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EVIDENCE OF ABNORMAL HIGH SILVER CONTENT IN A POLISH POLOTRAK COIN ISSUED IN 1624 AS CONSEQUENCE OF ADVANCED COPPER CORROSION

Nicoleta IGNAT[a], Emanoil PRIPON[b], Simona Elena AVRAM[c], Lucian Barbu TUDORAN[d,e], Gheorghe BORODI[e], Ioan PETEAN[a*], Marzena GROCHOWSKA-JASNOS[f*]

ABSTRACT. Long ground resting of coins small denomination might affect their microstructure due to advanced corrosion. It is well known that cleaning of silver-copper alloy artifacts leads to a surface enrichment of the silver amount due to the partial removal of the copper grains which are more corroded. We found a półtorak issued in 1624 with abnormal characteristics like lower weight and dull sound when it is thrown on the solid surfaces. It resulted to be made of very high silver content about 97 wt. % according SEM-EDX correlated with XRD in great discordance with the common półtoraks from 1624 having about 70 wt.% silver. Advanced investigation of the abnormal półtorak reveals a porous internal structure indicating complete dissolution of β grains and copper sheets within the eutectic. All observation pleads for a progressive corrosion involving partial leaching of product through the wet resting ground which might ensure the dissipation of the corrosion-product and affecting deeper layers. Such dynamic-corrosion for

[a] *Faculty of Chemistry and Chemical Engineering, Babes-Bolyai University, 11 Arany Janos Street, 400028 Cluj-Napoca, Romania.*
[b] *Zalau County Museum of History and Art, 9 Unirii Street, 450042, Zalau, Romania.*
[c] *Faculty of Materials and Environmental Engineering, Technical University of Cluj-Napoca, 103-105 Muncii Bd., RO-400641, Cluj-Napoca, Romania.*
[d] *Faculty of Biology and Geology, Babes-Bolyai University, 44 Gheorghe Bilascu Street, 400015 Cluj-Napoca, Romania.*
[e] *National Institute for Research and Development of Isotopic and Molecular Technologies, 65-103 Donath Street, 400293 Cluj-Napoca, Romania.*
[f] *Museum of Archaeology and History in Głogów, Brama Brzostowska 1, 67-200 Głogów, Poland.*
[*] *Corresponding authors: ioan.petean@ubbcluj.ro; marzena.grochowska@gmail.com*

300 years might explain this intragranular corrosion which transforms an Ag-Cu hypereutectic alloy into almost pure silver. This preliminary hypothesis must be further investigated on larger półtoraks hoards which might have such abnormally corroded coins and on suspicious random finds.

Keywords: *półtorak, microstructure, corrosion, copper loss*

INTRODUCTION

Półtorak coins issued by King Sigismund III of Poland had a great impact in the monetary circulation during 17th century with real impact in early 18th century supplying demand of small trustful silver coins. Their relative steady quality makes them desirable for daily commerce and is found in many hoards discovered in whole Central and Eastern Europe [1, 2].

Półtoraks, silver coins worth one-and-half groschen (pol. *grosz*) are among the most distinctive types of small money minted in the Polish-Lithuanian Commonwealth during the reign of Sigismund III Vasa (1587–1632). The introduction of this denomination in 1614 was a response to the shortage of small coins in the west border areas of the Polish Kingdom, which had been ongoing since the late 16th century, and to the growing influx of weaker German coins, including the so-called "apple" groschen from Brandenburg. In this way, the półtoraks became not only a means of payment within the country but also a component of Poland's monetary and economic expansion into neighbouring European markets.

Circulating alongside Hungarian denars, Imperial groschen and Czech groschen, they met the need for small change in everyday trade, whilst also serving as a tool for speculation and manipulation by experienced traders, who exploited the general monetary confusion to inflate the value of individual currency units [3]. This is evidenced by the fact that one-and-a-half-groschen (półtorak) coins are found alongside other small denominations minted at that time in Central European countries. The situation in the money market of Central and Eastern Europe was brought under control to some extent following a series of reforms implemented in 1659 by Emperor Leopold I in the Roman-German Empire, and in the early 1660s and 1670s in the Polish-Lithuanian Commonwealth, as well as through the imperial ordinances of Zinna (1667) and Leipzig (1690) [4, 5]. Półtoraks, even more than Polish half-groschen (pol. *półgrosz)* and 3-groschen (pol. *trojak*) coins, were the most common Polish coins in the first half of the 17th century in Austria, Bohemia, Moravia and Silesia, but also to the east and south-east of Poland – in Ukraine, Slovakia, Hungary and Romania, as well as other Balkan countries within the sphere of Turkish influence (Ottoman Empire) [3, 5, 6, 7].

The moment of the Polish półtorak entering Transylvania has long been disputed in Romanian numismatics. In 1964, Costin C. Kirițescu, referring to the monetary circulation in the period 1620-1625, stated that Polish półtoraks are present in large quantities [8]. Eugen Chirilă also advanced the idea of the półtoraks entering immediately after 1620, with the subsequent clarification that, since they needed four to six years to reach Transylvania, the maximum flow of coins occurred in the years 1627-1629 [9]. Judita Winkler rejected the idea of the massive penetration of Polish półtorak in the second half of the third decade of the 17th century [10], and the Hungarian numismatist János Buza also supported the idea of the massive penetration of półtorak into monetary circulation in Transylvania, since the first years of Gabriel Bethlen's reign, but demonstrates that these issues were not to blame for triggering the monetary crisis in the first half of the third decade, as was long believed [11].

In 2016, Corina Toma published the results of an analysis carried out on a batch of 38 monetary hoards (with over 19,900 coins, of which półtoraks represented 77%, present in 32 hoards), belonging to the chronological group 1625/1626-1668 [11]. According to this analysis, it places the penetration of Polish coins with a value of one and a half groschen, only after the death of Gabriel Bethlen, when a new wave of Polish currency, to which is added, in overwhelmingly smaller percentages, półtoraks issued in Elbing, Riga, Brandenburg-Prussia (Königsberg), in the second and third decade of the 17th century, still in circulation in Poland [11]. Although the first early attestation of półtoraks in hoards was made with the discovery of a hoard from Zalău with eight półtoraks issued during 1622-1625, we subscribe to the opinion that this monetary type entered Transylvania towards the end of the third decade-beginning of the fourth decade of the 17th century [7]. In the hoards of Transylvania, the issue of 1624 counts 2869 pieces [11].

A study conducted on a batch of medieval coins, part of a hoard of about 1400 coins discovered in Iași, highlighted the fact that some of the coins showed advanced intragranular corrosion, which led to their disintegration. Also, due to the long period of lying in the soil, the surface of the coins was affected by the selective corrosion process, resulting in an increase in the concentration of silver on the surface, in relation to the coin as a whole. The surface silver enrichment process is responsible for the apparent silvering appearance, observed in cross-section, by optical microscopy

[12]. Of course, the cross section metallographic investigation of a coin reveals valuable information of the surface and bulk microstructure but very often consists of complete damage of the investigated coin. However, the enriched silver outermost layer can be gently removed from a small, targeted area allowing a proper investigation of the coin's bulk without sectioning it.

