JOURNAL OF MATERIALS SCIENCE **39** (2004) 2767 – 2774

Study of ancient lead materials: A gallo-roman sarcophagus—contribution of the electrolytic treatment to its restoration

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The restoration of metallic archaeological artefacts needs the knowledge of ancient materials—their composition, their state of conservation and their manufacturing process—to avoid any inappropriate action in the restoration process. This paper is devoted to the study of a lead gallo-roman sarcophagus, found in a much corroded state after a long burial in a calcareous soil in the banks of the Rhône River at Lyon (France). From the metallographic observations, it was found that the lead sheets constituting the sarcophagus have been directly cast on a table covered with a bed of sand. In addition, the presence of a thick corrosion layer consisting of lead oxide, lead carbonates and some important penetrations of PbO in the metal explain the loss of lead ductility and the important brittleness of this ancient material. The mechanism of formation and growth of this PbO layer in a carbonated medium was studied using electrochemical experiments and metallographic observations. Finally, the comprehensive study of this complex material consisting of lead metals, a PbO/lead carbonate layer and some compounds of the soil allowed the setting up of a restoration process based on an electrochemical reduction method.

1. Introduction

Many problems arise from the restoration of metallic archaeological artefacts because of the presence of thick and important corrosion layers on the metal, which were formed whilst the object was buried in the archaeological site or during storage before restoration. Metallic archaeological materials are complex composite materials containing, in many cases, some compounds of the soil, several corrosion layers, and a metallic part. Besides the historical information of the object, such as ornamentations or marks of the artisan's tool used in the manufacturing process, is present in the corrosion layer, and must be conserved during and after the operations of restoration [1]. The composition, the state of corrosion and the manufacturing process of ancient materials are decisive in determining the course of restoration. Indeed, the restoration treatment must improve the visibility of the metallic surface and the historical details on the object and allow it to be exhibit in museums. For the metallic materials, mechanical or chemical treatments, such as pickling or dipping, are too aggressive on very corroded objects, and can destroy the historical details contained in the corrosive layer [2, 3]. Consequently, electrochemical treatments are often chosen to transform the corrosion layer into metal and to restore the initial metallic surface [4].

This study is concerned with the gallo-roman sarcophagi in lead belonging to the collection of the Museum of Gallo-roman civilisation of Lyon in France. During the gallo-roman period in Europe, lead was widely used for pipes in the water network, weights for clocks, looms, medals and especially as a material from which to make sarcophagi. In the banks of the Rhône River at Lyon in France, several lead sarcophagi were found in a very corroded state in the presence of a calcareous soil. Thus, they were in contact with an environment rich in carbonate species at a pH close to 8 for several hundreds of years. According to many authors, lead is relatively stable in this type of medium, forming different lead carbonate compounds such as cerussite $PbCO_3$, hydrocerussite $Pb_3(CO_3)_2(OH)_2$ or plumbonacrite $Pb_{10}(CO_3)_6O(OH)_6$ [5–7]. However, as the corrosion proceeds for several tens of years in museums, the surface of the lead artefact becomes incoherent and dusty, while the ductility of the metal decreases because of significant intergranular corrosion [8, 9]. This paper concerns a comprehensive study of the complex material of the sarcophagi, comprising a lead alloy and a thick corrosion layer. The mechanism

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of corrosion layer formation in a hydrogenocarbonate-enriched medium was studied by both electrochemical methods and metallographic observations. This allowed the history of this ancient lead to be revealed, and the conditions of the electrolytic treatment for the restoration of the metallic material of the sarcophagus to be selected.

2. Experimental techniques

After sampling the materials of the sarcophagus, metallographic cross-sections were prepared by embedding the samples in epoxy resin under vacuum followed by polishing in water with successively finer grades of SiC papers, and finally with colloidal silica dispersed in water (particle size: 0.1 μm). Then the samples were observed by a Scanning Electron Microscopy (HITACHI 250, equipped with a KEVEX Sigma energy-dispersive X-ray spectrometer). The composition of the samples was measured by Electron Probe MicroAnalysis (Cameca SX50). The corrosion products were accurately identified by X-ray diffraction (XRD) at room temperature (θ-2θ BRUKER diffractometer using Cu K_α radiation and equipped with a DACO MP acquisition system). The XRD diffractograms were analysed using the DIFFRAC AT Software with JCPDS Data Bank.

The electrochemical tests on pure lead in 0.1 mol$\cdot$l^{-1} $NaHCO_3$ were performed in a three-electrode electrochemical cell connected to an EGG PAR 273A potentiostat and driven by a computer. A circular and horizontal working electrode was placed at the bottom of the cell under a Pt-disk electrode. The reference electrode was a K_2SO_4-saturated Hg/Hg_2SO_4 electrode ($E = +0.658$ V/SHE), and all working electrode potentials are given versus this reference electrode. The working electrode was mechanically polished in the same way as the metallographic cross-sections.

