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A method of conserving ancient iron artefacts retrieved from shipwrecks using a combination of silane self-assembled monolayers and wax coating

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ABSTRACT

Iron artefacts corrode severely in a marine environment, and require further conservation after retrieval. This research proposes a novel conservation method, based on a bi-layered concept: a thin silane self-assembled monolayer serving as nano-scale barrier, covered by a thicker waxlayer, which is applied by dipping the object into a suitable solution. An accelerated corrosion test was performed, using modern cast iron and steel samples, and repeated on archaeological wrought iron artefacts retrieved from shipwrecks. This protection, which can be easily applied, was found to improve the corrosion resistance of the artefacts.

1. Introduction

1.1. Corrosion of iron artefacts retrieved from shipwrecks

Corrosion of archaeological iron artefacts in shipwrecks buried for a long period under sand is an electrochemical process in a non-equilibrium state in an aqueous electrolytic environment, which often involves anaerobic processes caused by sulphate-reduction bacteria [1–3]. When iron is buried in a marine environment, the oxide layers grow slowly, resulting in the formation of various oxide and oxyhydroxide compounds. The common iron oxides are: Haematite (α -Fe₂O₃), Maghemite (γ -Fe₂O₃), Magnetite (Fe₃O₄), and Ferrihydrite (5Fe₂O₃·9H₂O). The common iron oxyhydroxides are: Goethite (α -FeOOH), Akaganeite (β -FeOOH), Lepidocrocite (γ -FeOOH), and Ferroxhyte (δ -FeOOH) [3–6]. Iron hydroxychloride, β -Fe₂(OH)₃Cl, which actually consists of a mixture of β - and γ -Fe₂(OH)₃Cl, is also common in iron artefacts retrieved from a sea environment [5–8]. During the corrosion process of iron artefacts in marine environment the chloride ions from the sea water migrate into the metal, resulting in a chloride concentration three times higher than that in normal sea water [9].

The deterioration of ferrous archaeological artefacts buried for some centuries results in the formation of thick corrosion layers of thickness varying from a few hundred microns to a few millimetres [10]. The corrosion rate of such ferrous archaeological objects depends on various factors, including the composition of the object (presence of phosphorus inclusion particles and the carbon concentration in the alloy),

the heterogeneity of the alloy, structural defects and cracks, and residual stresses. Moreover, the corrosion rate is influenced by the undersea corrosion medium conditions (the temperature and pH of the water, its salinity, environmental changes during the burial period, such as water movement, waves, storms and rain), corrosion mechanisms (including biological processes and the creation of biofilm coatings), the composition of the corrosion product (CP) layers (including the formation of various oxides, oxyhydroxides, chlorides, sulphides, sulphates, and carbonates) as well as the quality, thickness and density of the concretion layers [10,11].

Such iron artefacts commonly suffer from severe long-term corrosion, and are covered with a layered structure of thick encrustation and concretion. Marine encrustation is a solid coating layer (crust), built up on the surface of metal objects, especially iron, during a long period under water [12]. Marine concretion is a hard compact material (mainly calcium carbonate, CaCO₃) formed by mineral precipitation around a nucleus (such as an iron object) [13]. The concretion creates a barrier between the artefact and the underwater environment. In the Mediterranean Sea the concretion process of iron objects usually involves marine organisms [12]. Three main regions are commonly presented on the cross-sections of archaeological iron artefacts retrieved from shipwrecks: (1) metal; (2) corrosion product; and (3) concretion layers. Chlorides, β -Fe₂(OH)₃Cl, and sulphides (FeS phases) tend to be located in the external surface of the corrosion layer, between the metal and the concretion coating [7,8]. These thick encrustation and concretion coatings, composed of sand particles, shell

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fragments and remains of various marine organisms that create layers of CaCO_3 , serve as a protective cocoon, which partially isolates the artefact from its environment, and shields the metal from further aggressive corrosion process [1,4,14–16].

During the underwater concretion formation process, the iron and its surroundings interact: the metal gradually dissolves, and its surface is slowly covered with encrustation. The thickness, composition and density of these layers depend on the environment and the burial period. In this corrosion process, the surface area of the metal decreases as the concretion thickness increases [4]. If the object eventually reaches a state of equilibrium with its surroundings it will survive. Such encrustation and concretion layers developed on the ancient artefacts which were the subject of this study. These were T-shaped wrought iron anchors retrieved from the Tantura F shipwreck [17,18]; the cast iron cannonballs and the iron nails retrieved from the Akko 1 shipwreck [19–21]; the iron deadeyes from the Akko Tower Wreck [22]; and the wrought iron and cast iron objects retrieved from the Dor 2002/2 shipwreck [15]. The thickness, density and hardness of the encrustation and concretion layers depend on the underwater burial environment conditions [11].

Since there may be a long time span between the underwater excavation and exhibition in the museum, archaeologists are increasingly adapting an in-situ approach of preventive conservation, by creating underwater museums and parks [11]. When an iron object is retrieved and its concretion cover is damaged and cracked, it is no longer in equilibrium conditions. After retrieving, de-concretion and corrosion processes of the objects begin; wrought iron corrodes around the inclusions, and the existence of chlorides in the metal accelerates the corrosion rate. Therefore, as-retrieved damaged concretion cover leads to a significant increase in the corrosion rate [4,13,23]. Orange-red drops (called ‘sweating’) tend to appear on the iron artefact’s surface, resulting from the presence of chlorides [13]. When cast iron is retrieved and exposed to the atmospheric environment it is further attacked in areas rich in graphite flakes, as well as in the boundaries between the graphite and the metal iron [3].