The półtoraks conservation state strongly depends on the long resting in the ground and its physicochemical parameters such soil composition and moistening degree. A minor mishandling of a półtorak issued in 1624 reveals abnormal characteristics like increased brittleness and fragile structure associated with reduced weight and dull sound when it is ringed on the solid surface. This behavior is completely different than well preserved półtoraks issued in the same year. Therefore, the aim of the present study is to effectuate a comparative physicochemical investigation between a regular półtorak issued in 1624 and the abnormal one. The microstructural investigations assisted by high resolution SEM coupled with EDX elemental analysis can provide useful clues for proposing a corrosion mechanism. Thus, an advanced intra granular corrosion of the coins facilitated by the long resting in a specific soil might involve with some hydro soluble product. Its repeated contact with pluvial water infiltration might leak copper from the microstructure altering the coins characteristics, a fact which will be further discussed.

RESULTS AND DISCUSSION

Most of the półtoraks were issued in the Bydgoszcz mint, having a constant design pattern. Photographs of the investigated coins are presented in Figure 1. The obverse feature Poland kingdom shield with Wasa family arms in the middle covered with the kingdom crown. The surrounding legend text feature SIGIS 3 D G REX PMDL divided by a small shield with numeral 3 (meaning equivalent to 3 half groschen) meaning Sigismund the III-rd by God's mercy King of Poland and Grand Duke of Lithuania. The reverse features an orb with a cross with inscription 24 below the cross meaning that 24 of such coins are equal to one thaler. The year is marked by numerals divided by the cross respectively 2 and 4 (1624). The surrounding legend feature MONE NO REG POLO meaning new coin issued by the king of Poland, divided by the grand treasurer's arms, a vertical arrow flanked by two stars with a moon crescent on the base, these symbols are surrounded by square brackets making the appearance of a smiley face.

Figure 1. Investigated samples: a) well preserved półtorak issued in 1624 and b) abnormally corroded półtorak from 1624.

Figure 1a, feature the general aspect of the good coin reference having the striken details very well preserved with a sharp detail. The abnormal półtorak is presented in Figure 1b revealing partly swelled details of the text and cross arms. There were found significant metrological differences between them, Table 1. Literature data reveal that pure silver density is about 10.49 g/cm^3 and copper density is 8.96 g/cm^3 [13, 14].

Table 1. Metrological characteristics of the investigated coins

Sample	Diameter, mm	Thickness, mm	Weight, g		Temp., °C	ρ_{water}, g/cm^3	ρ_{sample}, g/cm^3	Alloy, wt. %	
			air	water				Ag	Cu
a	19	0.56	0.9219	0.8298	22.1	0.9877	9.98	70.07	29.93
b	19	0.71	0.7414	0.6361	22.1	0.9978	7.02	-	-

Thus, the well preserved półtorak is situated in the hypereutectic domain closely after the eutectic position [15]. Copper amount increase causes a the alloy denisity decreasing. It would have been espected that the abnormally corroded półtorak to have too much copper but its density is far below than pure copper, Table 1. Since the abnormally corroded coin has a fine silvery aspect, we wonder what it might happened there to affect the density. Microstructural observations are required.

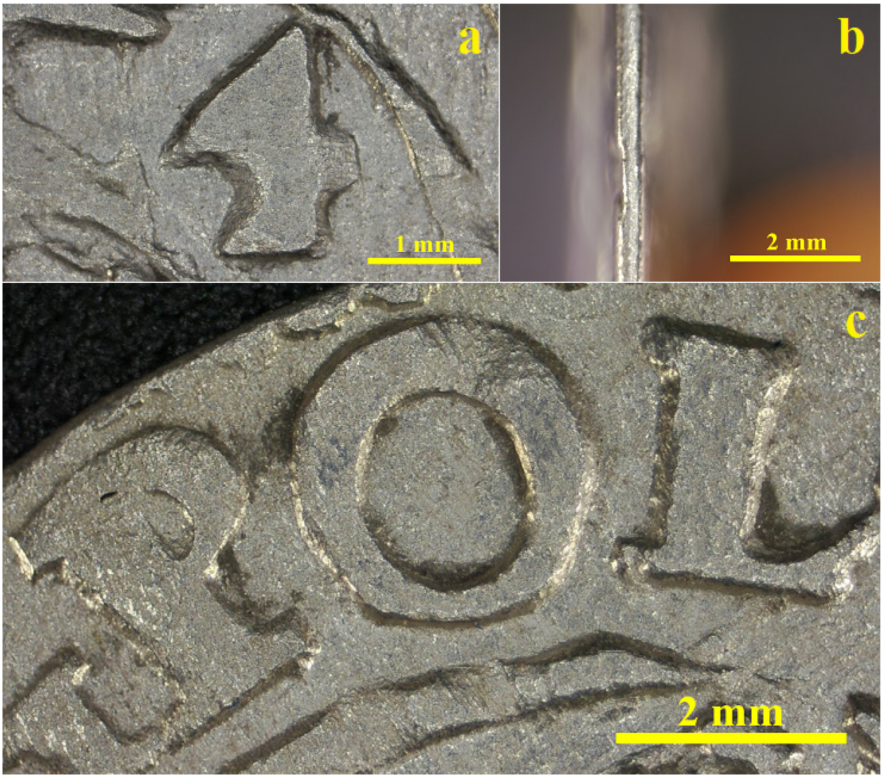

Figure 2. Macrostructural details observed at low magnification (x10) in reflected light of the well preserved półtorak issued in 1624: a) detail on year distinctive number 4, b) coin's edge aspect and c) aspect of the coin's text.

Figure 2 reveal the low magnification aspect of the well preserved półtorak surface. The date numeral 4 has a sharp edged shape well imprinted into the alloy and has heavy worn marks on the top as consequence of intensive circulation, Figure 2a. Since the coins were cleaned without aggressive chemicals the silver enriched areas are found only on the lower areas of the surface while the top of inscription are heavily worn and thus it makes them less prone to the silver enrichment [1]. Moreover, choosing a proper microstructural area like the numeral 4 or the character L for a micro polishing with 8000 grains sand paper followed by gentle felt brushing with colloidal alumina ensures a proper removal of the silver enriched layer and optimally prepares the targeted micro area for metallographic observation. The coin's edge, Figure 2b, is well defined without microstructural flaws.

