INVESTIGATING THE EFFECT OF $(NH_4)_2SnCl_6$ ON THE TIN PEST PROCESS

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Abstract

The so-called tin pest is a phase transformation of white tin (β(Sn)) into grey tin(α(Sn)), where the disintegration of tin materials occurs due to different thermodynamic stability of the phases with a transition at 13.2 °C. The degradation is relatively slow until -50 °C where the maximum speed is located. Therefore, one can trace research (over 100 years old) synthetizing pink salt $(NH_4)_2SnCl_6$ and use it together with α(Sn) particles inoculation to accelerate the tin pest process.

Because $(NH_4)_2SnCl_6$ was discovered in nature in 2009 in the volcanic dust of an Italian volcano, we decided to investigate its effect on tin material without the use of an inoculator, in aqueous and ethanol solution. To fully simulate the weathering conditions, we observed the samples at different temperatures.

Tin in ethanol solution showed the tin pest, and this after only 5 days and at a temperature of just 4 °C. In aqueous solution, rapid degradation also occurred already at room temperature, but this was not tin pest. Based on these results, pink salt poses a serious risk, not only in the vicinity of the volcano, but also many kilometres away because of volcanic fallout and already at temperatures above zero.

The samples were characterized with stereo microscope, scanning electron microscopy and Raman microscope.

Keywords: Tin pest, α(Sn), grey tin, pink salt, $(NH_4)_2SnCl_6$

1. INTRODUCTION

With the increasing use of tin solder, which is gradually replacing tin-lead solder [1], tin pest poses a risk to not just historical objects but also to many crucial modern objects and materials. The problem is that although tin degradation has been scientifically studied for over a century, there remains insufficient understanding of how to prevent or treat the process.

The degradation occurs when so-called white tin β(Sn) is converted to grey tin α(Sn) at a temperature below 13.2 °C, with the maximum conversion rate occurring at -50 °C [2-6]. Due to the different crystal lattice of the two phases, disintegration of the material occurs, accompanied by the formation of characteristic blisters and cracks, and can lead to complete disintegration into grey tin powder [7].Thus, the transformation process is influenced not only by temperature but also by exposure time, the tin-based composition and mechanical stress, with the first signs of tin pest manifesting themselves within a period ranging from just a few days to hundreds of years. In Cohen's study [4], tin samples with purity >99.99% undergo the first manifestations of pest in 1 day at temperatures around -50 °C, in 3 days at -22 °C, in 7 days at -11 °C, and at 0 °C the pest did not appear even after 62 days. These are the earliest times of manifestation mentioned. If we look at the variance of the results, the range is from 1 to 8 days at around -50 °C. In another study, at the same temperature, pest does not manifest itself even after 54 days [5]. Therefore, samples of untransformed tin were inoculated with particles of α(Sn) to accelerate and stabilize the experiment when investigating tin pest [8, 9].

A further improvement came with synthetizing of the so-called pink salt, $(NH_4)_2SnCl_6$, which can be first found in literature in 1861 [10]. At the beginning of the 19th century E. Cohen observed tin pest with help of $(NH_4)_2SnCl_6$ [11]. Samples were inoculated, exposed in the 10% aqueous solution of the above-mentioned salt, and then exposed to low temperatures [12]. At nowadays research, only the inoculator is used [13], the pink salt last worked with in the Cohen's and Tamman's researches [14]. Information about salt came again in 2009, but from another side. It was discovered in nature, specifically in the volcanic dust of La Fossa Crater, Italy [15]. The spread of volcanic fallout is not only a problem in the vicinity of the volcano, but often tens of thousands of kilometres away. This phenomenon was observed in the Czech Republic this year in the case of Saharan sand [16]. Thus, there is a risk of contact with tin materials, both industrial, such as solder joints in solar cells located at higher altitudes, and historical, such as organs located in unheated and imperfectly sealed churches. In addition, the idea of producing crystals for use in solar cells parts from synthesized pink salt and its subsequent crystallization are emerging [17].

Based on these findings, we decided to investigate the effect of pink salt on tin materials by simulating the weathering conditions of the environment. That means, without grey tin particle inoculation. The experiment consisted of observing the degradation process of pure tin due to pink salt solution in water and ethanol to also simulate the maintenance of tin objects. The observing temperatures were RT (room temperature), 4 °C and -18 °C, which again correspond well to real outdoor conditions.

