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Lead sheathing of ship hulls in the Roman period: Archaeometallurgical characterisation

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ABSTRACT

An archaeometallurgical analysis of samples of lead sheathing from five ships of the Roman period was carried out in order to determine their composition and microstructure, and to obtain a better understanding of their manufacturing processes. The examinations included optical microscopy of metallographic cross-sections, microhardness tests, scanning electron microscopy, including energy dispersive spectroscopy, and X-ray photoelectron spectroscopy. The results show that the samples were all composed of lead covered with an oxide layer. The sheet thicknesses, microhardness values and microhardness distribution, as well as the grain size distribution, led to the conclusion that all of the sheets were produced by the same technology, using hammering, and were probably used for the same purpose. The presence of antimony was observed in the sample from the Roman ship from Caesarea, which may hint at an Italian (Sardinian) origin of the material, and perhaps of the ship.

1. Introduction

In antiquity, mainly between the third century BC and the second century AD, ships' hulls were sheathed with lead. It is estimated that lead sheathing was applied on about two-thirds of ships' hulls in the Roman period [1]. The lead sheathing was a physical barrier against molluscs of the Teredinidae family, the genus Teredo, specifically the species *Teredo navalis* [2–5]. As lead is poisonous it also served as an antifouling agent. At the same time, it improved the waterproofing of the hull, which was made watertight mainly by the construction method, 'shell first', with the planking connected by mortise-and-tenon joints [6,7]. It also probably contributed to the ship's stability. The lead sheathing was formed into sheets, typically about 1 m square. The largest sheets measured 1.7–2 m [2,8,9], while the smallest were about 0.35–0.5 m [10]. The thickness of the sheets ranged between 0.9 and 2.5 mm, with an average of 1.25 mm [11]. The lead sheathing was nailed to the outside of the lower part of the hull, from the keel to about the first or second strake above the waterline. In several cases a woven textile was found between the lead and the hull planks (e.g., in the shipwrecks of Kyrenia [8,12], Marsala [2,13], Grand Congloué [14], St. Jordi [10], Nemi [9], Madrague de Giens [15]). The sheets were overlapped so that the water would flow smoothly over them from bow to stern [2,8,12]. The lead was attached to the hull by small tacks. Usually the tacks were of copper, with heads of an average diameter of slightly less than 2 cm, and length of just over 2 cm. The tacks created a diagonal or pentagonal pattern on the surface of the lead, with an average distance between them of about 7 cm [2,7,11,16,17 with many references under the entry 'lead sheathing' or 'lead sheathed' in the index].

2. Background to Research

Investigation of materials may indicate trade connections and interaction between cultures. This study combines typological

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considerations, as well as archaeometallurgic microscopic examinations using methods such as optical microscopy, scanning electron microscopy, microhardness tests, and chemical analyses. It extends the analyses, and may provide clues about the manufacturing process of metallic artefacts, and perhaps also about their origin.

Lead (Pb) is a very soft, usually 4–5 Vickers Hardness (HV), greyish metal with a face-centred cubic (FCC) unit cell, which is considered a heavy metal because its high density (10.66 g/cm^3). It has a low melting point of 327 °C, poor electrical and thermal conductivity, and is ductile and highly malleable, being easily extruded into rods, sheets and pipes.

During plastic deformation, dislocation motion begins and further dislocations are generated, resulting in a strengthening of the metal. The process of plastic deformation of metals at temperatures much below their melting point is called cold-working (or strain-hardening). The cold-working process increases the dislocation density in order to increase the strength and hardness of the metal. Lead is usually extracted from galena, which is a natural mineral of lead sulphide [18]. When pure lead is deformed it can recrystallise at room temperature [19,20]. Lead and its alloys are so soft that they are considered the most difficult materials for metallographic preparation, since distortion occurs during grinding and polishing. If the distortion layer is not removed, the true structure of the metal will not be exposed, since the deformation and heating develop recrystallisation of the surface and mask the true grain structure. Moreover, applying high pressure during grinding and polishing will cause penetration of the abrasive materials into the lead surface.