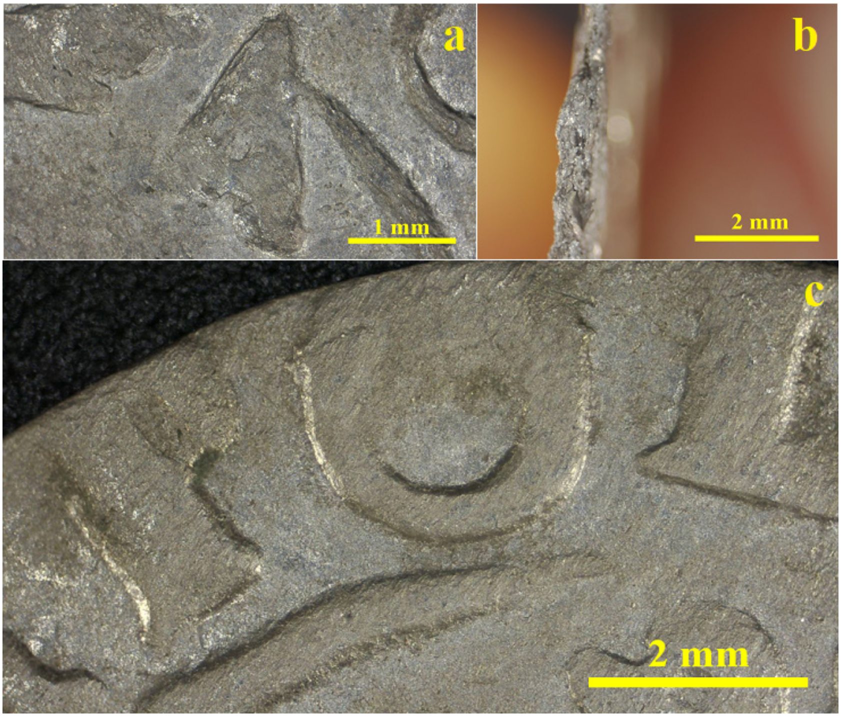

Figure 3. Macrostructural details observed at low magnification (x10) in reflected light of the abnormally corroded półtorak from 1624: a) detail on year distinctive number 4, b) coin's edge aspect and c) aspect of the coin's text.

Circular text of the coin is also well stricken into the coin blank with well defined characters, minor oxidation marks appear as dark spots on the O character from inscription. The abnormally coroded coin has a deeply worn year numeral, Figure 3a, with fuzzy edges partly generated by the intensive worn from caused by prolonged circulation, fact sustained by the faded inscription of POL in Figure 3c. The lower areas of the surface are well preserved showing a extremly good looking enriched silver layer (caused by the removal of the corrosion products) but top areas of inscription being heavily worn resemble better the bulk characteristics. The biggest surprise occurs on the coin's edge examination, Figure 3b. It is blunted featuring deeper internal fissures which causes the increase of the edge thickness which almost become double than the one of the well preserved coin. It is the first phisical proof that something abnormal issue affects the coin integrity. X ray diffraction (XRD) effectuated on the coin's reverse which was gently brushed with felt disc reveal the overall phase composition of the alloy, Figure 4.

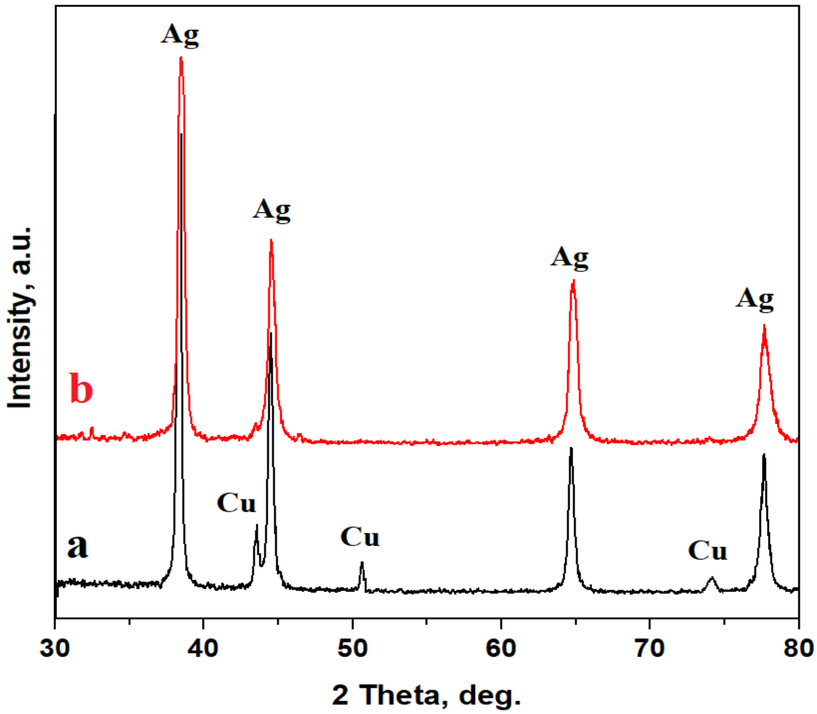

Figure 4. XRD patterns of the investigated samples: a) well preserved półtorak issued in 1624 and b) abnormally corroded półtorak from 1624. Peaks assignment according PDF 89-3722 for Ag and PDF 89-2838 for Cu.

The well preserved półtorak reveal an XRD pattern with well developed peaks belonging to Ag and Cu. Relative Intensity Ratio (RIR) method allow to calculate the mass participation of each identified phase corelating the relative intensity of the specific peaks with the corrundum factor of the identified phases [16, 17]. It results that the well preserved poltorak has a silver content of 69 wt. % and 31 wt. % copper which is in good accordance with the composition determined from the coin's density and agrees our previous observations on the poltoraks issued in 1624 [1].

On the other hand the abnormally corroded półtorak has an astonishing composition made of pure silver without copper. It is in a fragrant disagreement with the observations made uppon the density variation. Thus, the metallographic investigation of the bulk microstructure is mandatory, Figure 5.

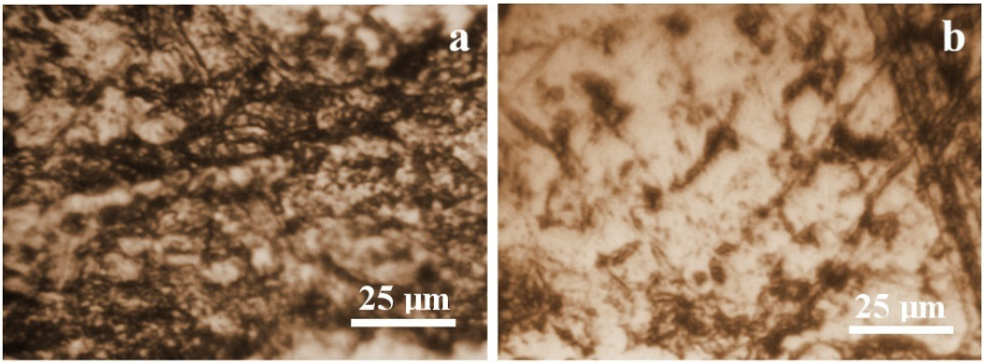

Figure 5. Metallographic microscopy images of: a) well preserved półtorak issued in 1624 and b) abnormally corroded półtorak from 1624.

The metallographic aspect of well preserved półtorak, Figure 1a, reveal a dense matrix of eutectic grains having white appearance with darken lamellas within alternating with compact dark grains of β phase. Both of the grains are elongated under the rolling dirrection and have a length of about 20 – 25 µm and a width of 8 – 12 µm. It confirm a normal microstructure of a hypereutectic Ag-Cu alloy which was subjected to rolling lamination and subsequent stricking.

