in our material.

The chemical composition was studied on the samples that underwent phase transformation at -50 °C. The damaged part was partially enriched by lead oxides but also contained higher amount of Zn.

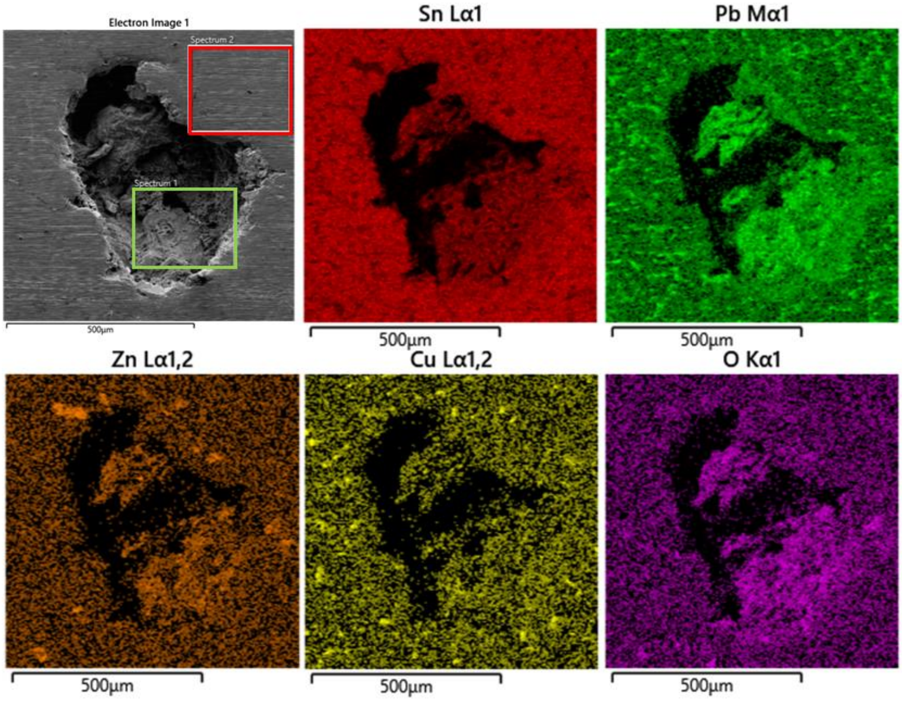

Figure 5 SEM micrograph of the material after exposure at -50 °C for 3 week

When we neglect the oxygen content, the comparison of chemical composition in the affected part (green labelled, spectrum 1) and non-affected part (red labelled, spectrum 2) is given in **Table 2**. It is clearly visible that in the affected part the Zn concentration is significantly higher. It indicates that the Zn content is above the solubility of Zn in Sn solid solution.

Table 2 EDS analysis of chemical composition from area shown in **Figure 5**

Element	**Spectrum 1** (wt%)	**Spectrum 2** (wt%)
Sn	69.0 ± 0.5	89.8 ± 0.4
Pb	26.8 ± 0.4	8.8 ± 0.3
Cu	1.1 ± 0.3	1.0 ± 0.3
Zn	3.1 ± 0.3	0.5 ± 0.2

Presence of Zn-rich regions creates a weak place that can be affected by tin pest although the material contains tin pest suppressing elements like Pb. This can explain the contradictions in the literature. Pb content may inhibit the tin pest but this effect may be compensated or exceeded by presence of minor elements like Zn.

4. CONCLUSION

In this work historical organ pipe material was studied. The composition was Sn with 12 wt% Pb, 0.9 wt% Cu, 0.2 wt% Zn and 0.2 wt% Bi. Although the material contained high amount of Pb, it underwent tin pest process (low temperature phase transformation) in 3 weeks at -50 °C. The affected parts of sample exhibited higher amount of Zn than average material. It seems that the effect of Zn on low temperature Sn behaviour is higher that effect of Pb.

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