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Deterioration of tin-rich organ pipes

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Tin-rich organ pipes are often affected by localised deterioration in the form of grey pustules, pinholes, cracks and exfoliations at the surface. Two main types of decay of tin-base materials that might have a similar appearance, i.e. the surface of the object covered with dark grey pustules, are known. The first is the allotropic transformation of white metallic tin into grey tin, the so-called "tin-pest". The second form of decay is due to corrosion in the form of localised oxidation of tin. The identification of the causes of deterioration is of main concern because, whereas oxidised material can be treated, an object that suffers "tin pest" cannot be reconstituted. In the present paper the results of investigations on ancient tin-rich organ pipes affected by localised degradation are presented. The study of the composition and the microstructure of the pipes has been coupled with the results of analyses on the corrosion products. It was shown that oxidation clearly has a significant role in the deterioration of tin pipes, but it was not possible to establish if the allotropic transformation took place or not, because of the low probability of detecting the residual grey tin.

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1. Introduction

Tin-rich alloys are often used for the construction of prospect pipes in pipe organs. Pipes manufactured with tin-rich alloys have a bright sound and typically look more shiny than pipes manufactured with lead-rich alloys, commonly used for pipes in the interior pipe work, hidden behind the prospect. Both lead-rich and tin-rich organ pipes may undergo some kind of degradation. Lead-rich pipes can be affected by corrosion in the inner surface as a consequence of the interaction between the metal and the environment inside the organ [1], whereas two main different types of degradation phenomena may affect tin-rich pipes: (i) interaction with the environment that leads to localised tin corrosion or (ii) the so-called "tin pest," that is a consequence of a change of tin crystal structure. In both cases, i.e. localised corrosion and tin pest, the morphology of the deteriorated area can be very similar: grey pustules, pinholes, cracks and exfoliations appear on the external surface of the pipe.

It is interesting to point out that the occurrence of "tin pest" has been observed for the first time in organ pipes: in 1851 Erdman [2] noticed a modification of the surface of tin-based prospect pipes in the organ of the church of the castle of Zeitz (Germany). Pustules, exfoliations and areas where the metal becomes "crystalline" and brittle on the external surface of tin pipes were visually observed by Erdman, who assumed that the degradation of the metal had to be due to some change of the crystalline structure, favoured by vibrations in speaking pipes.

As regards the interaction with the environment, it is known that atmospheric corrosion of tin in clean dry air is very slow and the main corrosion products are SnO and SnO_2 [3–5]; tarnishing of tin is sometimes observed in indoor atmospheric conditions [6].

The oxidation rate of tin increases with alloy additions (0.1 at%) of elements such as Mn, Sb, Bi, Pb, Fe and decreases with additions of Zn, In, Cd and P. Even small

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TABLE I Information on the organs

Sample[a]	Organbuilder, year	Location of the organ	Location of the deteriorated areas of the pipe (sampling)
A	Costanzo Antegnati, 1585	S.Nicola, Almenno S.Salvatore, Northern Italy	Uniformly distributed
N	Nacchini, first half of 1700	Castelferretti, Central Italy	Near the hook that keeps the pipe vertical
R	Cesare Romani, 1588	S.Stefano Cathedral, Prato, Central Italy	Uniformly distributed
S	Michelangelo Sanarica, 1763	Southern Italy	Zones in contact with the wooden pipe rack
T	Agati (?), beginning of 19th century	Florence, Central Italy	Uniformly distributed

[a] Samples were taken from tin-base prospect pipes.

additions of lead to tin impair the retention of its bright reflective surface in common atmospheres [7].

On the other hand, the so-called "tin-pest" is the allotropic transformation of white, metallic β-Sn (with a body-centred tetragonal structure) into grey non-metallic α-Sn (with a diamond cubic structure), which lacks cohesion and appears as a friable powder [8]. A 27% volume increase goes along with the $\beta \rightarrow \alpha$ transformation, which induces the formation of cracks and the typical lack of cohesion of α-Sn. Because of the large dilatational strains, the transformation starts invariably at the surface and then proceeds through the metal [9]. Several factors have an influence on the allotropic transformation.

