# CORROSIVE EFFECT OF ROLLING FAULTS INDUCED BY MICROSTRUCTURAL SEGREGATIONS IN A SILVER COIN **ISSUED BY GABRIEL BETHLEN IN 1626**

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**ABSTRACT.** Gabriel Bethlen's monetary reform in 1625 supposed to replace bad coins with good-quality silver issues. Some of these coins exhibit small, parallel surface lines caused by rolling faults in silver plates. This study investigates a 1626 silver groat minted at Baia-Mare, displaying prominent scratches extending from obverse to reverse. XRD and metallographic analyses reveal copper grain's oxidation to Cu<sub>2</sub>O, localized compositional inhomogeneities, and lamination-induced micro-cracks resulting from silvercopper segregation. The coin's high relief is worn due to the circulation while the lower areas preserve the initial state. Metallographic observation reveal that the lower relief contain silver (83.7 wt.% α phase and eutectic) while the worn areas contains debased silver (65.5 wt.% eutectic and β grains) generating large copper micro – segregations, confirmed by SEM – EDX. These structural defects facilitated corrosion across the rolling direction, becoming more visible after coin cleaning. Such micro faults would have been undetectable after coin issue. The findings indicate that such pseudoscratches represent not mechanical damage or intentional markings, but

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metallurgical anomalies associated with subtle debasement practices. This may suggest a controlled attempt to conceal minor reductions in silver fineness during Bethlen's monetary reform, intended to stabilize coin production while preserving the coin's visual and fiduciary integrity.

Keywords: Gabriel Bethlen, silver groat, microstructural segregation, corrosion

# INTRODUCTION

There are some actual silver alloys titles: 83.5 wt.% (used for the most of the modern coins like the emissions of Latin Monetary Union (Belgium, France, Italy and Switzerland) during 1865 to 1926. Many countries issued coins at this standard like Spain, Greece, Romania, Austro-Hungarian Empire (since 1892) which were in use until the end of first world war; 92.5 wt.% also called sterling silver is often found in British coins and Unites States of America silver dollars. The silver title decreases at 75.0 wt.% in some coins issued after the first world war depending on the monetary politics of each country. Unfortunately the silver title was less standardized in the pre-modern times and was more affected by the socio-political factors.

The start of 30 years war in 1618 implies issuing of large amount of counterfeited coins which were produced most likely in annex workshops of the official mints. Literature reveal that most effective silvering technique was the immersion of the copper strips into melted silver ensuring an thin layer attached to the core by an intermediary layer of eutectic [1, 2]. The official coins were also debased by reducing silver title to about 50 % [3]. All belligerent countries use this strategy and subsequently their vaults were filled up with forged or debased coins. In fact, it was a manifestation of enormous inflation that raised the conversion rate of small change coins to the greater commercial coins like silver thaler or gold ducats. Literature mention that a standard thaler worth 72 kreuzers in 1600; 124 kreuzers in 1619 and over 600 kreuzers in 1622 [4, 5]. A financial crisis called Kipper und Wipperzeit occur where the coins were clipped for verifying their core content and weighted for ensuring that the sides were not cut off. There are no records about the forged coins spread, but for sure the debased coins of Gabriel Bethlen were released on the Transylvanian circulation mainly as 1 groat and wide groat (equivalent to 5 conventional silver denars). The Northern find record of such groat belongs to Gdansk (e.g. from Łagiewniki in 2006) consisting in a groat issued in 1626. As professor Paszkiewicz writes, it likely reached Gdańsk via the Polish market [6]. A close look to the published photograph of the coin reveals some corrosive scratches on its obverse which might be related to the coin's core title.

Another inflation coins are the 24-kreuzer issued by Gabriel Bethlen in Opole circulating mainly in Silesia but not in the Greater Poland where only Transylvanian groat emissions were recognized as official Bethlen's emissions [7]. Most of these debased 24 kreuzers coins minted in Opole feature minor scratches oriented under the silver stripe lamination – rolling direction [8]. Such marks look to be a technological characteristic for the small value coins with low silver title.