On the opposite, the abnormal półtorak reveal a predominant α grains matrix spoted with corroded eutectic grain remains. The copper loss from the microstructure is evident, however the grain texturing clearly indicate elongation under the rolling dirrection but it is difficult to establish a precise size because of removal of the advanced intergranular corrosion product which let the grain boundaries fuzzy. The α grains can be estimated with a length of 20 µm and width of about 10 µm while the eutectic grains remains are about 25 µm length and width is difficult to be established. High resolution SEM images are required to elucidate better these microstructural aspects.

SEM investigation sustains the optical microscopy observation regarding the overview of the microstructural aspects of the well preserved półtorak, Figure 6a. It is clearly observed that the mild felt brushing let the lower areas untouched while the enriched silver outermost layer on the top worn areas was successfully removed revealing the true bulk microstructure as observed in the detail cached in Figure 6b.

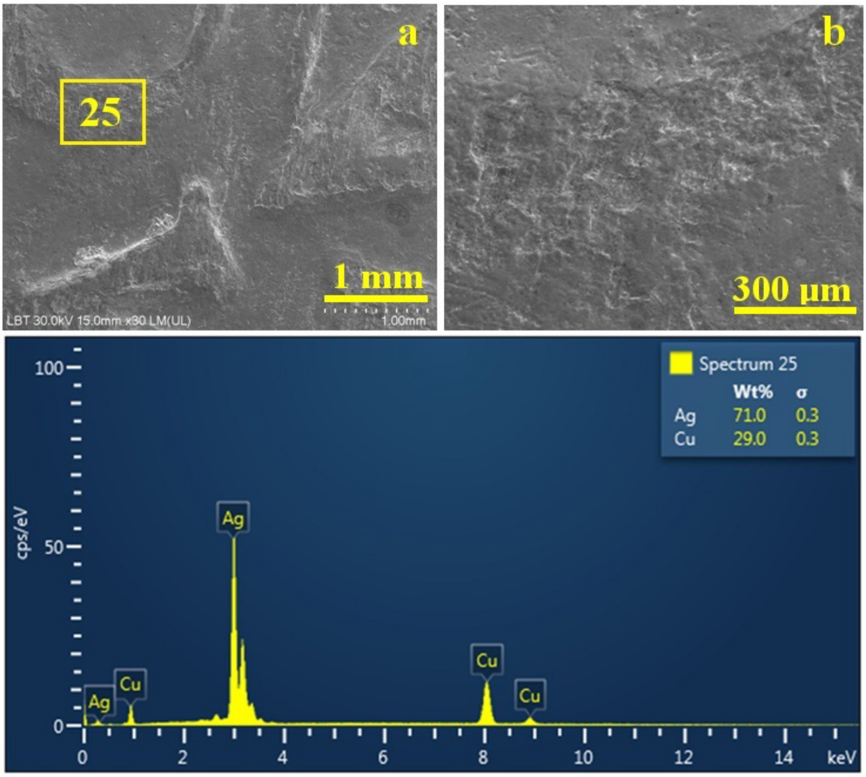

Figure 6. Overall aspect of the well preserved półtorak observed by SEM: a) macrostructure view, b) overall microstructure and c) EDS spectrum of overall elemental composition.

EDS spectrum was taken on these worn areas, spectrum 25 in Figure 6c. It reveals the elemental composition of the alloy resulting in 71 wt.% Ag and 29 wt.% Cu being in great agreement with the XRD and density related measurements. Since the density based calculation of the alloy composition is certainly related to the bulk composition, the confirmation of the surface based measurements like XRD and SEM-EDX prove the efficiency of mild felt brushing in removal of the cleaning silver enriched outer most layer within the worn areas. Moreover, the targeted metallographic preparation of such certain areas allows an optimal view of the grain's microstructure through SEM – EDS investigation, Figure 7.

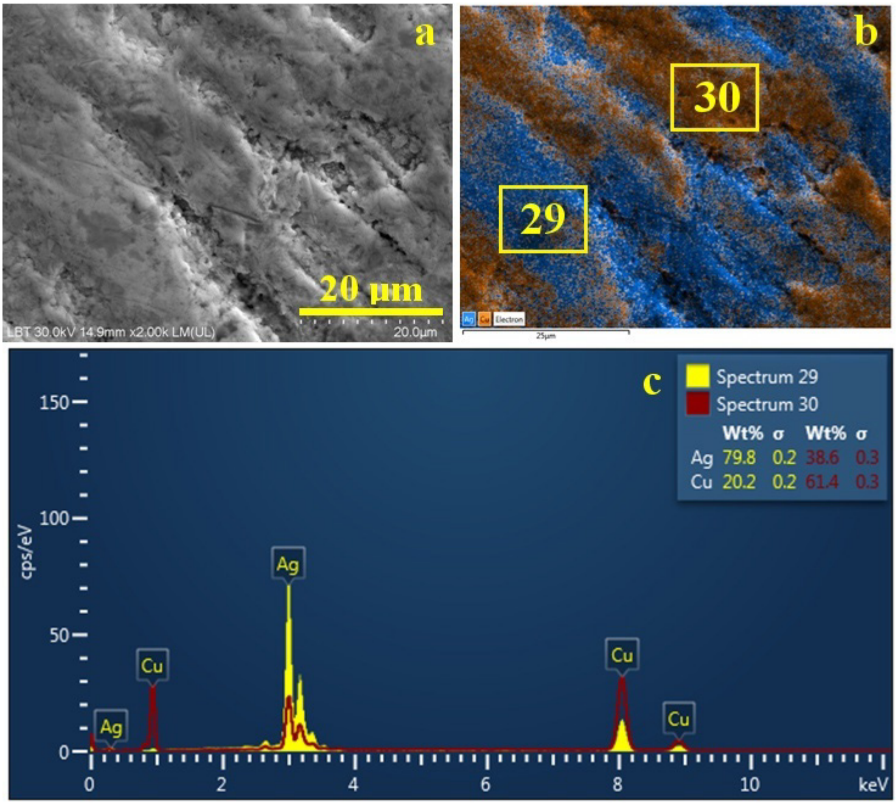

Figure 7. Microstructural constituents of the well preserved półtorak observed by SEM: a) SEI image, b) BSE image with superimposed elemental map, and c) EDS spectra comparison between eutectic grains (blue – spectrum 29) and β phase grains (orange – spectrum 30).

Secondary electron image (SEI) of the micro polished and lustred area of the well reserved półtorak reveal a smooth surface making rather difficult observing grains, some eroded eutectic grains are obvious in the central and lower right area of the image indicating partly breaking of the thin lamellas as consequence of intensive circulation worn as reported in our previous study [1]. Backscattered electron image (BSE) overlapped with the elemental distribution, Figure 7b, reveals better the grains microstructure. Eutectic grains have a blue appearance spotted with fine orange points while pure copper β has an orange aspect. They are elongated in the rolling direction proving the mechanical processing of silver alloy sheet prior striking. Grains elemental composition was investigated with targeted EDS spectra. Spectrum 29 was taken on the blue grains revealing an amount of 79.8 wt.% Ag and 20.2 wt.% Cu very close to the eutectic composition. Spectrum 30 was taken on a orange grain revealing dominance of copper as 61.4 wt.% within the β phase while the silver remains of 38.6 wt.% belongs to the eutectic grains boundaries that were partly caught in the EDS sampling spot.