From a compositional point of view, in the case of pure tin, the allotropic transformation is thermodynamically allowed at 13.2°C [10]. The presence of impurities such as Sb and Bi (below 0.1 wt%) in the alloy delays or hinders the $\beta \rightarrow \alpha$ transformation [9, 13]. Also Pb, Ag and Cd delay the transformation, whereas Al, Zn, Ge, and Cu accelerate it [12, 14]. About 0.5 wt% Ge or 0.6 wt% Si stabilize grey tin to 60° and 90°C respectively [9]. The amount of Pb in the alloy of the pipes analysed by Erdman [2] was surprisingly high (about 3.7 wt%), considering the present knowledge that Pb delays the allotropic transformation.

From the point of view of the kinetics, the transformation rate of pure tin reaches the maximum value at about –50°C [11]. Also the inoculation of β-Sn with α-Sn crystals accelerates the transformation [7].

The microstructure of the metal influences the allotropic transformation: the $\beta \rightarrow \alpha$ rate increases with decreasing grain size. Cold working without subsequent annealing allows the transformation to develop more rapidly [3].

From a mechanical point of view, the tendency to form grey tin is also increased when tin undergoes tensile stresses but not when it is compressed [12]. Other factors, which may be of particular importance in the case of organ pipes, are the amplitude and the frequency of vibration. In the areas of the pipes with the highest concentration of stresses induced by vibrations, the density of dislocations in the metal increases and activates the transformation [11].

The identification of the causes of deterioration is of main concern for the restoration and conservation of organ pipes because, whereas oxidised material can be treated, an object that suffers "tin pest" cannot be reconstituted [3, 4]. The reverse $\alpha \rightarrow \beta$ transformation of pure tin is possible above 13.2°C, but if α-Sn is converted back into β-Sn by raising the temperature, the metal will be porous and cracked until it has been remelted [12]. It is also worth noting that the $\beta \rightarrow \alpha$ transformation is considered irreversible if the grey tin particles have already undergone peripheral oxidation and would therefore not smelt into a metallic body at the melting point of tin [4].

In any case, if the pipe is too much deteriorated, i.e. there are through-thickness holes in the pipe wall, the only solution that allows the pipe to speak again is the integration of the missing parts with new material.

In the present paper the results of investigations on ancient tin-base pipes affected by localised degradation are presented. The study of the composition and the microstructure of the pipe has been coupled with the results of analyses on the corrosion products, in order to get a deeper understanding of the deterioration processes.