2. EXPERIMENTAL, RESULTS AND DISCUSSION

Sn foil samples with 99.99+% purity and 0.05 mm thickness were placed in 10 % $(NH_4)_2SnCl_6$ solution in demineralized water and exposed to RT, 4 °C and -18 °C. Samples from the same foil were placed in a saturated solution of $(NH_4)_2SnCl_6$ in ethanol (0.25 g/100 ml) and exposed to the same temperatures.

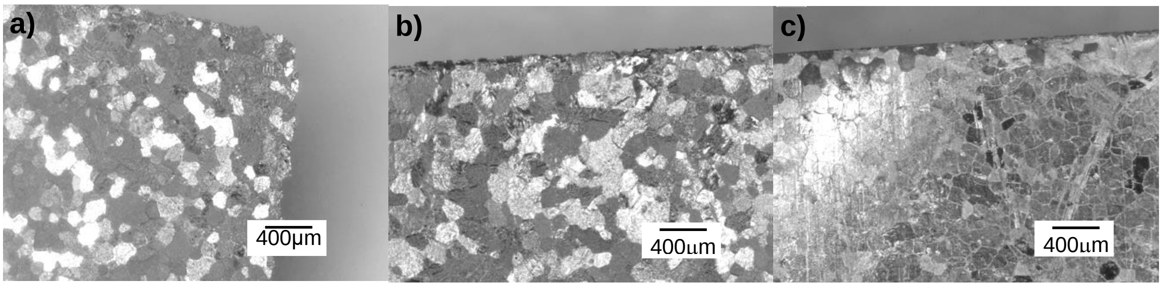

Figure 1 Sn foil in aqueous solution of $(NH_4)_2SnCl_6$ after 5 days: a) RT, b) 4 °C, c) -18 °C, observed with stereo microscope SZX10 IE Power Kit

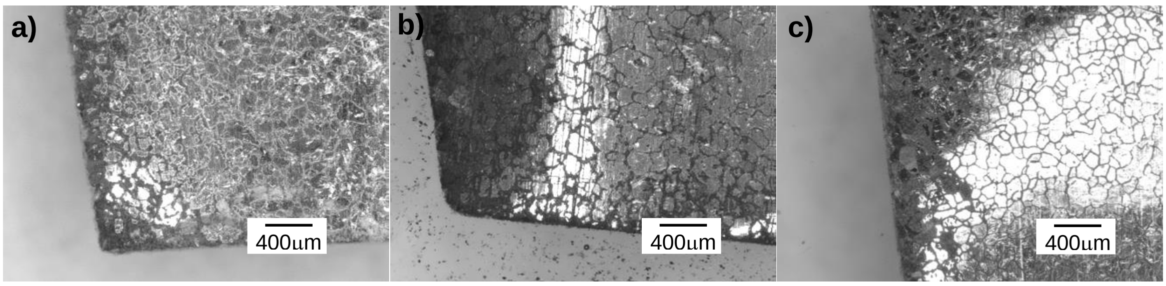

Figure 2 Sn foil in ethanol solution of $(NH_4)_2SnCl_6$ after 5 days: a) RT, b) 4 °C, c) -18 °C, observed with SZX10 IE Power Kit stereo microscope

Using evaluation from an optical microscope, the fastest decay of the Sn foil in water was observed at RT, but it was not a tin pest (**Figure 1**) due to the absence of dark grey coloured parts. In ethanol, all samples were hit by the tin pest, with the fastest rate at 4 °C occurring as early as 5 days (**Figure 2**).

The structure of the samples in aqueous solution at RT and in ethanol at 4 °C were further investigated by SEM. The degradation differed, with the foil grains in water always degrading throughout their entire surface area (**Figure 3**), whereas in ethanol there was preferential damage to the grain boundaries (**Figure 4**).