In order to determine the optimum operating conditions for the electrolytic restoration treatment, experiments were carried out on samples of about 10 cm^2 taken from the sarcophagus. A three-electrode cell was also used: the sample of the sarcophagus as the working electrode, a flexible stainless steel wire gauze (surrounding the working electrode) as the counter electrode, and the reference electrode.

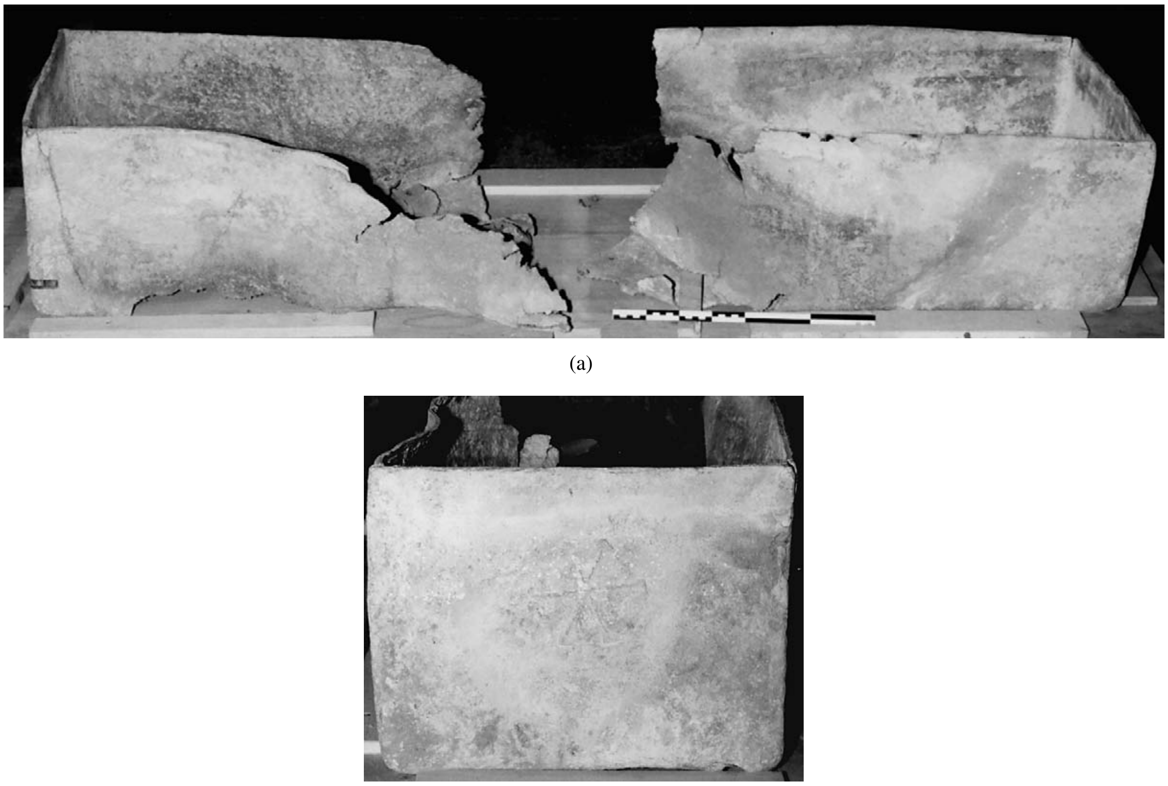
3. Results

3.1. Description of the state of sarcophagus

The sarcophagus consists of a lid in a relatively good state of conservation, and a box with numerous parts missing (Fig. 1a), of dimensions: $L = 172$ cm, $1 = 39$ cm and $h = 32$ cm. Some ornamentation, partially covered by the corrosion layers, as well as square-shaped, longitudinal handles are visible on the lid. Some figures with six branches are present on the outside faces of the box (Fig. 1b). These lead sheets show numerous zones of fracture and are deformed. In addition, numerous parts are completely detached from the chest.

3.2. Composition and microstructure of the metal

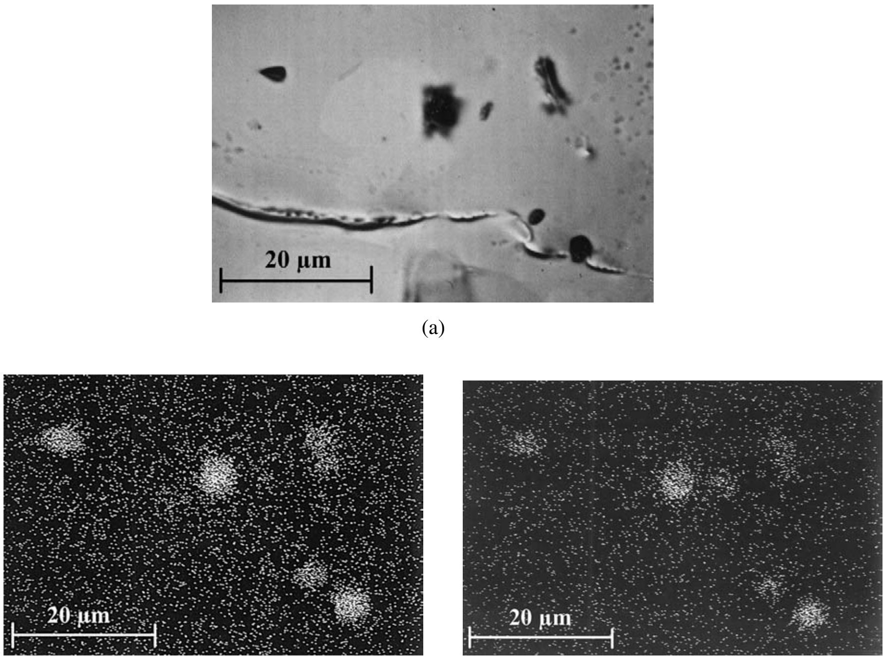
The lead contains around 0.5 wt% of tin and some traces of copper. As can be observed in Fig. 2 traces