Monetary reform implemented by Gabriel Bethlen prince of Transylvania (1613-1629), in 1625 was designed to replace debased and forged coins with good silver issues produced under strict control. This reform followed a period of monetary instability caused by excessive minting of underweight coins what have been started during the preceding reigns. Bethlen's aim was to restore public trust in Transylvanian coinage and to demonstrate the principality's independence from the Habsburg monetary system [9, 10].

These new issues were preferred for hoarding as observed in the hoards discovered in Salaj County [11] as well in the hoards discovered in other places from Transylvania [12]. Surprising, some of them also feature minor scratches oriented in the rolling - lamination direction like those observed for debased coins. It is clearly that these marks are not generated by the circulation worn but were formed during the coins production. Circulation worn only could enhance their aspect because of local friction forces of the coins high relief. On the other hand, such scratches are rarely found on the high denominations like thaler which are made of good silver over 80 % fineness. Some of these valuable coins were deliberately marked with specific symbols related to the personal ownership marks, commemorative marks or bullion fineness marks (even alchemical symbols) described in literature as graffiti [13]. It is also reported that smaller denomination were not subjected to such deliberate inscriptions.

Another characteristic of the high denomination is their significantly increased width of about 1.5-2 mm while small denomination is very thin < 1 mm. Such an advanced thickness reduction within silver stripe of the small denomination implies supplementary rolling. The excessive rolling without annealing process induces progressive cold hardening of the grains and their subsequently failure through the development of dislocations forests within the tensioned grains [14]. The dislocations progress into fine micro-cracks predominantly oriented perpendicularly on the rolling direction which further induces macroscopic fissures if the annealing treatment is not applied [15]. On the other hand, silver has good deformability ensuring a proper rolling supporting large strain [16], perhaps this is the reason for less observation of these specific scratches on the high denomination. Smaller denominations are very often debased having uneven composition and microstructure produced in a metallurgical process without precise control of the temperature. In

consequence grain segregation most likely occurs at the ends of the silver alloy ingot due to the uneven cooling rate between ingot's surface and core [17]. Thus, the scratches formed along the rolling direction indicate a potential microstructural failure of some atypical segregated grains. Such hypothesis requires advanced physicochemical investigation to figure out the scratches nature and their possibility to be specific marks of the debased coins.

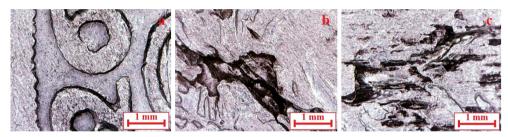
### RESULTS AND DISCUSSION

A random discovery of a 1626 silver groat from Baia Mare (Nagybánya) provides valuable insight into the technical implementation of the reform of Gabriel Bethlen (Figure 1). Although visually well-preserved, the coin displayed a dark (black-brown) tarnish, induced by the advanced degradation of the copper grains within the silver alloy. The presence of such patinas and corrosion traces aligns with the high-temperature and rolling conditions typical of early-seventeenth-century minting technology. Silver sheets were laminated multiple times to ensure uniformity, but uneven cooling and imperfect alloying often induced micro-segregations of copper, which later served as preferential corrosion sites. At first sight, the coin seemed well preserved but covered with a dark brown-black oxide layer (Figure 1). Cleaning removed this patina and revealed parallel linear features on both obverse and reverse. These were initially interpreted as scratches caused by circulation but further examination proved them to be structural faults.



**Figure 1.** Photograph of the investigated coin before and after cleaning: silver groat issued by Gabriel Bethlen in 1626 minted at Baia Mare (N.B.). Medals alignment ↑↓.

Reflected light microscopy, taken a low magnification, confirms that the upper relief of the coin – especially Madonna and Child and inscription characters – is worn by the circulation (Figure 2a). However, the lower areas are well preserved, without circulation worn. Such parallel defects (Figure 2a–b) are consistent with lamination defects ("rolling faults") that appear when cold-worked Ag–Cu alloys experience localized strain hardening and copper segregation during the final rolling stage before striking coins.

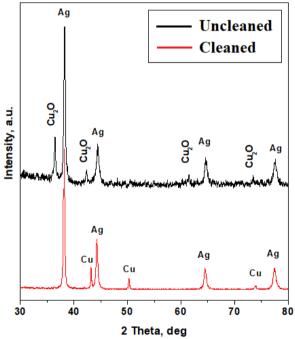


**Figure 2.** Reflected light microscopy of the coin surface: a) normal areas with worn relief and intact lower details, b) scratches on the obverse and c) scratches on the reverse.