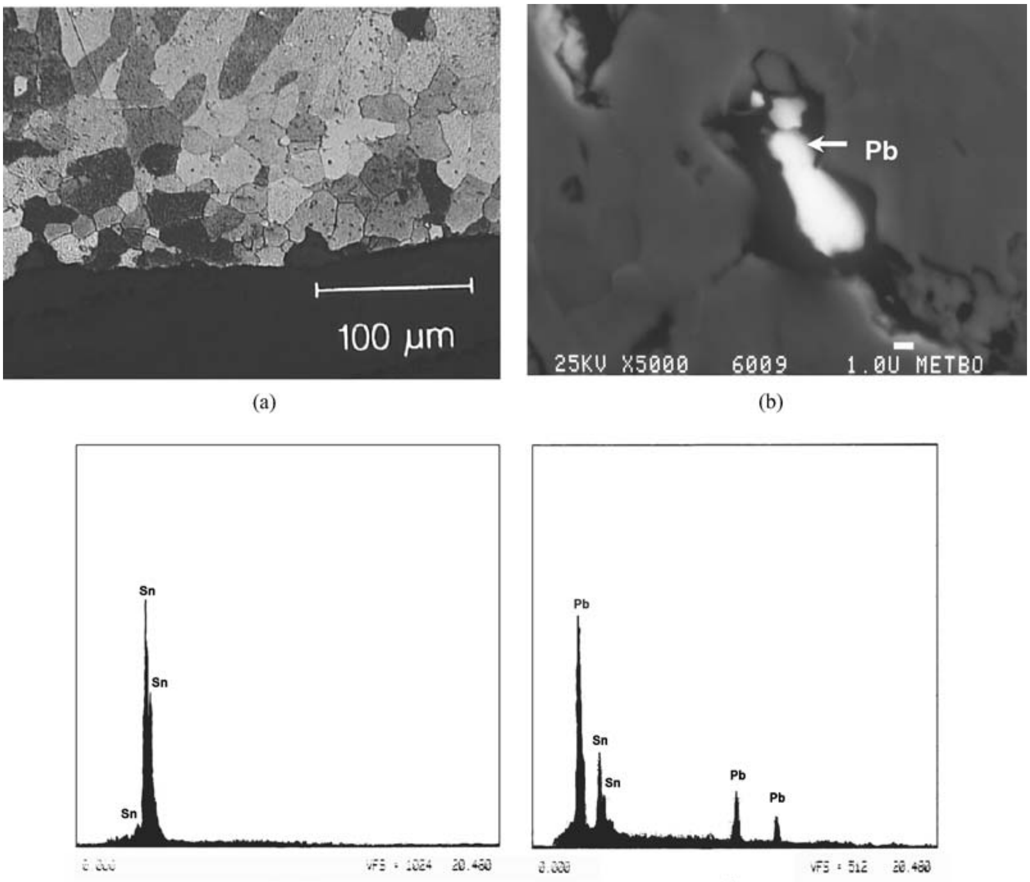
2. Experimental

Several organs, which are briefly described in Table I, were taken into account in this research. Tin-rich prospect pipes affected by corrosion were selected and samples from the deteriorated areas were collected (Table I). As an example, an image of the tin-rich flue pipes in the prospect of the Antegnati organ of Almenno S. Salvatore (Northern Italy) can be seen in Fig. 1a.

The morphology of the deteriorated areas was observed by stereomicroscopy (SM) and Scanning Electron Microscopy (SEM). Corrosion products in selected areas were analysed by X-Ray Diffraction (XRD) using a computer controlled goniometer (0.02 $2\theta°$ step, 1 s counting time) and Cu k_α radiation. XRD analyses were performed directly on deteriorated areas of the pipe metal and on powders taken from pustules in these areas. When possible, small samples were taken from the pipes using a fine jeweller's saw. Samples were then cold mounted in epoxy resin and polished for metallographic analysis of both the surface and the cross section of the pipe, according to standard metallographic procedures for tin alloys [15]. The microstructure of the mounted samples was studied by Optical Microscopy (OM) and SEM. Energy Dispersive Spectroscopy (EDS) was used for localised compositional microanalyses. Etching with alcoholic ferric chloride was carried out in order to reveal grain boundaries; samples

(a) (b)

Figure 1 Organ in the church of S. Nicola at Almenno S. Salvatore (Bergamo, Northern Italy) (a) and general view of the deteriorated prospect pipes (b).



(a) (b) (c) (d)

Figure 2 Representative microstructures of non-deteriorated areas (etched with alcoholic $FeCl_3$/HCl); sample T with equiaxed twinned grains in the tin-rich matrix (a); sample S with lead-rich inclusions at grain boundaries (b); EDS spectra of tin-rich matrix (c) and precipitates (d).

TABLE II Composition of pipe metal samples, wt% (FAAS)

	Pb	Ag	As	Bi	Cu	Sb
A	0.30	–	0.12	0.09	0.05	–
N	–	–	–	–	0.19	–
R	0.12	–	0.02	0.07	0.05	–
S	1.34	–	0.09	0.07	0.14	–
T	0.13	0.06	0.10	0.08	0.44	–

were observed both before and after etching. Samples for wet chemical quantitative analysis (about 0.01 g) were also taken with small twist drills (1 mm diameter). Care was taken to get the samples from the uncorroded core metal. Flame Atomic Absorption Spectroscopy (FAAS) was used to determine the chemical composition of the pipe metal samples.