(a)

(b)

Figure 1 (a) Photographs of the box of the lead gallo-roman sarcophagus before restoration and (b) Details of the decoration present on the outside faces of the lead sheets of the box.



(a)

(b) (c)

Figure 2 EPMA analysis of Cu-Sn intermetallic precipitates: (a) Backscattered electron image of precipitates, (b) Distribution of copper, and (c) Distribution of tin.

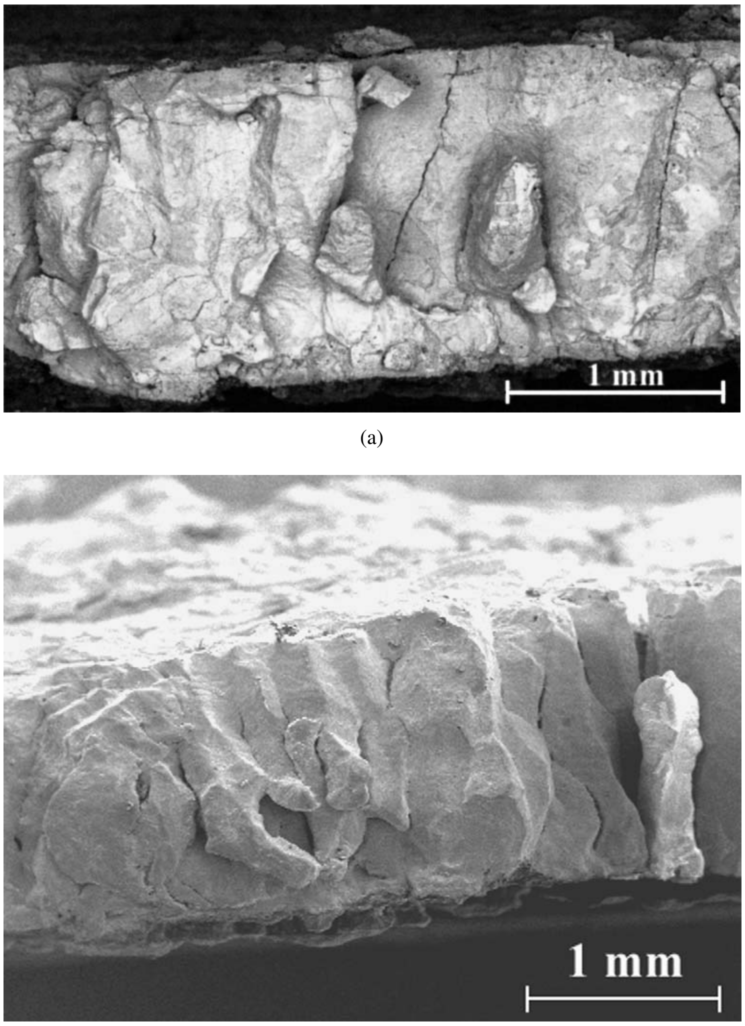
of copper are concentrated in small Cu-Sn precipitates, which are a few micrometres in size. Some parts of the lead sheet can be easily fractured. The observation of fractured parts by SEM shows a very basaltic structure with large grains preferentially aligned in the direction perpendicular to the two interfaces of the sheet, which are indicative of the presence of a temperature gradient during solidification (Fig. 3a and b). In some parts, the grain size is of the same order of magnitude as the sheet thickness, about 1 mm. These large grains also reveal a slow cooling rate of the metal after casting.