The coin obverse has a deep scratch with a length of about 7 mm and a mean width of 600  $\mu$ m, its detail can be observed in Figure 2b. The worn area belonging to Madonna's knees and hand surrounds the scratch having firm rims. The scratch borders are irregular having the shape of some missing microstructural grains that were removed through the corrosion process. The scratches on the reverse start appearing approximate on the point where the obverse scratch disappears beneath the worn silver. These are distributed in shorter parallel branches of about 1 – 1.5 mm length and width of about 200 – 250  $\mu$ m, Figure 2c. Their orientation keeps the rolling direction similarly to the obverse scratches. Their shape and spatial positioning indicate that the microstructural defect pass through the coins core.

X Ray Diffraction (XRD) analysis (Figure 3), confirmed that the initial patina of the coin contained copper oxide  $\text{Cu}_2\text{O}$  (crystallized as cuprite) while silver grains remained well preserved revealing their metallic state. After cleaning, the oxide layer fell below the diffractometer's detection limit (e.g. 1 wt. %), demonstrating efficient removal of surface corrosion products. Unfortunately, the resting environment of the coin is unknown and no connection with the corrosion type can be followed. However, the coexistence of metallic silver with cuprite indicates an advanced oxidation of the copper grains within the coin surface microstructure particularly affecting the more reactive copper component. Ag does not possess a protective native oxide film and relies on natural immunity for corrosion protection in mild environments [18].

The complete cleaning of the coin removes oxides from its surface at a level below detection limit of the diffractometer (e.g. 1 wt.%). Removing the oxidized crystals from the copper grains make them available to the diffracting X-ray beam and become completely detectable. The XRD pattern reveals specific peaks for Ag having strong intensities and narrow aspect followed by Cu peaks having lower intensities but keeping their narrow aspect. It indicates that both silver and copper appear on the well developed grains. It is interesting finding since one of the phases should have been finely divided as thin lamellas within the eutectic composition according to the binary phase diagram [17]. Such refinement of the dispersed phase induces a significant broadening of the XRD patterns [19], a fact which was not observed in our case.



**Figure 3.** XRD patterns for the coin surface before and after cleaning process.

The overall silver and copper amount can be established on the XRD pattern in Figure 3 by applying the Relative Intensity Ratio Method (RIR) which correlates the relative intensities of Ag and Cu peaks with their corundum factor [1]. Finally results an overall weight composition of 76.12 % Ag and 23.88 % Cu. This result would indicate a good silver alloy situated in the hypoeutectic zone of the Ag-Cu phase diagram, just like the mint master

would have been wanted. The nice and good-looking aspect of the completely cleaned coin sustain this impression making this coin very desirable in 1626 to be kept from the circulation and nowadays to be exposed in a collection. But the obvious discordance between the shine of the worn surfaces regarding the preserved ones tells another story that the overall silver content might be uneven distributed into the coin surface.

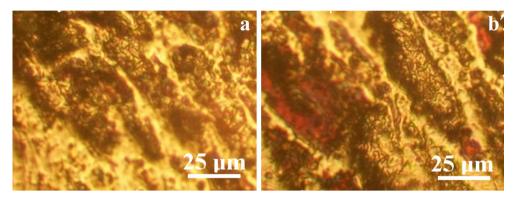
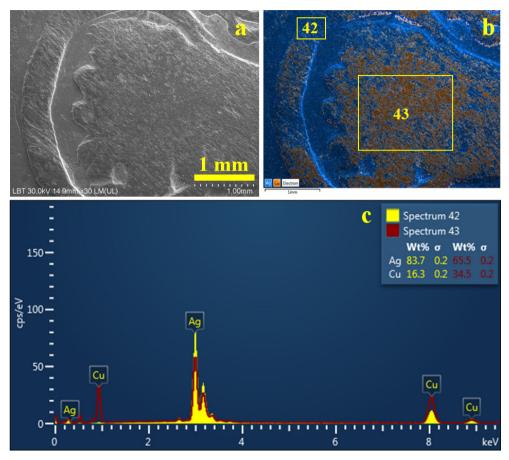


Figure 4. Metallographic observations: a) intact lower relief and b) worn high relief.

