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Identification of Corrosion Products on a Medieval Copper-Silver Coin[1]

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Abstract—This work relates a study on a medieval coin found during archaeological works carried out at the site of Senhora do Castelo in Urros (Torre de Moncorvo, Portugal). The artefact has been identified as a coin of D. Afonso IX of Leon (1155–1188). The substratum showed composition typical of bullion, Cu–Ag (30–33%) with minor elements (1% Pb + 0.2% Sn + 0.4% Zn). The corrosion products developed on the coin during the archaeological burial was studied by means of optical microscopy (OM), scanning electron microscopy combined with energy dispersive spectrometry (SEM-EDS), energy dispersive X-ray fluorescence (EDXRF), and X-ray diffraction (XRD). The results show the presence of cuprite, atacamite, chalcocite, native silver, silver oxide and silver sulphide on the outer layers of the coin, which allows deducing the importance of the environment in the corrosion phenomena.

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INTRODUCTION

The interaction of archaeological artefacts with the neighbouring environment becomes very important in the field of preservation and corrosion.

Indeed, compared to centuries or millennia of burial, the data coming from those systems reflect true steady-state conditions. Most studies of different environmental conditions (soils [1, 2], atmosphere [3, 4] and water [5, 6]) tried to establish the correlation between the chemical composition of the artefacts, the surroundings, and the structure of patina. Those works are also a reference for the interpretation of the effect of stable compounds on the surface of metals and their mode of preservation.

The copper patina, initially, is mainly composed by cuprite (Cu_2O, 5–15 μm) formed near the metal. On the surface appears a brown color that turns black along the time. Depending on the environmental conditions, an external porous layer (5–40 μm) of brochantite ($Cu_4SO_4(OH)_6$) or atacamite ($Cu_2Cl(OH)_3$) may grow on the Cu_2O according to the following reactions:

$$4Cu + O_2 \rightleftharpoons 2Cu_2O, \qquad (1)$$

$$2Cu_2O + SO_4^{2-} + O_2 + 4H_2O \rightleftharpoons CuSO_4 \cdot 3Cu(OH)_2 + 2OH^-, \qquad (2)$$

$$Cu_2O + Cl^- + 1/2O_2 + 2H_2O \rightleftharpoons Cu_2(OH)_3Cl + OH^-. \qquad (3)$$

The thermodynamic stability of copper in these environments may be synthesised in the potential-pH (Pourbaix) diagrams for the $Cu–H_2O–S$ and $Cu–H_2O–Cl$ systems [7, 8]. It is clear the higher stability of cuprous oxide over cuprous chloride at neutral and alkaline pH values. Furthermore, it is possible to observe that the brochantite, tenorite and atacamite exist only in oxidizing conditions, while the cuprite (Cu_2O), chalcocite (Cu_2S) and nantokite (CuCI) exist in the reducing conditions typical of the burial.

The metallic elements added to copper to form alloys significantly change its corrosion behavior. The more noble (Ag) accelerate the corrosion, while the most active (Pb, Zn, Sn) promotes its cathodic protection during a certain period in function of the environmental aggressiveness. This is deduced by analyzing the relative stability of those metals in water through their Pourbaix diagrams [9].

Silver does not react readily with the oxygen at ordinary temperature in dry air. Adsorbed water layers into the oxide structure promote irregularities that allow the penetration of corrosive ions. The chlorides and sulphide ions, likewise, tend to widen crystalline defects of silver oxide leading to corrosion by local cells. Silver sulphide is a better electrical conductor than silver oxide which means an increase of thickness of corrosion bed with the time.

The knowledge of the place of burial is very important to understand the mechanism of the phenomena responsible for the patina. However, the archaeological finds occur in soils modified over time by human

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activities and climatic conditions. In the case of recent burials, aspects of geology, chemical composition, grain size, resistivity, water phreatic level, and soil pH are key elements to define similar conditions in accelerated tests.

EXPERIMENTAL

Archaeological Site

The artefact has been identified as a coin of D. Afonso IX of Leon, lost in a medieval universe with others artefacts, found during archaeological works carried out at the hill of Senhora do Castelo, parish of Urros, council of Torre de Moncorvo (Portugal).

The archaeological site is a medieval village, in an occupational continuity from Roman times, located at the foot of the hill, near the St. Apolinário's church. At the top of the hill exists a chapel; the analyses made to the plaster found revealed the chemical element gold suggesting the presence of paintings or fresh in agreement with the typical composition of the mortars used in that time. This chapel, possibly of Romanic architecture, is associated with a necropolis where eighteen burials were found.