3. Results

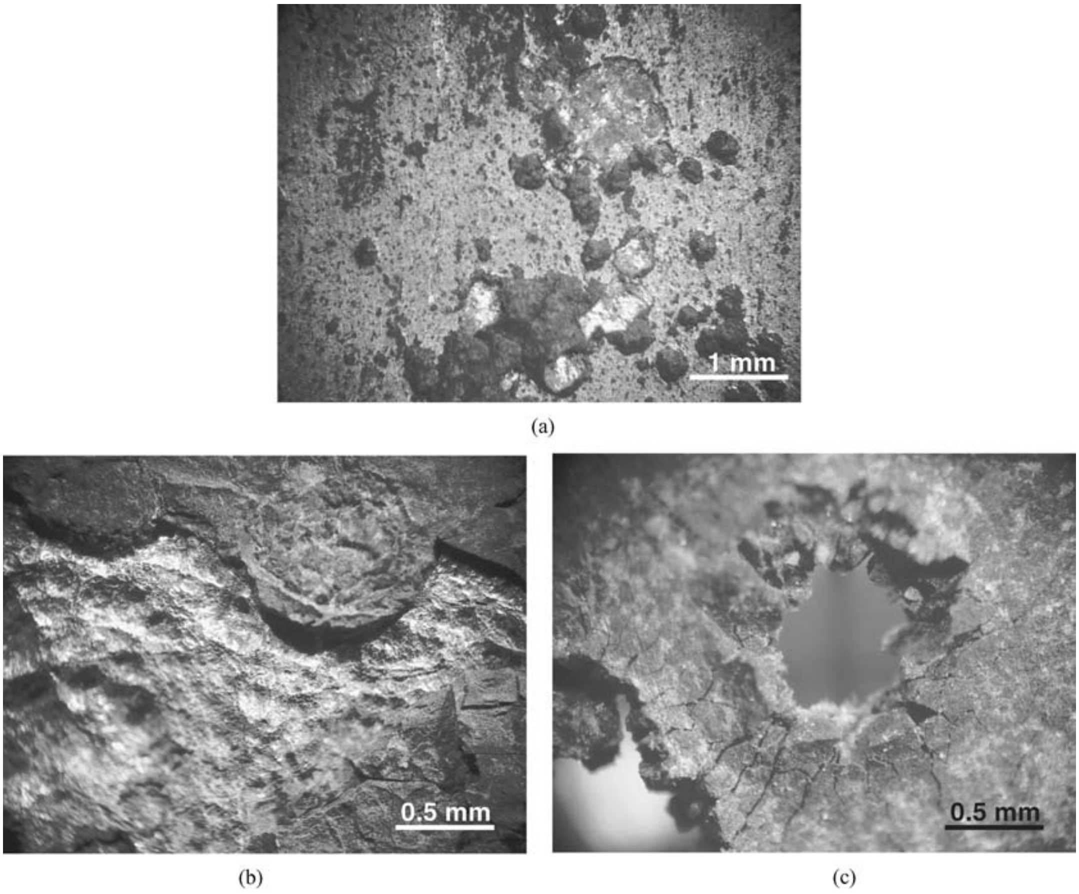
In agreement with compositional data (Table II), the microstructure of the pipes in non-deteriorated areas consists of a tin-rich matrix with equiaxed twinned grains (Fig. 2a); lead-rich precipitates at grain boundaries (Fig. 2b–d) were observed only in sample S, that contains the highest amount of lead among these samples.

An example of the visual appearance of the pipes can be observed in Fig. 1b; the typical morphology of the deteriorated areas is shown at higher magnification in the stereomicrographs of Fig. 3. Grey pustules on the surface of the pipe (Fig. 3a) are often covered with interconnected cracks (Fig. 4). The pustules are partly or completely disintegrated; when the pustules spall off, the exposed underlying metal appears typically rougher than the surrounding non-deteriorated areas (Fig. 3b). In some cases the crater under the pustule is very deep or generates a hole (Fig. 3c).

As to the distribution of pustules on the outer surface of the pipes, in the case of pipe N pustules are located near the hook that keeps the pipe vertical (Fig. 5), whereas in pipe S the pustules are mainly located in the zones in contact with the wooden pipe rack. In pipes A, R and T the pustules are more uniformly distributed, both in the body (upper cylindrical part) and in the foot (lower conical part) of the pipe.

The cross section of the sheet in deteriorated areas always shows a greyish corrosion products layer with a banded morphology. A crater-like interface separates the corrosion products layer from the uncorroded metal (Fig. 6a). The corrosion layer is neither compact nor adherent and therefore it affords no protection to the underlying metal. Traces of pitting corrosion can also be observed (Fig. 6b).

The metallographic observation of the external surface of the sheet reveals intergranular corrosion around the



(a)

(b) (c)

Figure 3 Morphology of deteriorated areas: sample A (a), sample R (b), sample T (c).