3.3. Analysis of the corrosion layers

As seen from Fig. 1, the surface of the sarcophagus is completely covered with a compact layer of corrosion products. After scraping away some of the layer, an X-ray diffraction analysis of the powder was carried out. Fig. 4 shows the corresponding diffractogram which reveals that this layer is essentially lead oxide (PbO tetragonal and Pb_3O_4 in small amounts) and lead carbonates ($PbCO_3$ cerusite and $Pb_3(CO_3)_2(OH)_2$ hydrocerusite). Some products resulting from the burial, such as calcium carbonate ($CaCO_3$), are also present on the surface of the sarcophagus. The cross-sections of several parts of the sarcophagus, presented in Fig. 5, show the distribution of the corrosion products. Directly in contact with the soil environment, a porous external layer, which consists essentially of cerusite and hydrocerusite compounds, is observed and it has a thickness of 500 to 1000 μm. This layer is found to mix with some soil residues containing calcium. A very compact internal layer with a thickness of 100 to 200 μm is observed at the metallic interface. Chemical analysis by EPMA shows that this layer is lead monoxide, PbO. The PbO layer penetrates into the bulk of the sheet by following the metallic grain boundaries. These penetrations, which involve mechanical stress, tend to disconnect the metallic grains, and weaken the metal by inducing cracks (Fig. 5a). The weight of these lead panels and the mechanical weakness due to the oxide growth have induced cracking, leading to the breakage of some parts, as shown in Fig. 1a.

3.4. Study of the corrosion of lead in 0.1 M $NaHCO_3$ solution

The stabilisation and the growth of a thick and dense PbO layer are surprisingly in a calcareous soil which is a hydrogenocarbonate enriched environment. Indeed, according to the literature [10], lead tends to become passive in soils by the formation of lead carbonate compounds. According to the thermodynamic data in the system $PbO\text{-}CO_2\text{-}H_2O$ and the potential-pH diagram of lead in these conditions, the lead monoxide PbO is not stable in the presence of carbonate species [5, 11]. In order to understand the formation of this thick PbO layer, the electrochemical behaviour of pure lead in a 0.1 M $NaHCO_3$ has been studied by voltammetry. As can be seen in Fig. 6a, the pure lead has a passive behaviour beyond -800 mV after the A1 anodic peak, characterised by a passive current less than 10 $\mu A \cdot cm^{-2}$. The first anodic double peak noted as A1 corresponds to the formation of the two forms of lead carbonate (cerusite and hydrocerusite). The reduction peak of these two compounds is noted as C1. At high potentials, the A3 and C3 peaks are assigned to the oxidation of Pb(II) species to Pb(IV) and to the reduction of Pb(IV) to Pb(II) respectively. The C2 reduction peak can be assigned to the reduction of PbO, which was formed on the passive plateau between approximately -800 and $+200$ mV. The formation of a very dense PbO layer was confirmed by the metallographic cross section of



(a)

(b)

Figure 3 Microstructure of the lead sheet of the sarcophagus after fracture.

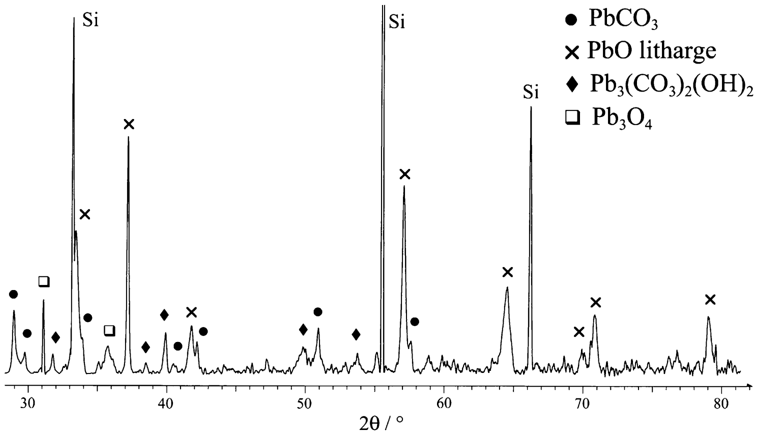


Figure 4 XRD pattern of the corrosion layer on the lead sheets of the sarcophagus with silicon as reference (Si is added to the powder as a standard).

the pure lead after oxidation at 0 V for 7 days in 0.1 M $NaHCO_3$ (Fig. 6b).

The formation of this duplex corrosion layer, PbO/lead carbonate, was also observed after immersion of pure lead in 0.1 M $NaHCO_3$ for 19 months. XRD analysis reveals clearly the presence of PbO litharge and a mixture of lead carbonates (cerusite, hydrocerusite and plombonacrite) which are also organised in a duplex structure as can be seen in Fig. 7. These experiments confirm that the formation of the thick PbO layer on the metal of the sarcophagus is due to being buried in a hydrogenocarbonate medium over several hundreds of years.

3.5. Study of the electrolytic process of restoration

The process of restoration should retrieve the original surface of the metal as much as possible in order to restore the historic information of the object. Electrochemical treatments or consolidative reduction was