Overall, the well preserved półtorak issued in 1624 has a good cohesion of the internal microstructure explaining the metallic sound when it is thrown on the solid surfaces (e.g. table, floor, and pavement). Such testing method was very popular when these coins were in circulation to distinguish them from the lead and thin forgeries which have dull sound when they are throw on solid surfaces [18, 19]. Despite the dull sound, our abnormal półtorak is made almost pure silver having an abnormal density. It clearly indicates severe microstructural flaws which require advanced investigations.

Its surface is well preserved as a consequence of the striking dies punching alloy ensuring a smooth and uniform lower areas, Figure 8a. The inscriptions are relatively swelled having a large curvature connection with the lower areas instead of the sharp connection implying a small curvature radius observed on the normal półtorak, in good agreement with optical microscopy. SEM imagining confirms that the top of inscriptions is deeply worn. Figure 8b presents a microstructural detail of the worn areas. The grains are quite eroded due to the intensive circulation of the coin but have extra eroded patterns as scaly structure suggesting in depth erosion of the microstructure via intra-crystalline corrosion.

The internal microstructure of the abnormal półtorak is properly observed on the damaged margin observed by optical microscopy in Figure 3b. SEM investigations were conducted to catch both damaged margin and a small part from adjacent lower areas from the coin surface, Figure 8c. The lower right corner evidence of excoriation of the top surface layer revealing deeply corroded microstructure beneath.

The surface has a smoother appearance compared to the damaged margin which reveals a deeply corroded microstructure of the coin. BSE image with elemental distribution map in Figure 8c reveals a uniform distribution of silver both on the surface and in the bulk of the coin (uniform blue color). Small orange points represent copper distribution which is very scarce on the surface and slightly more present in the damaged margin. Thus, spectrum 19 taken on the coin surface reveals a composition of 98.6 wt.% silver and 1.4 wt.%, Figure 8e. Spectrum 20 reveals the slightly appreciation of the copper content to 2.6 wt.% in the damaged margin. It suggests that the initial state of this coin contained much more copper in the bulk most likely a similar content as observed in the normal półtorak.

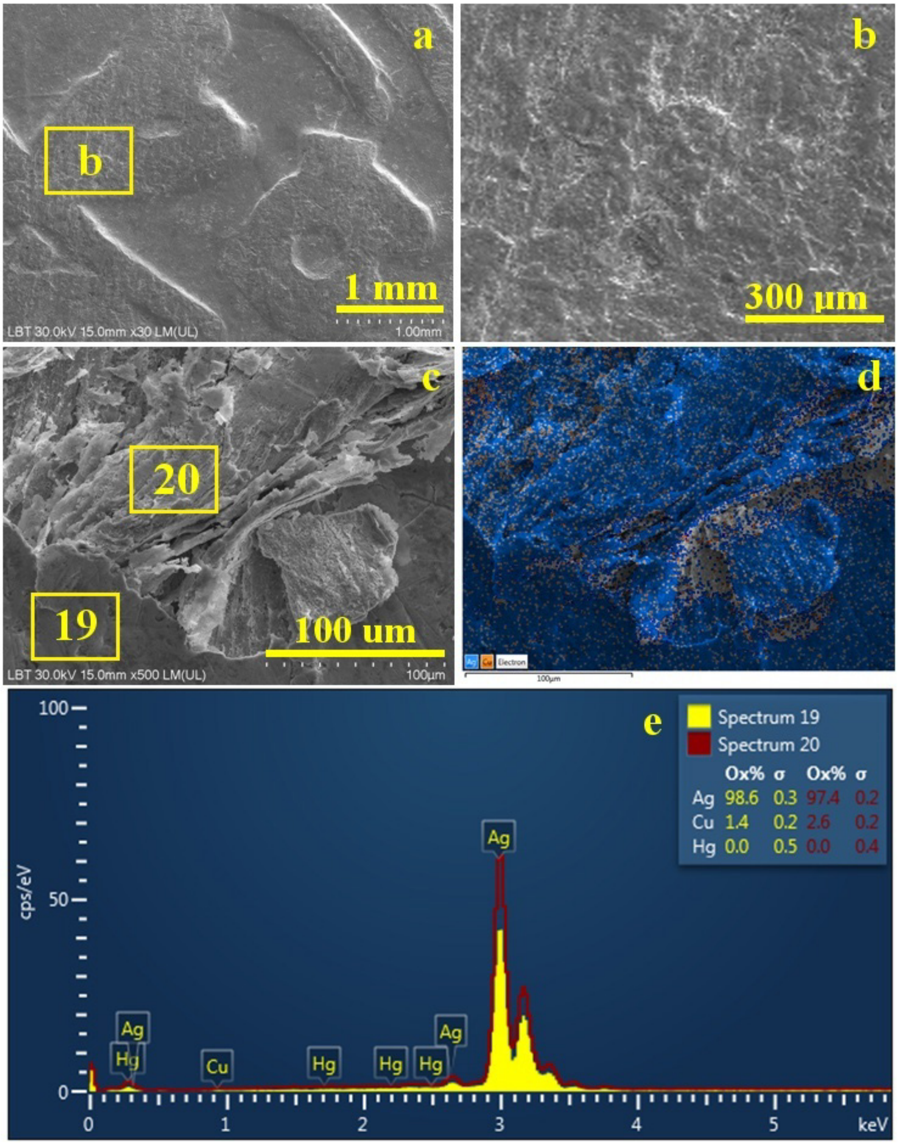

Figure 8. SEM images of the abnormally corroded półtorak: a) macrostructure view, b) overall microstructure and c) SEI image of microstructural detail of damaged margin of the coin, d) BSE image superimposed with the elemental map of the damaged margin of the coin, and e) EDS spectra taken on the coin surface and on the damaged margin.

Abnormal półtorak bulk microstructure, Figure 9a, is formed by grains elongated under the rolling direction respecting the pattern observed in the normal półtorak. Their length ranges from about 15 to 20 µm and their width ranges from about 3 – 8 µm. The abnormal aspect is given by the elongated pores resembling to the β grains within the normal alloy. The other grains are merely eroded into thin silver sheets, a fact better observed at high magnification in Figure 9b. Both abnormal situations are confirmed by spectrum 22 which reveal their composition as 97.8 wt.% Ag and only 2.2 wt.% Cu, Figure 9c.