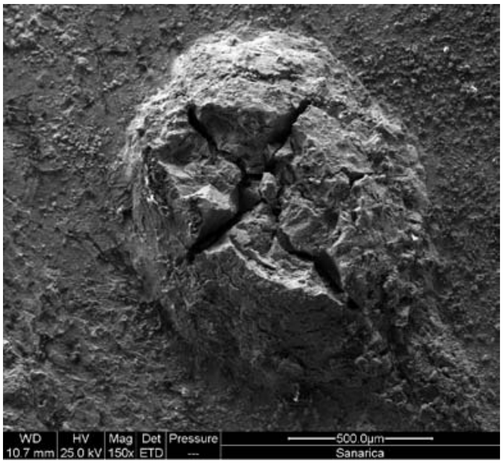


Figure 4 SEM image of a pustule on the surface of sample S.

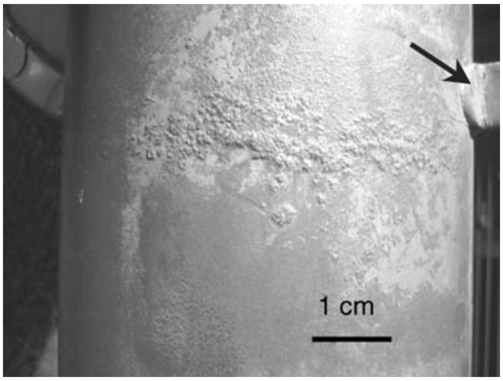


Figure 5 Pipe from the Nacchini organ: the zone of the pipe underneath the hook (indicated by the arrow) that holds the pipe in place is covered with pustules (sample N).

pustules in the deteriorated areas of all samples (Fig. 7). Intergranular corrosion also outlines grain boundaries in unetched metallographic samples (Fig. 6a–b) and leads to the formation of cracks (Fig. 7a). Pustules are located in areas with corroded grain boundaries (Fig. 7b).

Elemental X-ray maps show that tin and oxygen are the main components of the dark grey pustules (Fig. 8), where XRD patterns actually reveal β-Sn, SnO and SnO_2 as the main phases (Fig. 9). Moreover, XRD analyses of the powders taken from the pustules in these areas confirm that SnO and SnO_2 are the main corrosion products on all the samples (Fig. 9a). It has to be noticed that α-Sn has never been detected.

4. Discussion

The pipes examined in this study consist of nearly pure tin; the alloys also contain lead, which is commonly present in alloys for this kind of components. The lead content is relatively low, with the exception of sample S, as shown in Table II. The presence of lead-rich precipitates in sample S is due to the low solubility of lead in tin at room temperature [16].

The tin-rich alloys also contain traces of elements that might favour (Cu) or hinder (Pb, Bi, Ag) the $\beta \rightarrow \alpha$ transformation. However, it is important to take into account that the effects of the composition described in the literature have been measured in binary alloys, whereas in these alloys different trace elements are simultaneously present.

The presence of tin oxides and the absence of α-Sn in deteriorated areas indicate that the degradation of tin pipes studied in the present work is due to a more complex phenomenon than the plain $\beta \rightarrow \alpha$ transformation. The intergranular attack that leads to the localised formation of pustules consisting of tin oxides is clearly a significant part of the degradation process, as observed also by other authors [6, 17] that studied historical tin artefacts. The impossibility to detect α-Sn may not be an indication that the $\beta \rightarrow \alpha$ transformation never occurred. It is worth noting that α-tin is not commonly detected in naturally deteriorated tin-base objects, but only in samples where tin pest was artificially induced [3, 4, 11, 17, 18]. For instance, in the case of the French organ in Bordeaux, built by dom Bedos de Celles in 1766, XRD analyses performed on deteriorated areas of nearly pure tin pipes did not detect α-Sn, but only tin oxides [11]. However, the occurrence of tin pest was deduced by the authors on the basis of the morphology and the microstructure of the deteriorated material.