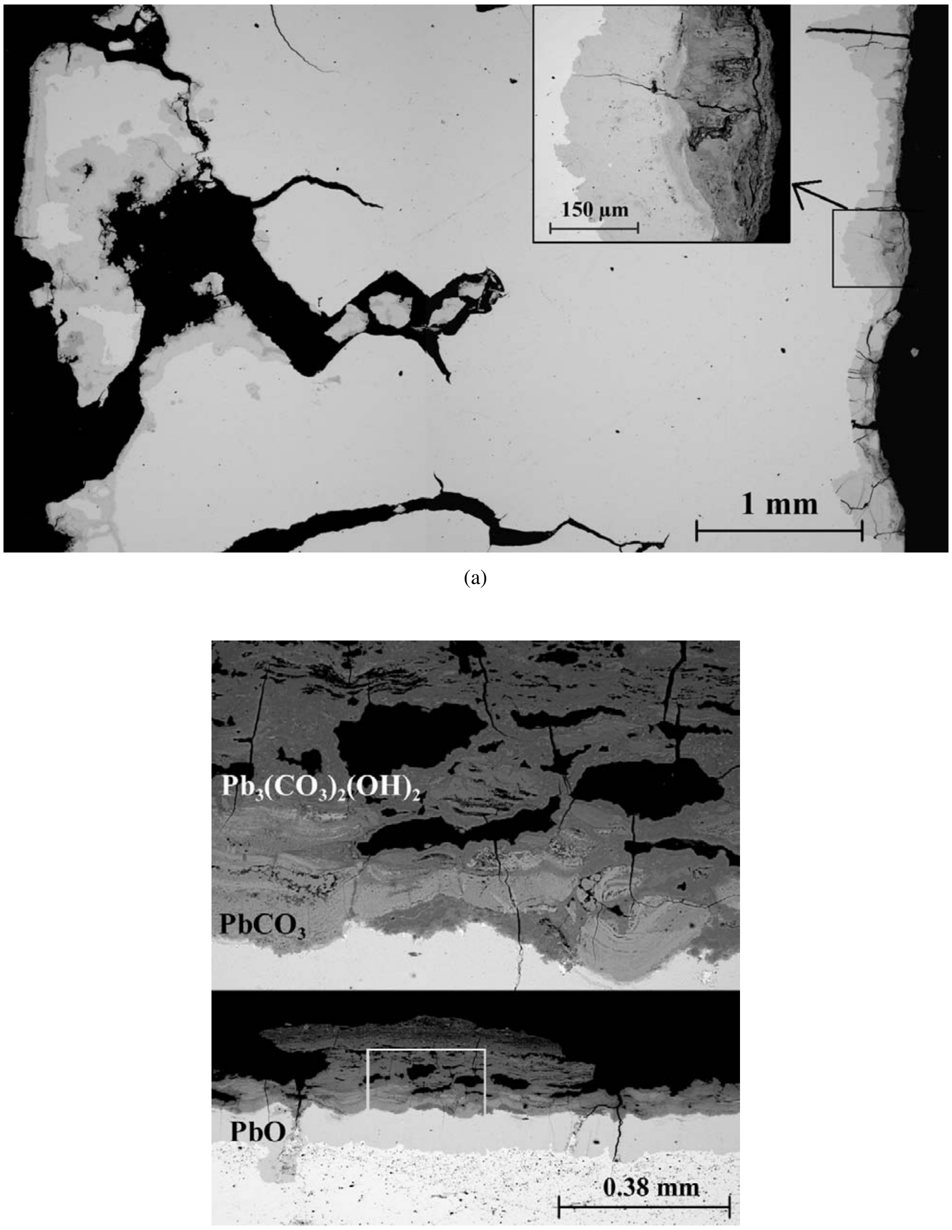


Figure 5 Typical cross-sections of the corrosion layers on the lead sarcophagi.

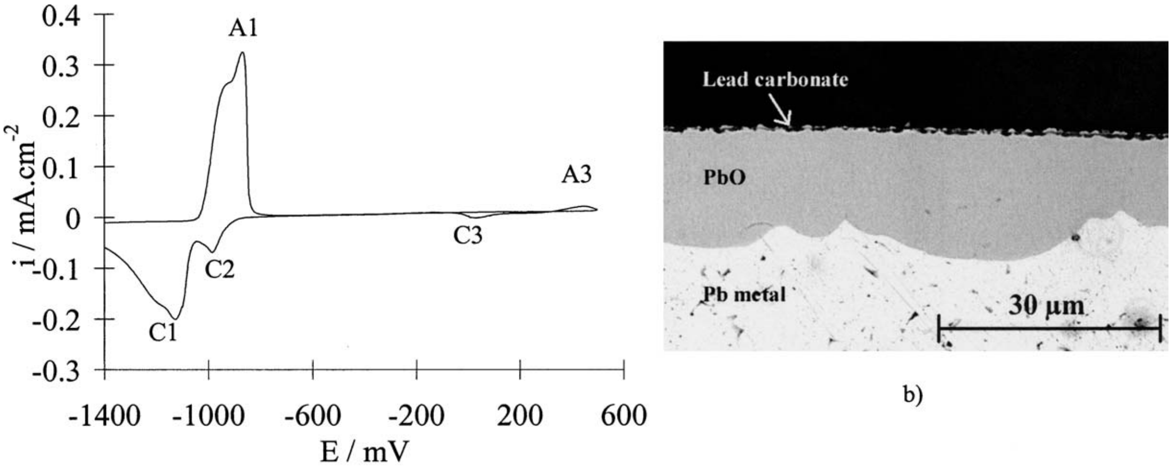


Figure 6 (a) Current density as a function of potential for pure lead in 0.1 M $NaHCO_3$ and (b) cross-section of pure lead oxidised at 0 V for 7 days.