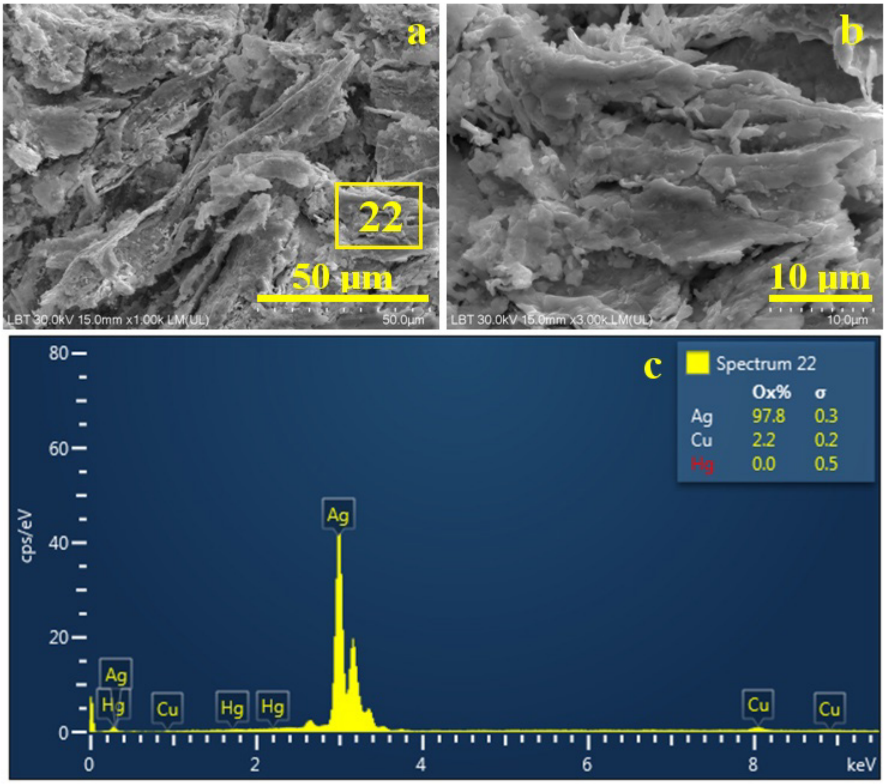

Figure 9. SEM images of the abnormally corroded półtorak broken side: a) overall microstructure, b) microstructural detail, and c) EDS spectrum of the microstructural detail.

SEM advanced microstructural investigations confirm that lower density of the coin is caused by large internal voids produced by an advanced corrosion which extract progressively copper from the microstructure. The evidence is strongly sustained by all employed physicochemical investigation methods. Thus, we wonder how it was possible to extract selectively copper from the coin. It is well known that silver is more noble than copper and then is prone affected by corrosion [18]. Thus, a corrosion mechanism can be established based on literature.

Wet underground conditions induce the galvanic corrosion of the microstructure activating copper microstructural components as anode because of its higher reactivity while silver microstructural components play cathode role [19]. Thus, the microstructural decuprification occurs through the β grains and Cu lamellas within eutectic oxidization with formation of tenorite and cuprite:

$$2Cu + O_2 \rightarrow 2CuO \quad (1)$$

$$4Cu + O_2 \rightarrow 2Cu_2O \quad (2)$$

where CuO crystallizes as Tenorite having black color and Cu_2O crystallizes as cuprite having brown color [20, 21]. These further react with the salts dissolved in soil. The most aggressive enhancers of the underground corrosions are chlorides like sodium chloride which denaturizes copper oxides transforming them in sodium dichloro-cuprate:

$$Cu_2O + 4NaCl + H_2O \rightarrow 2Na[CuCl_2] + 2NaOH \quad (3)$$

The sodium dichloro-cuprate has a water solubility of 22.7 g/(100 mL) at 25 °C representing a high solubility that makes this corrosion product susceptible to dissolving in high moisture and prone to removal through the liquid dispersion through the ground particles. However, this reaction is very slow, taking a longer time to generate the soluble products [22, 23]. The laboratory reaction can be accelerated by acetic or hydrochloric acid.

Carbonate minerals from soil like calcite and aragonite $CaCO_3$ also interacts with copper oxides generating malachite as main corrosion product [19, 24]:

$$2Cu_2O + 2\,CaCO_3 + 4H_2O + O_2 \rightarrow 2Cu_2(CO_3)(OH)_2 + 2Ca(OH)_2 \quad (4)$$

where: $Cu_2(CO_3)(OH)_2$ is malachite which is insoluble in water but the other product $Ca(OH)_2$ slacked lime has a water solubility of 1.73 g/L at 20 °C and thus it might affect the natural balance of the corrosion products in high wet ground moisture facilitating corrosion products dissipation.

Literature reveals that sulfide that might occur in the resting ground does not directly react with copper or with copper oxides but however might affect the balance of the other reaction products [25].

Several corrosion products like tenorite, cuprite and malachite are practically insoluble in water than their tight deposits formed on the coins surface act as a shield preventing mineral loss. On the other hand, sodium dichloro-cuprate has a high solubility and slaked lime also has a limited water solubility facilitating the corrosion products evacuation through the moisture flow within the resting ground. Mineral diversity within resting ground could generate complex copper chlorides like atacamite $Cu_2Cl(OH)_3$ having a more complex chemical structure than sodium dichloro-cuprate and it is insoluble in water. However, its occurrence is strongly related to the arid conditions which imply moderate moisture. Considering the slow reaction rate of sodium dichloro-cuprate formation within high salted moisture soil facilitates slowly and progressive dissipation of this copper corrosion product into the adjacent environment. Continuing this process for several hundreds of years explains progressive decuprification of the półtorak microstructure preserving silver grains relatively untouched.

The corrosion products chemistry reveals that almost all copper-based compounds are practically insoluble in water excepting sodium dichloro-cuprate that forms into the aqueous state when halite crystals (sodium chloride crystallized in cubic system) are dissolved by pluvial water. Thus, the proposed mechanism explaining the abnormally corrosion pattern observed in 1624 półtorak works in sedimentary soil rich in calcium carbonate minerals like calcite and halides like sodium chloride.

Such soils are common in the Transylvanian basin due to the evaporitic deposits formed during Badenian age as consequence of intensive evaporation of water from Tethys Sea (covering actual areas of Transylvanian Basin and Pannonian Field) generating large deposits on the Praid – Sovata – Dej line up to Salaj County [26, 27, 28]. These salty soils are common in the półtorak discoveries areas and thus we might assume that some of the random finds might be affected by intensive corrosion.

Malachite belonging to carbonate minerals is situated in the noble patina components while atacamite is generate by resting grounds rich in halides altering the noble patina [29]. However, the patina stratification depends on the subsequent interactions and the coexistence of malachite and atacamite is reported as bronze disease where chlorides transform the compact noble patina in a green powdery corrosion product [30].

Pluvial water infiltration within such soils dissolves halite crystals generating sodium chloride aqueous solution which reacts directly with the copper oxide formed on the coins surface and generate sodium dichloro-cuprate in aqueous solution which is dissipated away along with the water flux reducing the copper content. Considering this progressive corrosion pattern over few hundreds of years the decuprification affects deeply the alloy microstructure which losses the copper content enriching in silver, a fact in good agreement with literature data regarding intra-crystalline corrosion [12]. Moreover, it is confirmed by the oxygen presence in the elemental analysis of the broken side of abnormal półtorak but the content was subtracted from the analysis quantification to reveal only the alloy composition (the fact is properly displayed as Ox wt.% in the label of spectra 19, 20 and 22 in Figures 8e and 9c.