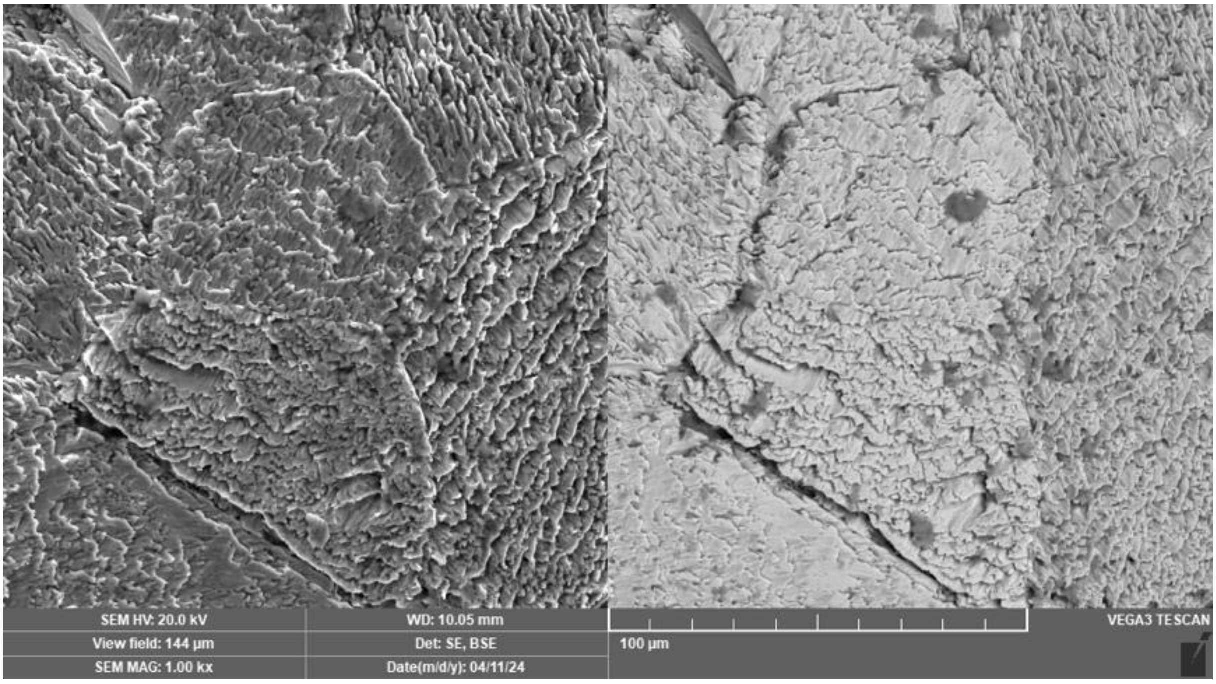

Figure 3 Sn foil in aqueous solution of $(NH_4)_2SnCl_6$ after 5 days at RT, observed with SEM MIRA LMU 3