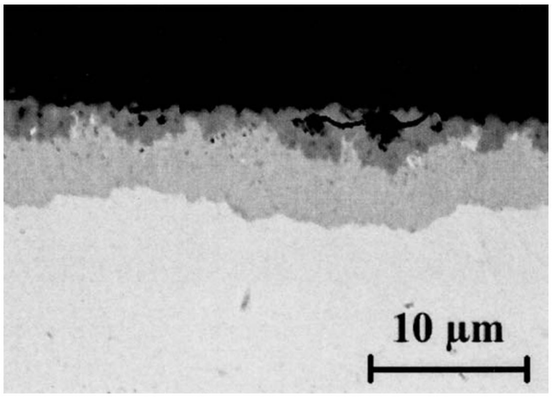


Figure 7 Cross-section of lead after an immersion in 0.1 M $NaHCO_3$ solution for 19 months.

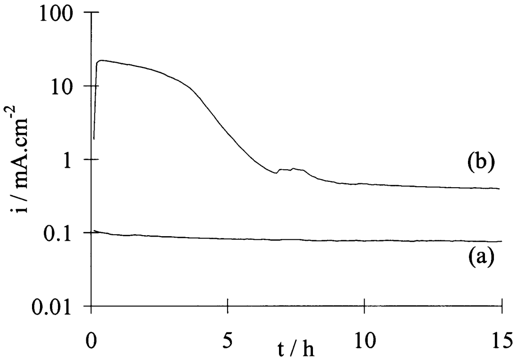


Figure 8 Typical current density as a function of time during the electrochemical reduction of the corrosion layer at −1.4 V (a) and at −1.7 V (b) in 0.5 M Na_2SO_4.

proposed in the 1960's to restore and consolidate very corroded metallic objects with powdery corrosion products [12, 13]. The electrochemical reduction process at low current has been extensively studied and used on lead artefacts in the case of very powdery corrosion layers of lead carbonate, because the porosity of the corrosion products allows the access of the electrolyte to the metallic surface. Generally the electrochemical reduction is carried out under potentiostatic conditions to avoid any local hydrogen evolution which can damage the brittle materials. According to Degrigny *et al.* [14], the reduction of the lead carbonate compound can be carried out at −1.4 V in 0.5 M Na_2SO_4 which is the potential for the reduction of lead carbonate in this medium. So, two reduction potentials, −1.4 and −1.7 V, were tested on two fragments of the sarcophagus in a 0.5 M Na_2SO_4 electrolyte (see Fig. 8). The measured current during the experiment at −1.4 V is very low and no change is observed on the piece after 24 h of reduction, whereas a high current is measured during the first hours of reduction at −1.7 V and the surface appearance of the fragment becomes more metallic. The metallographic cross-section displayed in Fig. 9a shows that after 2 h of reduction at −1.7 V, the unreduced PbO layer is present at the metal corrosion layer interface. Consequently, the reaction of the electrochemical reduction seems to occur at the corrosion layer/electrolyte interface and progresses inside the PbO layer towards the metal. After 24 h of reduction, the corrosion layer is completely reduced to lead metal, and the buried soil compounds, such as $CaCO_3$, remain on the metal and can be easily removed by mechanical cleaning of the object (Fig. 9b).

4. Discussion

According to the results of this study, the history of the sarcophagus lead material can be recounted: the making of the lead sheets by the plumber, their corrosion in a carbonated soil over several thousands of years, and their restoration by an electrochemical technique before exhibition in a museum.

Two main processes were used to make panels or sheets in lead: casting then rolling to make fine sheets, and casting at the required thickness on a table covered by a bed of damp sand. This second process easily allows ornamentation in relief to be pressed on the panels from the sand moulds. The metallographic study of the lead sheets revealed a very oriented structure with large grains, perpendicular to the faces of the sheets. These observations are consistent with the Encyclopaedia of Diderot et d'Alemenbert [15], which describes the casting techniques of large sheets of lead on tables. The low cooling rate of the metal at room temperature with a face in contact with cold damp sand induces the formation of large grains mainly oriented in the direction of the temperature gradient. To form the sarcophagus, the different panels were bent and soldered with a Pb-Sn alloy.