The lack of corrosion products associated with the abnormal półtorak and unknown resting ground consists of a main limitation of the present study. The proposed in deep progressive corrosion mediated by chlorides present in the resting ground consist in a good start point for advanced research implying fresh archeological discoveries of such coins, case in which soil samples and corrosion product samples can be collected properly and investigated prior to the complete cleaning of the coin.

Certainly the proposed corrosion mechanism is only a hypothesis that requires more advanced investigation on larger representative samples number preferably with the discovery place known. The lack of knowledge about the abnormally corroded poltorak makes difficult searching for soluble corrosion products that might explain more precise the leakage of copper from the microstructure. A fresh archeological discovery from scientifically investigated sites would be of great importance compared to random finds because the resting ground sampling will be possible as well as targeted collection of corrosion products from the coins surface prior cleaning. All these samples subjected to physicochemical investigations like the one performed in the present research will give important data for refining the advanced corrosion mechanism.

NUMISMATIC SIGNIFICANCE

Of course, large silver numismatic pieces such as thalers are more impressive from a numismatic point of view and on the other hand are less exposed to corrosion of the deeper layers. But, the everyday monetary circulation of ordinary people, such as buying and selling at the market, was mainly ensured by small coins, the basis being provided by półtoraks. This brings them to the forefront as the basis of monetary circulation. Data from the literature show that półtoraks issued by King Sigismund III of Poland were considered reliable coins, surpassing local circulation and being recognized and appreciated throughout Central and Eastern Europe.

Numerous 17th-century hoards and coin accumulations contain significant quantities of półtoraks. Many of these are discovered in what is now Poland, but the literature reports significant hoards and coin accumulations of this type in Transylvania.

Polish mint implication under grand treasurer Nikolai Daniłowicz had ensured a good standard of półtoraks production in large quantities. King's Sigismund III półtoraks emissions ceased after 1627 three years after Nikolai Daniłowicz death under new grand treasurer Hermolaus Ligęza. The 1614 Crown półtorak coins weighed 1.576 g and, with a fineness of 0.469, contained 0.739 g of silver. In 1619, their mint rate raised from 128 to 164 minted coins from the Kraków mark (201.802 g). From 1619 onwards, the półtoraki had the following specifications: weight 1.230 g, fineness 0.406, and 0.500 g content of Ag. Finally, mint regulation of 1623 devalued półtorak more, so that they weighed 1.201 g and, with a fineness of 0.375, contained 0.450 g of pure silver, and from then on, 168 one-and-a-half-groschen coins were minted from the same Krakow fine. Półtoraks minted from 1619, were almost equal to the two Austrian kreuzers of 1625 (weight 0.567 g), and the youngest póltoraks, minted from 1623, were approximately equal to 1.5 kreuzer (half of Imperial groschen) minted after the monetary reform of 1623–1624 [5]. This relation meant that they became readily exchangeable currency on the Central European market and effectively supplemented the supply of small change in circulation. This is confirmed by numerous finds of one-and-a-half-groschen coins in Central European hoards dating from the 1620s to the 1660s.

The findings show that the oldest, i.e. better, emissions are favoured and occur more often and in greater quantity. Although, mass issues of the półtoraks, particularly from the 1620s, which account for such a large proportion of coin finds from the Polish state and Hungary, including Transylvania, in the 17th century, did not reach the Austria, Bohemia, Moravia or Silesia market in the same quantities. The first one and half groschen coins in the Kingdom of Bohemia are recorded in hoards dating back to the 1620s. In 1623, Czech and Moravian sources show a break in the influx of coins from Poland. At that time, a coinage reform introduced by Ferdinand II (great kalada) was carried out in the Bohemia (Czechia, Moravia, Silesia, Lusatia), successfully overcoming a severe monetary crisis. At the same time, a new coinage regulation in the Polish state introduced a coin of lower quality, which could no longer play an active role in the finally stabilized Czech market. This contrasts with Hungary and Transylvania, where, despite access to silver deposits, there was still a deficit in the production of medium and small denominations, and the demand for this type of coin was met by imports from

Polish-Lithuanian Commonwelth and the Roman-German Empire. Their proportion in hoards in those territories, likewise in Poland, declined markedly after 1663, when new denominations were introduced as part of reforms in the Holy Roman Empire and the Polish-Lithuanian Commonwealth [7, 31].

In hoards from the territory of the Kingdom of Poland, one-and-a-half-grosch coins have been found as early as 1614. At least nine hoards containing this denomination, dating from immediately after its introduction, have been recorded. Such an early and relatively frequent presence of półtoraks in hoards may indicate that users recognised their more favourable metal composition — the silver content was approximately 11% higher than that of the groschen coins in circulation at the time. These groschen coins were struck from silver of a fineness of V 3/4 lute (lute is a medieval and pre-modern way to express the silver fineness where 16 lutes correspond to pure silver, in consequence V 3/4 lute corresponds to 75% silver and 25 % copper), weighing approx. 1.580 g and containing approx. 0.571 g of pure silver, which corresponds to a fineness of 359 3/8‰ (i.e. 36.139%) [5].

The large scale of the issue of one-and-a-half groschen coins, their novelty and their relative ‘overvaluation’ compared to the grosch may have encouraged their withdrawal from circulation and hoarding, a trend reflected in the composition of the earliest hoards. Between 1615 and 1623, there was a decline in the number of hoards containing półtoraks, as well as a reduction in their proportion within individual hoards. This phenomenon may be linked to the outflow of this coin beyond the borders of the Polish-Lithuanian Commonwealth, a fact confirmed by finds from neighbouring regions. A renewed increase in the frequency of półtoraks in hoards occurred from 1624 and—despite some annual fluctuations—persisted until the 1660s. In the following decades (the 1670s and 1680s), these coins continue to appear in hoards, though their significance gradually declined. In the 1690s, there was a marked decline in the presence of one and half groschen coins in hoards, although isolated examples still appeared sporadically at the beginning of the 18th century [32, 33]. The evidence gathered suggests that Polish coins—particularly the półtorak—served a supplementary role to the local monetary system in Silesia, especially in the case of small denominations. Their presence was constant, though usually limited in quantity. Exceptional accumulations from the years 1656–1667, however, should be interpreted as the result of extraordinary factors linked to population migrations and political instability in the region [32, 33].