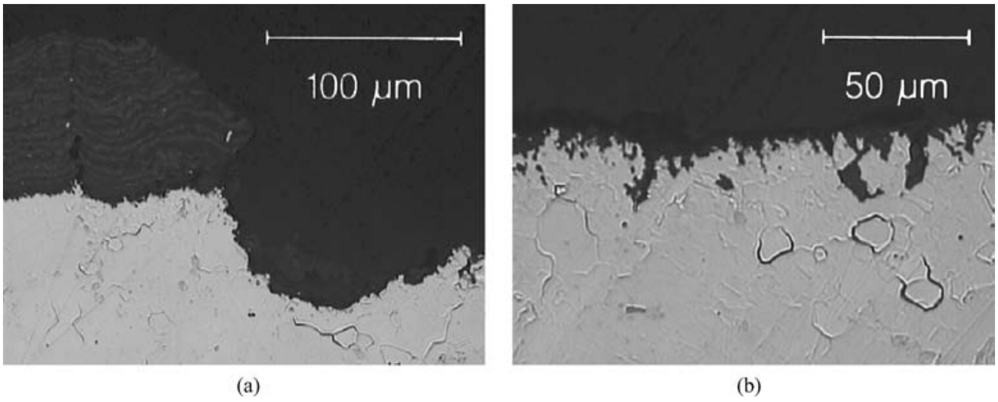
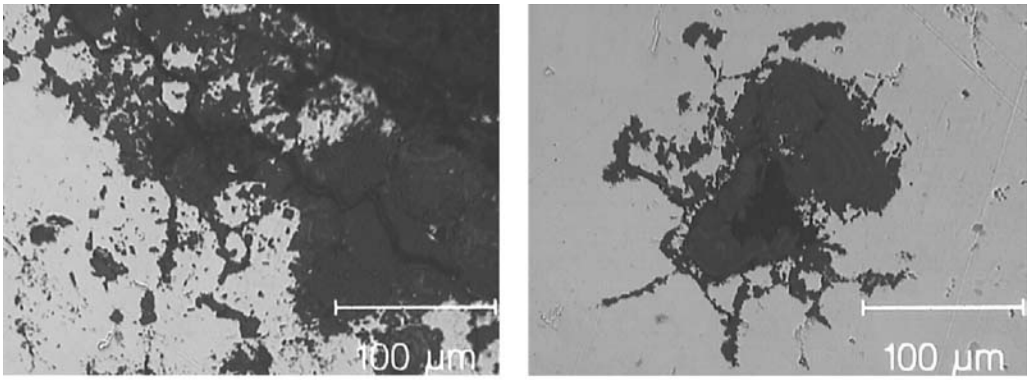


Figure 6 Cross section of deteriorated areas in sample S (unetched): crater-like interface between layered corrosion products and the underlying metal (a); pitting corrosion (b).



(a) (b)

Figure 7 Surface of deteriorated areas (unetched). Intergranular corrosion outlines the recrystallised microstructure and an intergranular crack is visible in sample S (a); pustule growing from an intergranular corrosion zone in sample S (b).