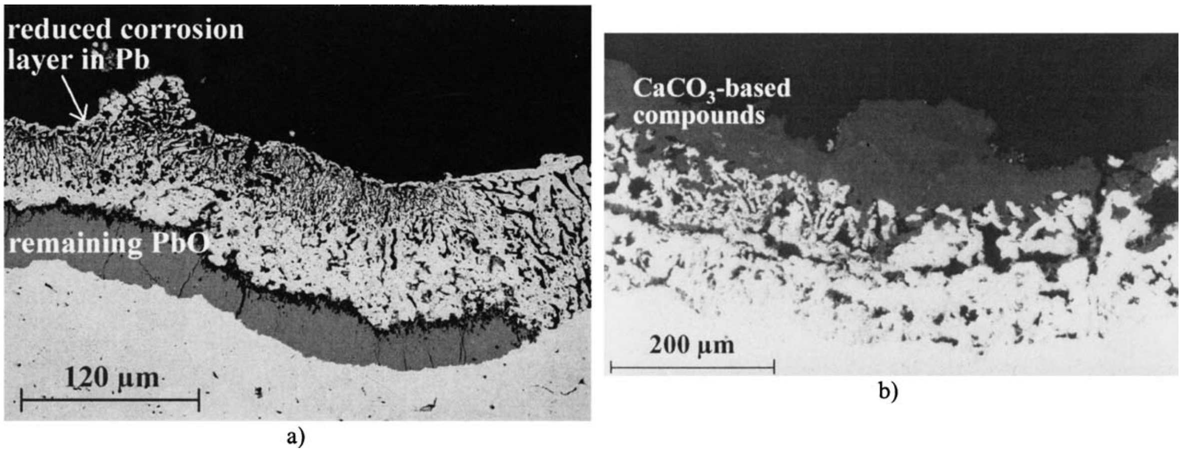


Figure 9 Cross-sections of the corrosion layer after (a) 2 h at −1.7 V and (b) at the end of the electrochemical reduction after 24 h.

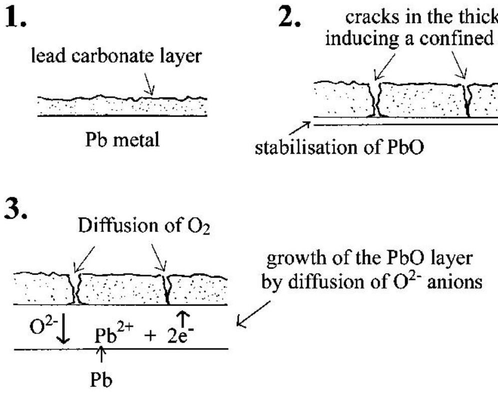


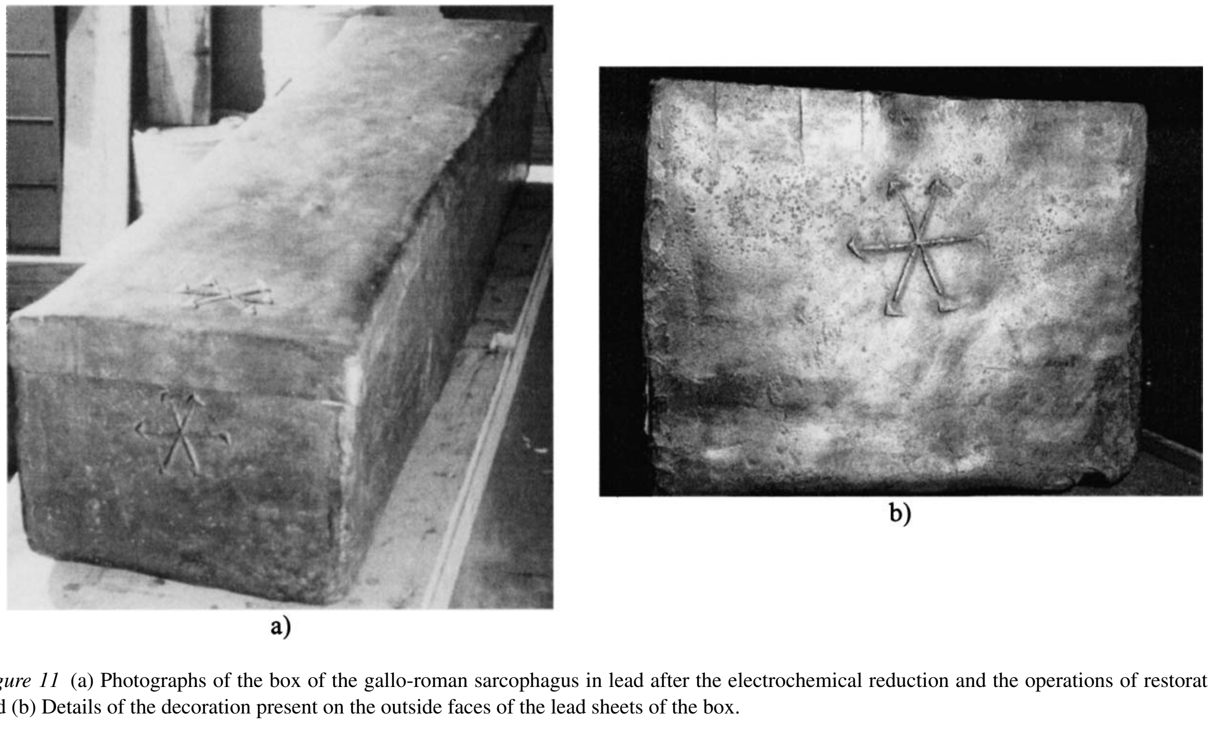
Figure 10 Schematic diagram of the mechanism of lead corrosion in $\mathrm{NaHCO_3}$.