This sacred space, suffered the effects of the unstable period of reconquest in Portugal, since this is a border area to control the Douros's river, and therefore has a strategic position, serving as refuge of people in times of war resulting from political conflicts again the kingdom of Leon [10]. It is thus the appearance at the top of Senhora do Castelo of a coin of D. Afonso IX of Leon and other archaeological finds from Roman and medieval times.

Morphological Characterization

The exhumed coin (SB1 00, No reg. 29) characterized in Table 1, is a coin of Afonso IX of Leon (Fig. 4) dated from 1155–1188 [11]. This coin is named as a "bullion", because its chemical composition shows a copper-silver alloy.

Table 1. Morphological characteristics of the coin

Weight, g	Minimum diameter, mm	Maximum diameter, mm	Thickness, mm	Axis
0.71	17.01	18.27	0.41–0.77	12

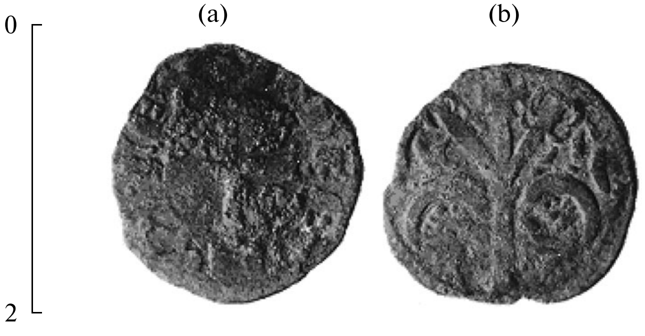

Fig. 1. Medieval coin: (a) Anvers—an equilateral cross, bordered by flowers, with the caption, + A (L) DEF (O) NS · REX; (b) Reverse—tree surmounted by a cross and decorated flower, flanked by two Hons.

Methods of Analysis: SEM-EDS, XRD, FRXED and Optical Microscopy

The morphology, microstructure, and chemical composition of corrosion products developed on the artefact were studied using a combination of nondestructive analytical techniques.

An optical microscope Nikon Eclipse L150 model, equipped with a camera, allowed obtaining images with various extensions.

The images of scanning electron microscopy (SEM) and analysis by energy dispersive spectroscopy X-ray (EDS) were made with an equipment FEI Quanta 400FEG, fitted with a probe for micro analysis EDAX Genesis X4M. The conditions of observation of the analysis varied slightly from sample to sample in order to highlight aspects of interest in each situation. In all cases, the pressure inside the chamber was about 6×10^{-2} Pa. The distance between the objective lens and the sample, ranged between 6 mm and 10 mm. There were used three accelerators of energy (10 keV, 15 keV and 25 keV) to measure changes in the composition's depth.

The X-ray diffraction (XRD) spectra were recorded in the equipment Panalytical XPER PRO with slits

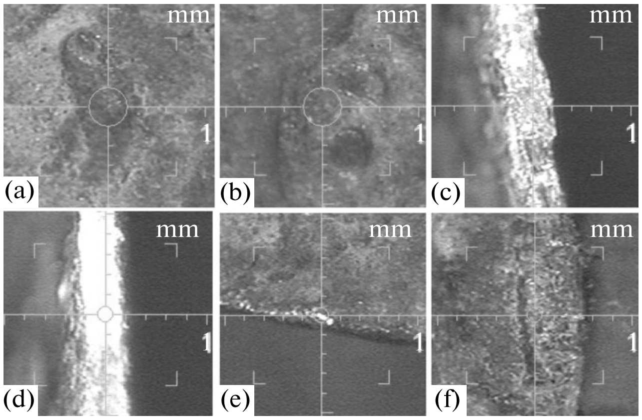

Fig. 2. Optical photographs in several points of the coin: (a) pitch-dark reddish surface area; (b) yellow-greenish surface area; (c) border scrapped reddish area; (d) border scrapped area with metallic lustre; (e) edge greenish area with metallic lustre; (f) pitch-dark reddish border area.

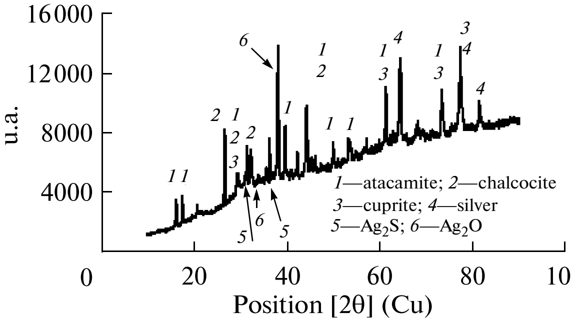

Fig. 3. X-ray diffractogram of the coin.