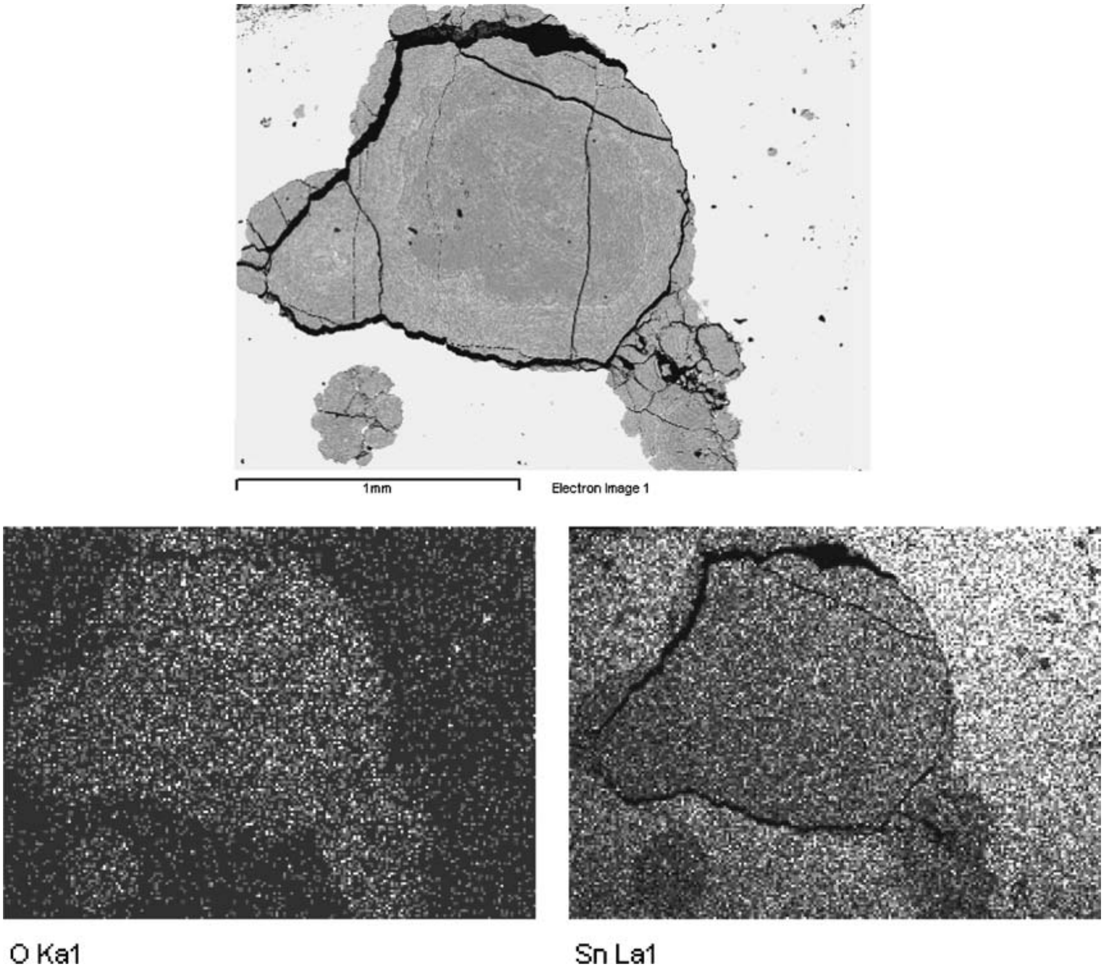


Figure 8 Backscattered electron image and RX maps of a pustule on the surface of sample S.

Actually, in the case of ancient samples affected by tin pest, both (i) oxidation of α-Sn and (ii) the reverse $\alpha \rightarrow \beta$ transformation at room temperature might decrease the probability of detecting the residual α phase even if the transformation occurred.

Firstly, α-Sn as well as β-Sn might be affected by atmospheric corrosion namely in the form of localised oxidation [4]. It is worth noting that the powdery consistency of α-Sn causes a high surface area to be exposed to the environment, thus favouring the oxidation process.

Secondly, the prolonged exposure of the object to temperatures higher than the transformation temperature during warm months, might revert the transformation thus leading to the local formation of brittle and non-coherent β-Sn. This is demonstrated for example by the results of XRD analyses on transformed areas of samples where tin