Once completed, the sarcophagus was buried in a carbonated soil in the bank of the Rhône river at Lyon (France) for about 1500 years. After excavation, a thick duplex layer consisting of $\mathrm{PbO/PbCO_3/Pb_3(CO_3)_2(OH)_2}$ with significant intergranular corrosion was observed. Even though in a medium rich in carbonate species such as $\mathrm{HCO_3^-}$ and in contact with a significant partial pressure of oxygen due to the microbial activity in the soil [16], the lead monoxide PbO is not stable. Indeed, the thermodynamic data of lead compounds show that the lead carbonates (cerusite, hydrocerusite and plombonacrite) should be the most stable corrosion products. Nevertheless, according to these experiments, the formation of the duplex corrosion layer PbO/lead carbonate is possible by electrochemical oxidation at 0 V in 0.1 M $\mathrm{HCO_3^-}$ or by immersion in the same medium for a long time. In lead-acid batteries, the formation of PbO in sulphuric acid has also been observed [17, 18]. In this case, the lead is covered with a layer of lead sulfate $\mathrm{PbSO_4}$ under which PbO grows because of a local modification in the concentrations at the metal/$\mathrm{PbSO_4}$ interface [19].

TABLE I Evaluation of the parabolic constant K of the Wagner's model for the PbO growth on pure lead and the ancient lead of the sarcophagus

Conditions of oxidation	Oxidation time	PbO thickness (μm)	K/μm·month^{-1}
Pure Pb in a 0.1 M $\mathrm{NaHCO_3}$ solution	19 months	5 +/− 1	1.15 +/− 0.25
Ancient lead in a carbonated soil	1800 +/− 200 years	150 ∀ 50	1.02 +/− 0.45

In the same way, in a carbonated medium, the lead carbonate layer seems to act as a membrane inducing local conditions of pH and concentration at the Pb/lead carbonate interface. So, a local decrease in the concentration of carbonated species and an increase in the pH due to the reduction of dissolved oxygen are responsible for the stabilisation of a PbO layer (after 19 months of immersion) (as shown in Fig. 7). A schematic representation of the PbO growth in a $\mathrm{HCO_3^-}$ solution is shown in Fig. 10. Previous studies, using sulphuric acid solutions, have shown that the growth of the PbO layer under potentiostatic control is due to the diffusion of $\mathrm{O^{2-}}$ anions, because PbO litharge has sufficient ionic conductivity to ensure the transport of electrons and $\mathrm{O^{2-}}$ anions [20, 21]. In the case of the oxidation of lead in a carbonated medium at open-circuit, the compactness and the regular thickness of the PbO layer seem to indicate that a solid-state process governs the growth mechanism. Consequently, by assuming that Wagner's law for oxide growth at high temperature can be applied to the PbO growth, the parabolic constant, K can be calculated from the data in Table I using $w(t) = K \times \sqrt{t}$, where w is the thickness of the oxide, and t is the time of oxidation. It is worth noting that the values of K calculated for 19 months of oxidation



a)

b)

Figure 11 (a) Photographs of the box of the gallo-roman sarcophagus in lead after the electrochemical reduction and the operations of restoration and (b) Details of the decoration present on the outside faces of the lead sheets of the box.

and for 1800 years have the same order of magnitude. Thus Wagner's model may be invoked, to a first approximation, to explain the PbO growth in an aerated and carbonated medium at room temperature.

After the corrosive action of the carbonated burial medium, the sarcophagus needs restoration before exhibition in a museum. A process of electrolytic reduction was chosen. Contrary to the Pb/lead carbonate system [13, 14], the presence of a compact PbO layer seems to reduce the efficiency of the reduction current due to an important ohmic drop in the layer. The use of a very low potential is then necessary to produce sufficient hydrogen gas, which improves the penetration of the electrolyte within the internal layers. Consequently, the electrolytic reduction of the corrosion layer is favoured. In addition, the local mechanical action of the hydrogen release weakens the buried products remaining on the object, which facilitates the last operations of restoration. After the electrolytic treatment, the sarcophagus underwent a soft mechanical cleaning followed by rinsing with water and ethanol. Fig. 11 shows the state of the sarcophagus after reassembly. The electrolytic treatment gave rise to improved visibility of the ornamentation and the retrieval of some marks made by the artisan's tool.

5. Conclusions

To avoid any inappropriate restoration which could damage artefacts or delete historic information, a comprehensive study of the ancient materials is necessary. In the case of the gallo-roman sarcophagi in lead, the study of the metallic part of the material has allowed the casting process of the large sheets of lead to be deduced. After a long burial, the sheets of lead were corroded by a carbonated soil, leading to the formation of a very thick PbO/lead carbonate layer. Subsequently, an electrolytic treatment has been identified to retrieve the original metallic surface containing the historic information.

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Received 15 April
and accepted 5 December 2003