When the concretion layers are removed, the retrieved objects are exposed to a rapid oxidation process, with chloride ions playing a major part, which could destroy the metal surface [24]. Hence, as soon as possible after excavation the conservator must cautiously remove the concretion coating layers, and only then begin the conservation treatment, avoiding the use of unsuitable materials whose future removal would further damage the artefact [4]. Therefore, it is recommended first, before removing the concretion, to perform an X-ray or gamma-ray radiographic test (RT), as for example, was made on the two wrought iron anchors from the Tantura F shipwreck [17] and the wrought iron deadeyes from the Akko Tower Wreck [22].

During the time between the removal of the coating and the start of anti-corrosion treatment, the corrosion may accelerate, and the artefact might be severely damaged [25]. It is therefore necessary to find a practicable solution to prevent accelerated corrosion of iron objects retrieved from shipwrecks.

After removal of the concretion, mechanical (such as by chisel, scalpel, and/or sandblaster) and/or chemical (immersion and/or electrochemical cleaning treatments) methods should be employed to remove external layers of corrosion products and marine microorganisms. The nature of the artefact, its preservation condition, and its hardness will determine which cleaning methods should be used. For electrically conductive metals the electrochemical cleaning treatments involve cathodic polarization [11]. Since ferrous archaeological artefacts retrieved from marine environments contain CPs, the archaeological object should be treated as soon as possible to remove chloride ions [5,26]. Electrolysis is used to clean large archaeological objects, such as anchors and cannons (for several years of treatment), and also to remove chlorides from the retrieved object (dechlorination) [7,8,11,24]. For metals, the stabilization treatments of the corrosion process mainly focus on the removal of chloride ions. The chloride ions

may be distributed in the corrosion layer in several forms: (a) free chlorides may be located inside pores, notches and cracks; (b) they may be trapped inside an iron hydroxychloride structure; and/or (c) they may be adsorbed at the surface of grains of different corrosion products [7]. The kinetics of the dechlorination treatments are mainly related to chloride diffusion through the corrosion layers, and are therefore promoted by high temperatures [27]. For large and/or chloride-contaminated objects, the electrochemical treatment is the most effective stabilization method [11]. However, electrochemical techniques are considered to be complicated and dangerous, and the treatment requires specialist expertise [11,24]. Furthermore, while many archaeological artefacts are treated by electrochemical methods and procedures, the exact effect of such electrochemical processes on ancient objects and their corrosion layers is not yet completely understood [28]. Many methods have been developed to remove the chlorides, among them simple immersion methods, which remove the chloride by diffusion in alkaline solution (such as NaOH solution), and the complicated hydrogen plasma treatment [7,27]. Nevertheless, today it is still complicated and challenging to be completely certain that a treated archaeological object will not present any remaining chloride ions that may cause future corrosion [5].

The cleaned and stabilized ancient artefact is then dried by a controlled process, and only then does the object undergo long-term conservation [11], such as coating with beeswax or paraffin wax (for example, with paraffin wax dissolved in benzene, or by dipping the metal into molten paraffin wax), and/or addition of inhibitors [23,29].

1.2. Common conservation solutions for preventing accelerated corrosion of archaeological iron artefacts

For archaeological iron artefacts excavated from soil environment (with no development of concretion), studies of protective coatings are common [30,31]. The main requirement for such protective coatings is corrosion resistance stability. Sadat-Shojai and Ershad-Langroudi examined the efficiency of various coatings (silicates, polyacrylates and alkoxy silanes) on the stability of historical metal artefacts [32]. Silicates adhere well to metals and also provide good protection in many aggressive environments; however, such coatings require ongoing treatment and are therefore not practical for some cases.

The common polyacrylate coating materials used for the protection of archaeological metal artefacts are Paraloid™ B-72 and Paraloid™ B-67 [30]. Watkinson compared the protective properties of Paraloid™ B-72 with those of wax, and found wax to be less effective in the short term [33]. However, although acrylic-based polymers have high adhesion capabilities, relatively good hydrophobicity, and also have high rigidity, they tend to decay with time [32]. Researchers have therefore explored the copolymerization of acrylic materials, and their blending with other resins. Polyacrylate and alkoxy silane blends, as well as fluoropolymers, have a potential as protective coatings. These materials are stable in sunlight, repel water and oil, and have good wettability. However, fluoropolymers tend to be expensive, their synthesis requires very high temperatures, and their application presents safety hazards and archaeological complications [32]. On the other hand, it has been suggested to apply copolymers of fluoropolymers and acrylic or silane-based polymers as protective coatings [34–36]. It seems that, although these copolymers have potential as protective coatings, their synthesis does not meet the requirement of being simple to use.

One of the more promising coatings that have received much attention in the last few years is ceramers – hybrids of organic and inorganic materials [37]. These hybrids have high adhesion, strength and flexibility, as well as good corrosion resistance [32]. However, their corrosion protection is strongly dependent on the environmental conditions, including temperature and pH [37].

Another coating that has been investigated in recent years involves plasma polymerization, a process in which the polymer is formed from

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