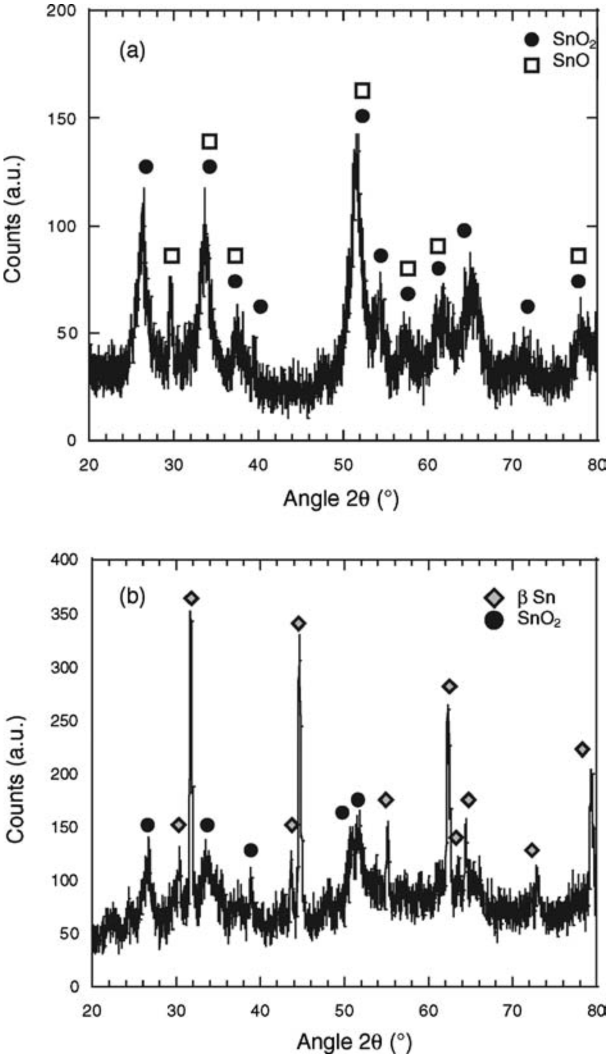


Figure 9 XRD patterns (Cu k_α radiation) measured on powders taken from dark grey pustules (a) and on deteriorated areas (b) of sample S.

pest was artificially induced: both peaks of α- and β-Sn were detected, thus proving the occurrence of the reverse $\alpha\rightarrow\beta$ transformation during measurements performed at room temperature [14].

For these reasons, and also because in some samples many of the conditions favourable to the allotropic $\beta\rightarrow\alpha$ transformation are satisfied (i.e. presence in the alloy of elements that favour the allotropic transformation, concentration of stresses due to sound generation, low temperatures in the environment of the organ) it is impossible to exclude the formation of α-Sn as one of the intermediate steps of degradation even if α-Sn has not been detected.

The distribution of pustules and the composition of the alloys might give some hints on the likeliness of the $\beta\rightarrow\alpha$ transformation. In the case of sample N, that consists of rather pure tin with only a very low amount of copper (Table II), the location of pustules near the hook that keeps the pipe vertical might indicate that the concentration of stresses in that area favoured the allotropic transformation. When the $\beta\rightarrow\alpha$ transformation takes place, the new powdery α phase has a low cohesion and a higher surface area than the corresponding amount of non-trasformed β phase, therefore the α phase is likely to oxidise more extensively than the massive metal. Furthermore, the lack of cohesion of the α phase that easily flakes off, exposes fresh metal to oxidation. For these reasons, the allotropic transformation might have actively contributed to the degradation of sample N.

On the other hand, the pipes from which sample A, R and T were taken are generally covered with pustules not located in a specific area related to stress concentration. In these cases, the degradation of the pipes is probably due to atmospheric corrosion of tin: all the samples contain delaying elements such as lead and bismuth and therefore the $\beta\rightarrow\alpha$ transformation is much less likely to have occurred. It is worth noting that sample T contains low amounts of lead and bismuth but also a noticeable amount of copper that favours the $\beta\rightarrow\alpha$ transformation. However, copper also has an influence on the corrosion behaviour of tin, since it segregates at grain boundaries, where it creates cathodic regions that decrease the overall corrosion resistance [19]. Also the location of pustules suggests that the degradation of pipe T is to be ascribed to atmospheric corrosion. In the case of sample S, mainly the high lead content but also the geographic location of the organ in a warm southern region, suggest to exclude the $\beta\rightarrow\alpha$ transformation as a cause of degradation.

5. Conclusive remarks

On the basis of these results, the degradation of tin pipes studied in the present work appears to be due to a more complex phenomenon than the plain $\beta\rightarrow\alpha$ transformation. We can express the following remarks on the degradation of tin pipes:

- The main alteration products on the external surface of deteriorated pipes are tin oxides SnO and SnO_2.
- Intergranular corrosion and localised formation of oxide pustules are observed.
- The product of the allotropic $\beta\rightarrow\alpha$ transformation, i.e. α-Sn, is never detected.

Oxidation has a significant role in the deterioration of tin pipes, even if many of the conditions favourable to the allotropic $\beta\rightarrow\alpha$ transformation are satisfied: presence in the alloy of elements that favour the allotropic transformation (or absence of elements that hinder it), low temperatures in the environment of the organ, plastic deformation by hammering of the sheet used for the production of the pipes and stresses due to sound generation. These considerations do not consent to exclude the formation of α-Sn as one of the intermediate steps of degradation in the case of samples with lower amounts of impurities and pustules located in areas where stresses concentrate, such as sample N.

In general, the chemical composition of the alloy, with particular regard to impurities that have an influence on the $\beta \rightarrow \alpha$ transformation, and the distribution of pustules along the pipe, can give hints on the likeliness of the allotropic transformation.

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