Lead has high resistance to corrosion, including to sea water, because it forms protective films, such as oxides (PbO, PbO_2, Pb_3O_4), sulphates and phosphates [21,22], but sulphate-reducing bacteria can attack the metal [2,14,15,23–25]. When extra corrosion resistance is required, lead containing around 0.06 wt.% copper is used. This kind of lead is resistant to sea water, as well as to acids, such as sulphuric, chromic and hydrofluoric acids [21]. Metallic lead is rare in nature, and lead is usually found in ores such as galena (PbS), anglesite ($PbSO_4$), cerrusite ($PbCO_3$), pyromorphite ($Pb_5(PO_4)_3Cl$), hydrocerrusite ($Pb_3(CO_3)_2(OH)_2$), and leadhillite ($Pb_4SO_4(CO_3)2(OH)_2$) [18,25,26]. Lead ores may also contain other elements, such as arsenic, antimony, bismuth, zinc, copper, silver, or gold. Lead has been used for thousands of years because its ore is widespread and easy to mine, and the metal is easy to smelt, melt and cast; and simple to work due to its ductility. It was used in classical times in water piping, anchors and sheathing of ships' hulls [18,25]. Numerous lead objects recovered from Roman shipwrecks have been found in underwater surveys along the Israeli coast, including hull sheathing, anchors, containers, fishing gear, sounding leads, lead ingots and cooking equipment [7,27–32].

Formation of stable oxide on a metallic alloy surface, which improves the alloy's resistance to uniform corrosion, may be destroyed by mechanical action (creep-strain) or by chemical attack. The mechanical action damaging the passivating film may be a result of residual stresses from the manufacturing processes as well as temperature changes. The chemical attack may result from exposure to an aqueous underwater environment [33]. When the passive layer is damaged, an unoxidised metallic surface is generated, behaving as a sacrificial anode in a galvanic couple. This results in cleavage crack propagation mechanisms of brittle fracture into the ductile material. The repassivation process of the exposed metallic film is suppressed by the presence of chlorides as well as continuous creep under stress, resulting in changing the mode of fracture from ductile dimple rupture to brittle intergranular cleavage or quasi-cleavage fracture [33].

3. Experimental Methods and Tests

Five samples of lead sheathing from ships, whose site locations and dates are summarised in Table 1 (Fig. 1), were studied in order to understand their manufacturing process. In all lead samples, cracks were observed in the brittle oxide film. Several methods were used, including metallographic optical microscopy (OM), scanning electron microscopy (SEM) examination, scanning electron microscopy–energy dispersive spectroscopy (SEM–EDS), X-ray photoelectron spectroscopy (XPS) measurements, and microhardness tests. All lead sheets were found to be covered with corrosion layers on both sides.

Table 1 – Sources of five samples of lead sheathing.

Sample no.	Site name	Location	Date	Reference/comments
1	Baratti, Pozzino B	Gulf of Baratti, near Livorno, Italy, (42°59.9′N, 10°30.1′E)	140–120 BC	[41], and Riccardi pers. comm.]. [a]
2	Grand Congloué 1	Near the island of Grand Congloué, near Marseilles, Southern France, (43°10.7′N, 5°24.0′E)	130 BC	[14 Fig. 83, 153 Fig. 84, 169, 171 pl. XXIX]. [b]
3	Madrague de Giens	Giens Peninsula, near Toulon, southern France, (43°02.7′N, 6°06.1′E)	75–60 BC	[15 pp. 85–87, Fig. 12, pl. XXXIV]. [c]
4	Caesarea	Caesarea, Israel, (32°30.5′N, 34°53.5′E)	1st century AD	[7 pp. 168, and pl. 38.1–2, 218; 32 pp. 185, 186 Figs. 11, 12].
5	Femina Morta	Between Punta Secca and Punta Bracetto, near Camarina, southern Sicily, (36°48.2′N, 14°28.6′E)	AD 300	[42] p. 625; [43], pp. 50–57, and Parker pers. comm.]. [d]

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[b] The lead sample was kindly provided with the help of Dr. Daniel Burette, the then Science Attaché of the French Embassy in Israel.
[c] The lead sample was kindly provided by Prof. Patrice Pomey.
[d] The lead sample was kindly provided with permission of Camarina Museum, Sicily.