An analysis of the Głogów hoard indicates that the półtoraki coins originated from numerous mints, which clearly illustrates the wide scope of their circulation. Hoard primarily issues from crown mint represented by circ 2300 pieces from Bydgoszcz (1618–1627), several hundred exemplars from:

the Duchy of Prussia in Königsberg (1621–1633), from the municipal mint in Riga (1620; 1623–1626; 1644–1649), including issues from Livonia (1648), as well as municipal issues from Elbląg during the Swedish occupation (1628–1633) and Swedish issues minted in that city between 1632 and 1637. Such a diverse minting structure confirms that the półtorak functioned as a supra-regional coin, easily crossing political borders. Particularly noteworthy is the fact that this hoard — alongside regular issues — also contains imitations of półtoraks, which constitutes significant evidence of their international influence. Noted here are both a Transylvanian poltur from 1638 (minted at an unknown mint, other Transylvanian sources mention the same coin issued in Koloszvar – actually Cluj –Napoca mint having CV mark inscribed on a small circle below the cross orb on the obverse) and six so-called dreipölker minted in Koszalin in 1621–1622by Prince-Bishop Ulrich of Pomerania and Cammin (pol. Kamień). These imitations form part of a wider trend of adapting the półtorak in Central and South-Eastern Europe. Particularly in Transylvania, the półtorak served as a model for local issues (poltura) minted between 1636 and 1638, which were adapted to the local monetary system whilst retaining the form and function of a small silver coin useful in regional and international trade. Similarly, in the area of Western Pomerania and the Kamień Bishopric, issues of the dreipölker type constituted a deliberate imitation of the Polish półtorak, often with reduced specifications, intended for circulation in neighbouring markets, mainly within the Polish-Lithuanian Commonwealth. The presence of both original issues and their imitations in a single hoard indicates that the półtorak functioned not only as part of the Polish monetary system, but also as an important monetary standard in the region. Its popularity encouraged the creation of numerous imitation issues, which — often with a lower silver content — circulated beyond the region and were used in cross-border transactions [34, 35].

Such a large spread of półtoraks from the issuing place to all over Central and Eastern Europe in numerous hoards and random finds imply their exposure to various resting grounds with different humidity degrees and pluvial water infiltration. It normally leads to different conservation state and slightly variation of patina compounds subscribed to the triangle formed by oxides – carbonates and halides. Such advanced intragranular corrosion like observed in our abnormal półtorak most likely was previously observed by the archaeologists and numismatists investigating the previously mentioned hoards. Thus, the advanced corrosion hypothesis discussed in the current article should be further investigated on the larger number of affected coins from different sources consisting in a future research work.

CONCLUSIONS

The abnormal density and extremely high silver content of the unusual półtorak issued in 1624 is caused by a progressive intra-crystalline corrosion which implies the decuprification through complete dissolution of β phase grains and copper lamellas from the eutectic grains leaving behind a porous microstructure of almost pure silver grains as observed by SEM-EDX in agreement with optical microscopy and XRD observations.

Sodium dichloro-cuprate is the single corrosion product having high water solubility while copper oxides, malachite and atacamite are practically insoluble in water. Thus, all aspects plead for a progressive corrosion in a high moistened soil containing evaporitic deposits of sodium chloride crystallized as halite. Moisture water circulation can ensure a progressive removal of sodium dichloro-cuprate during few hundreds of resting years causing deeply decuprification of the coin generating a porous microstructure explaining the dull sound when it is ringed on solid surfaces.

The proposed corrosion mechanism needs further investigations regarding the resting ground soil composition and a precise investigation of the patina layer formed on the coin surface prior to its complete cleaning. Such investigation should be further conducted on the fresh archeological discoveries of random finds and monetary accumulations. Also, it would be interesting to effectuate a search for such abnormally corroded półtoraks if they occur in large hoards.

EXPERIMENTAL SECTION

Numismatic examination of some półtoraks issued by Sigismund III King of Poland in early XVII century reveal one coin from 1624 having abnormal properties line relative low weight and a dull sound when it was ringed on the table. A manipulation accident occurs chipping its edge revealing deep internal structural flaws which were further investigated by physicochemical methods. The normal etalon was considered in a similar coin issued in the same year 1624 at the same place in Bydgoszcz mint.

Coins density was measured using an AX120 Shimadzu hydro-balance with a measuring range from a minimum of 10 mg to a maximum of 120g. Each coin’s mass was measured in atmosphere and in water. The density is given by following equation:

$$\rho_{solid} = \frac{m_{air}}{m_{air} - m_{water}} \cdot \rho_{water} \tag{5}$$

where: ρ_{solid} is the coin's density, m_{air} is the coin's mass measured in atmosphere and m_{water} is the coin's mass measured in water, ρ_{water} is water density at the measurement temperature which was 21 °C respectively 0.9978 g/cm^3. Knowing the coin density and assuming its standard composition within Ag-Cu binary system the weight percents of silver ω_{Ag} and of copper $\omega_{Cu} = 1 - \omega_{Ag}$ can be calculated with the following equation:

$$\frac{1}{\rho_{solid}} = \frac{\omega_{Ag}}{\rho_{Ag}} + \frac{1-\omega_{Ag}}{\rho_{Cu}} \tag{6}$$

where: ρ_{Ag} = 10.49 g/cm^3 and ρ_{Cu} = 8.96 g/cm^3.

Both coins are well cleaned under the museum's standard procedures, being free of corrosion products at visual inspection. According to the literature, such cleaning procedures might enrich the silver content of the outermost layer. Therefore, their reverse featuring the orb with cross was subjected to a gentle brushing with felt disc to remove the enriched silver layer from the heavily worn areas from the top of inscriptions and representations while the lower areas on the surface remaining undisturbed.

Furthermore, there were identified certain spots on the worn areas at the top of inscriptions that were further mild micro-polished with very high granulation sandpaper i.e 8000 grains and micro-lustred with colloidal alumina using felt pointers. The chemical etching was effectuated at the room temperature (20 °C) by swabbing method using a reagent containing ferric chloride and sodium thiosulfate applied with a small cotton cloth for 5 seconds followed by rinsing with deionized water. The procedure was gently effectuated to avoid damaging the coin surface but enough precise to allow metallographic analysis and SEM investigations.

Reflected light microscopy was effectuated using a Bresser WiFi 1080P 2L microscope equipped with an integrated computer aided image acquiring system working on the Windows platform using png high resolution output format 720 x 1080 pixels.

Metallographic microscopy was effectuated with an IOR MC8 metallographic microscope (IOR, Bucharest, Romania) equipped with a digital image capture camera Sony 14 MPx (Sony Co., Minato, Japan).

X ray diffraction (XRD) was performed with a Bruker D8 Advance diffractometer with Cu kα monochromatic radiation having a wavelength of 1.540562 Å. The patterns were registered at a speed of 1°/min. in the range of 10 – 80°. Crystal phase identification was made upon the XRD peaks using Match 1.0 software (Crystal Impact Company, Bonn, Germany).

Scanning Electron Microscopy (SEM) was done with the Hitachi SU8230 operated in high vacuum mode at an acceleration voltage of 30 kV. The samples were coated with a thin layer of Pt to ensure proper electrical conductivity. The elemental analysis was effectuated with the Energy Dispersive Spectroscopy (EDS) detector X-Max 1160 EDX (Oxford Instruments, Oxford, UK). The Pt component was subtracted from the EDS results.

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