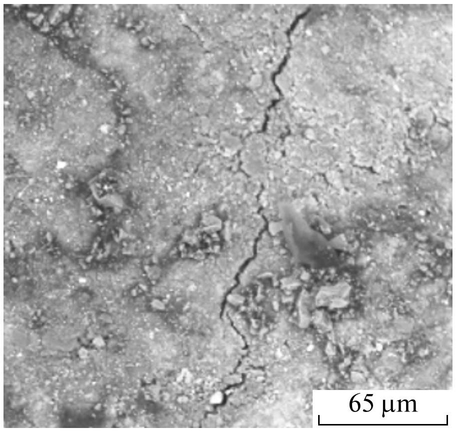

Fig. 4. SEM image of the coin.

fixed (divergence slit of 1° and Soller 0.04°). The beam copper anti-cathode was used at a scanning rate of $0.0006° s^{-1}$ 1 from –10° to 90° (2θ). The species identification was performed trough the High Score Plus software Panalytical with the ICDD database.

The chemical analysis by X-ray fluorescence energy-dispersive (FRXED) were performed on the equipment Spectro X-test, with a field of view with a diameter varying from 3 mm to 10 μm and up to 3 μm deep.

To preserve the samples, the tests to determine there chemical composition were made directly on their border after scraping.

RESULTS AND DISCUSSION

The optical observation in several zones of the coin, Fig. 2, and the respective FRXED analysis, Table 2, show the following: a structural changes in the surface with a pitch-dark reddish brown base, on which products are green, yellow-greenish and occasionally with metallic lustre; the dark reddish areas are linked to the silver and the brown areas to interactions of metal with the ground; the scrapped border areas with reddish colour and the metallic brightness zones are related, respectively, with copper and silver; the corrosion products of red-brown colour should be cuprite (Cu_2O), the yellow colour hematite (Fe_2O_3), the yellowish greenish colour atacamite ($Cu_2(OH)_3Cl$), the dark-brown colour silver oxide (Ag_2O) or silver sulphide (Ag_2S), and green colour malachite ($Cu_2(OH)_2CO_3$).

The analyses performed on the areas in the Figs. 5c and 5d show the copper as the mainly element in the coin. The chemical composition of this artefact belongs to the class of Cu–Ag alloys. It is a coin called "bullion" with a low content of silver and with minor elements (Pb 1%, Zn 0.3% and Sn 0.2%).

According to the monetary system based on gold-bullion at the time (since 1085) [12], the first mintages of bullion have about 30% Ag [13]. The quantity of silver in the coins of Leon has a range variety of 0.27 g to 0.18 g between the first and last time in the emission of Afonso IX [14]. The analysis made in this coin point to a bullion with 30–33% of silver.

The presence of areas in the coin with higher content of silver is a normal behaviour in Cu–Ag alloys due to the low solubility of silver in copper, and vice versa, at room temperature [14]. Indeed, the solubility of Cu in Ag is of 8% at 780°C (eutectic temperature), and practically zero at room temperature. During the

Table 2. FRXED analysis in several points of the coin

Area analysed	Elemental composition (%)						
	Cu	Ag	Pb	Fe	Sn	Zn	Ca
Fig. 2 a; face without scraping	65.8	26.3	2.1	2.0	–	–	3.8
Fig. 2 b; face without scraping	52.8	29.3	2.5	5.2	0.7	–	9.5
Fig. 2 c; border with scraping	79.6	18.9	1.0	–	0.2	0.3	–
Fig. 2 d; border with scraping	58.7	39.1	0.9	0.7	0.2	0.4	–
Fig. 2 e; edge without scraping	56.9	37.8	2.2	3.1	–	–	–
Fig. 2 f; edge without scraping	45.6	51.7	2.7	–	–	–	–

Table 3. Identification of chemical elements of the outdoor layers of the coin by EDS

Spectra	Elemental composition (%)												
	C	O	Cu	Ag	Pb	Fe	Ca	Al	Si	Mg	P	Cl	K
10 keV	36.5	31.8	9.8	0.8	1.4	1.9	3.2	3.6	5.6	0.2	3.5	0.6	1.1
15 keV	34.2	30.4	12.4	1.4	1.6	2.0	2.8	3.5	5.6	0.2	4.0	0.7	1.2
25 keV	35.5	30.6	12.8	1.0	1.9	1.6	2.4	3.0	5.5	0.2	3.7	0.8	1.0

cooling, the system separates each component in the pure state with the same reticular structure as the one in the supersaturated solid solution. So, the formation of rich areas of silver dispersed in copper matrix depends on the rate of cooling and thickness of the sample [15–18]. However, it is worth noting that hammering operations associated with any cycles of heating (200–300°C) in the manufacture of coins can also promote macroscopic or microscopic segregation. The little content of Pb, Zn and Sn is concerned with the extraction of silver from ores containing galena, spharelite and cassiterite.