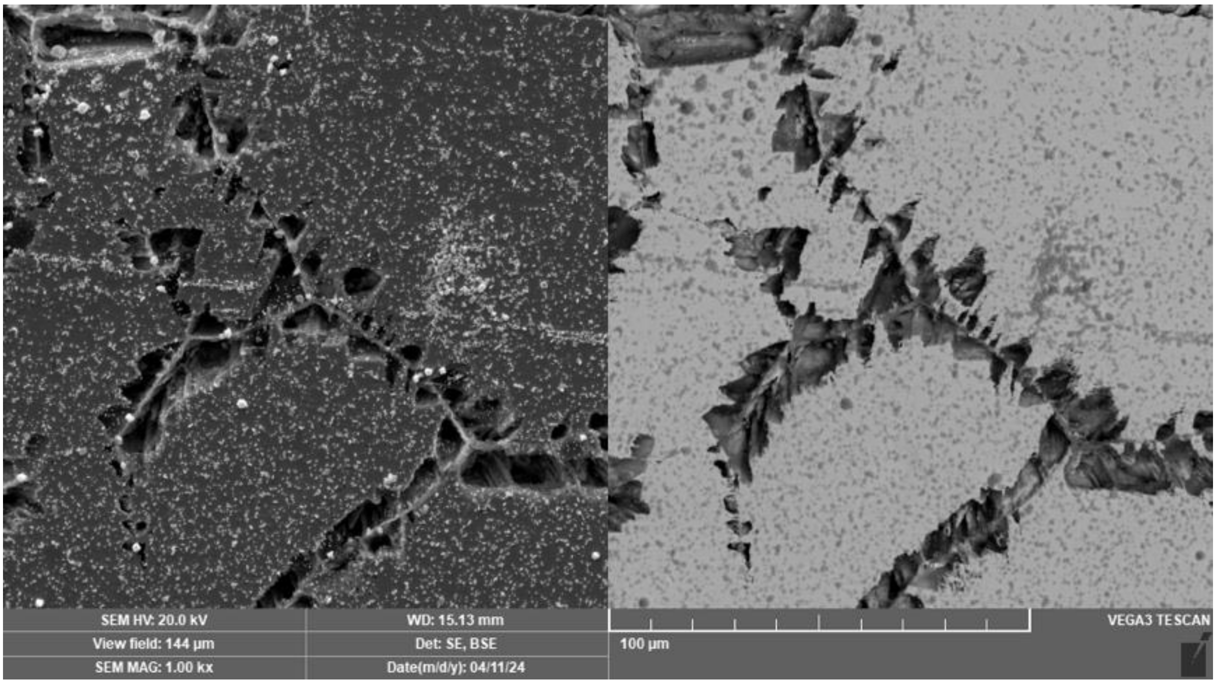

Figure 4 Sn foil in ethanol solution of $(NH_4)_2SnCl_6$ after 5 days at 4 °C, observed with SEM MIRA LMU 3

The presence of β(Sn) and α(Sn) was verified using a Thermo Scientific DXR Raman Microscope, where the sample in aqueous solution (RT) contained only beta tin (~130 cm^{-1}) (**Figure 5**), while the sample in ethanol solution (4 °C) indeed confirmed the presence of alpha tin (~195 cm^{-1}) (**Figure 6**).

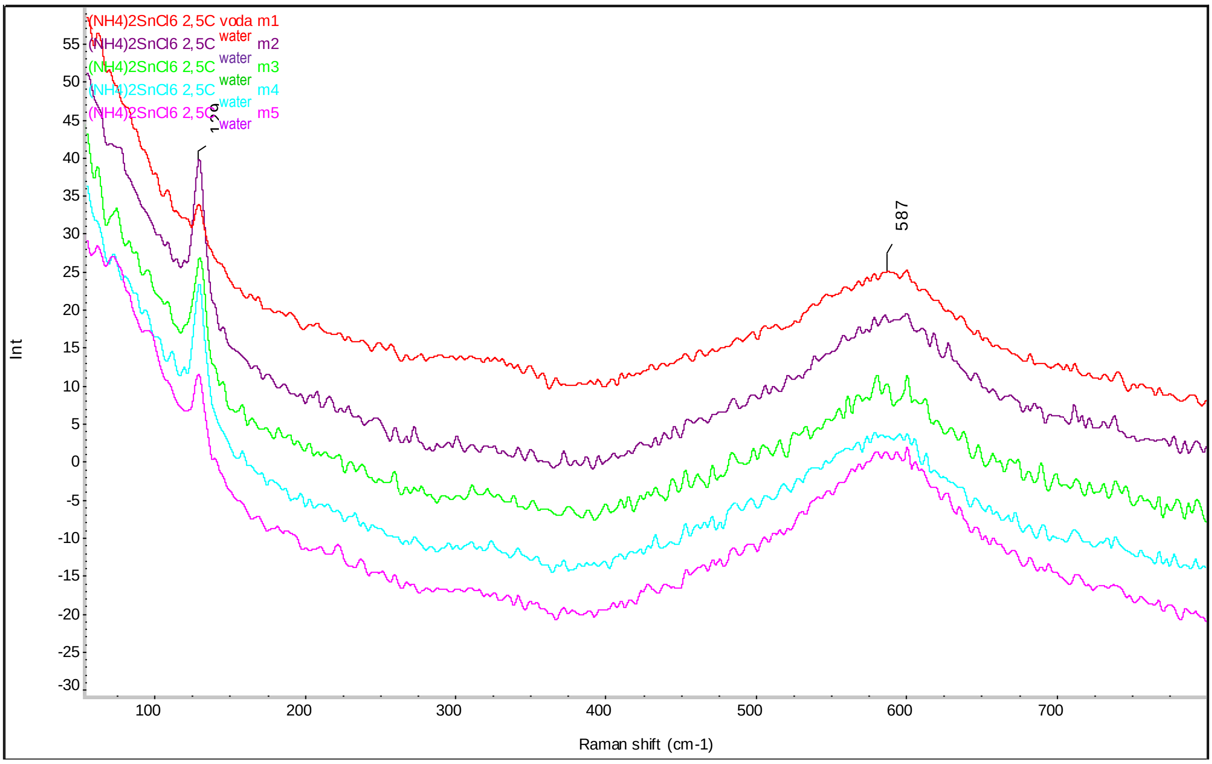

Figure 5 Raman spectrum of Sn foil in aqueous solution of $(NH_4)_2SnCl_6$ after 5 days at RT

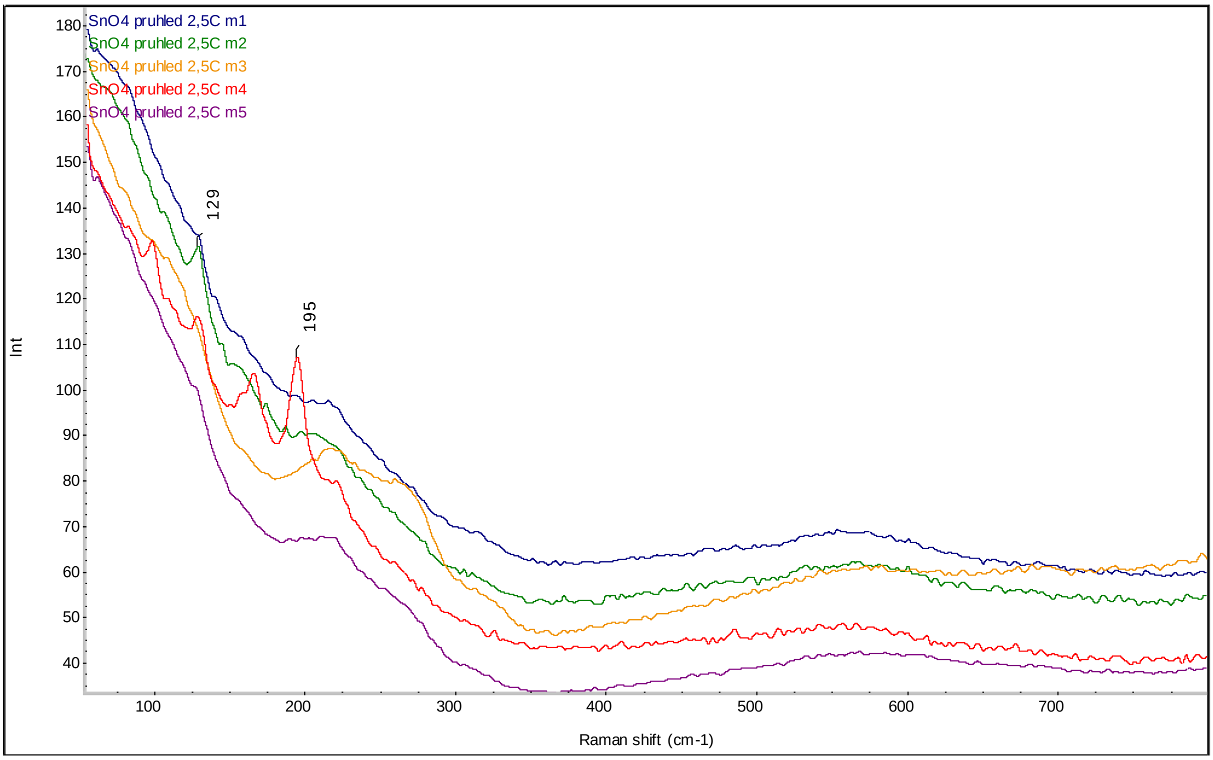

Figure 6 Raman spectrum of Sn foil in ethanol solution of $(NH_4)_2SnCl_6$ after 5 days at 4 °C

3. CONCLUSION

This study is the first to revisit pink salt in relation to tin pest in almost a century. This is due to the discovery of the salt in nature earlier this century, which changed the nature of the risk to tin objects outdoors. We have adapted our experiment accordingly, exposing tin to an aqueous and ethanol solution of $(NH_4)_2SnCl_6$. In an aqueous environment, it violates the tin at room temperature and can cause serious damage in as little as 5 days. At the same time, tin pest attacks in an ethanol solution at 4 °C. For comparison previous studies showed that the pest acted fastest at -50 °C, while at 0 °C no degradation occurred even after 62 days. The effect of water is also revealing from another reason, where with the α(Sn) inoculation and salt it acted as an accelerator of tin pest, while without inoculating it now acts as a strong etchant. Based on these results, it is strongly recommended to keep an eye on meteorological forecasts of volcanic dust fallout, which often has a range of several thousand kilometres, and to pay attention to maintenance. In as little as five days in a humid environment, the tin material can be severely damaged. With subsequent careless maintenance, rapid damage can then occur from the tin pest.

ACKNOWLEDGEMENT

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