The elements Ca and Fe present in the artefact, come from soil contamination, as well as Si, Mg, P, Al, CI and K detected by EDS analysis, Table 3.

The contact between different metals promotes galvanic couples in the presence of an electrolyte, which corrosion phenomena can also originate structural heterogeneities. Considering the standard electrode potentials of silver, copper, lead, tin and zinc, vs. NHE, respectively, 0.800 V, 0.337 V, –0.126 V, –0.136 V and –0.763 V, the thermodynamic tendency for corrosion of these metals is: Zn > Sn > Pb > Cu > Ag.

The outdoor layer composition of the coin points clearly to a preferential dissolution of lead, with its subsequent deposition on the surface. Indeed, the relative percentage ($r_i = M_i/\sum_{i=1}^{3} M_i$) between the three metallic elements on the surface is: $r_{\rm Cu} = 81 > r_{\rm Pb} = 12 > r_{\rm Ag} = 7$. These results show an increase of lead content in the surface of the order of twelve times in relation to its share in the chemical composition of the artefact, $r_{\rm Pb} = 1$. However, $r_{\rm Cu} = 81$ is larger than the value for the alloy composition, $r_{\rm Cu} \sim 70$, hence the greater amount of corrosion products of copper on the surface. The crystalline compounds identified by X-ray diffraction, Fig. 3, were cuprite (Cu_2O), atacamite ($Cu_2Cl(OH)_3$), chalcocite (Cu_2S), native silver (Ag), silver oxide (Ag_2O) and silver sulphide (Ag_2S). The sulphur element does not appear in the spectra by EDS analysis because the overlap of spectral lines of S and Pb.

The development of corrosion on the artefact can be seen initially as the selective dissolution of copper in the coin-soil interface, while silver remains cathodic. The cuprite is formed on the surface, and later converted into other chemical compounds in agreement with the environment. The atacamite suggests the presence of chlorides in the place of burial, while chalcocite the presence of an anaerobic reducing environment. However, despite being the silver cathodic in galvanic couples with copper it may also suffers corrosion due to local action cells according to the following reactions:

$$2Ag + 2NaCl + 1/2O_2 + H_2O \rightleftharpoons 2AgCl + 2NaOH \quad (4)$$

$$2Ag + H_2S + 1/2O_2 \rightleftharpoons Ag_2S + H_2O \quad (5)$$

$$2Ag + 1/2O_2 \rightleftharpoons Ag_2O \quad (6)$$

The presence of chlorides may induce an autocatalytic corrosion of copper, according to the following reactions:

$$1/2O_2 + 2H_2O + 2CuCl \rightleftharpoons Cu_2(OH)_3Cl + HCl \quad (7)$$

$$HCl + Cu \rightleftharpoons CuCl + 1/2H_2 \quad (8)$$

The silver can also suffer attack by copper (II) ions in the presence of chloride ions according to the reaction (9) [19]:

$$Cu^{2+} + 2Cl^- + Ag \rightleftharpoons AgCl + CuCl \quad (9)$$

The silver chloride, although insoluble in water, does not grow as a protective coating on the surface. So, and taking into account also the solubility of cuprous chloride in water (2.95×10^{-3} g mol cm^{-3}) [19, 20], this reaction is rendered decisively corrosive in the copper enriched areas and is induced by oxygen and humidity.

At observed in Fig. 2f and Fig. 4, the coin presents fractures and fissures along the thickness. The brittle behaviour of coins or other articles of Cu–Ag alloys is not uncommon. The weakness can result from chemical composition and microstructure, as well as from metallurgical processes, heat treatment and/or mechanical during the manufacture.

Some cracks observed in the patina may result from changes in volume resulting from corrosion, which favours the transfer of elements from the soil to the artefact promoting its intergranular corrosion.

The extent and depth of the corrosion phenomena will be depend on several variables, such as physical and chemical characteristics of the place of burial, type of electrolyte and the alloy microstructure.

CONCLUSIONS

The combined action of non-destructive analytical techniques of SEM-EDS, XRD, OM and FRXED allowed interpreting the nature of corrosion products formed on the medieval coin during the archaeological burial. The analyses show the presence of chlorides on the outdoor layer of the artefact that means a catalytic corrosion process.

The presence of chalcocite beyond atacamite indicates a burial under anaerobic conditions.

The interaction of the environment with the metallic material was evidenced by the EDS spectra, through the presence of the elements Cl, Mg, Ca, K, Si, Fe outside the alloy composition of the artefact.

The existence of rich areas in silver in the coin was also justified from the binary diagram of Cu–Ag alloys, in the manufacturing process, and phenomena of selective corrosion.

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