For metallographic observation, local spots of a few millimeters in size were manually selected, taking care to preserve the artifact's good condition. The lower relief areas reveal a good silver composition typical for hypoeutectic region of Ag - Cu phase diagram (approximately 83.7 wt.% Ag) revealing pure silver ( $\alpha$  phase) grain having bright nuance mixed up with eutectic grains having a lamellar structure of silver and copper interlocked sheets (Figure 4a). The grains are elongated under the lamination direction indicating that the final stage of silver plate was kept without re-crystallization.

In contrast, the worn regions have a completely changed microstructure (Figure 4b). It contains predominantly eutectic grains with tiny elongated ( $\alpha$  phase) surrounding their border. The abnormal microstructure is represented by copper segregation derived from the eutectic grains having dark red color (Figure 4b). In fact the coin's core is closer to the eutectic composition of Ag – Cu system (approx. 65.5 wt.% Ag) but the significant copper segregation move the alloy slightly into the hypereutectic region.

Such segregation appears in bigger ingots at their ends (e.g. head and the foot of the ingot when it is cast in vertical position). This inhomogeneity while visually imperceptible—may reflect intentional economic optimization: slightly reducing silver content in deeper, non-visible layers of the coin while maintaining a higher fineness on the surface to preserve trust in the currency. SEM investigation coupled with EDS spectroscopy fulfill this requirement.



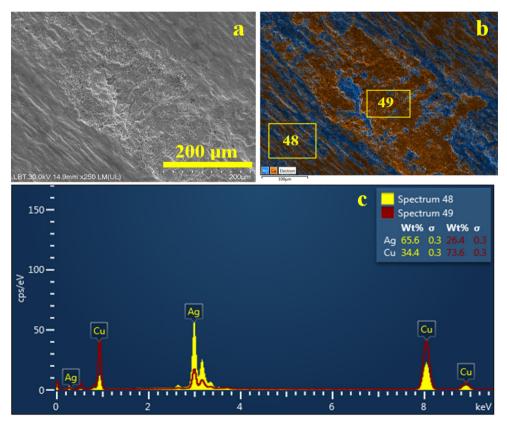
**Figure 5.** SEM investigation of the large area of the coin surface: a) SEI image, b) BSE image displaying elemental map and c) EDS spectra taken on specific positions.

Low magnification Secondary Electron Image (SEI) imaging (x30) reveals the overall aspect of the coin obverse (Figure 5a) in a complementary mode that reflected light microscopy does in Figure 2a. The worn areas (Madonna's head and halloo) reveal a grainy structure indicating that the eutectic grains were affected by the friction between circulating coins, in good observation with our pervious observation on worn coins [1]. The microstructural aspect of the lower relief confirms its well-preserved state without worn marks.

The backscattered electron image (BSE) display the elements distribution over the surface superimposed on the morphological details consisting in an elemental map (Figure 5b) Each element was assigned to a specific color such as blue for Ag and orange for Cu. The worn areas

clearly evidence a hypereutectic structure based on a dense mixture of eutectic grains (blue with fine orange spots) and  $\beta$  phase (e.g. pure Cu) phase. The microstructural observations are confirmed by the elemental composition of this area revealed by spectrum 43 (Figure 5c) having 65.5 % wt.% Ag and 34.5 wt. % Cu. The preserved areas reveal a different microstructure based on  $\alpha$  phase (e.g. pure Ag) grains mixed with eutectic grains belonging to the hypoeutectic region of the phase diagram. The fact generates a compact blue appearance spotted with small orange points. Spectrum 42 reveal the elemental composition of 73.7 wt.% Ag and 16.3 wt.% Ag. It indicates that the coin was covered by a thin layer of standard silver while the core is made of debased silver.

The obvious scratch on the obverse is too deep for obtaining a reliable image and therefore we took a microstructural detail at the lower end of the scratch revealing a significant copper segregation (Figure 6).



**Figure 6.** SEM investigation of the segregation overview: a) SEI image, b) BSE image displaying elemental map and c) EDS spectra taken on specific positions.

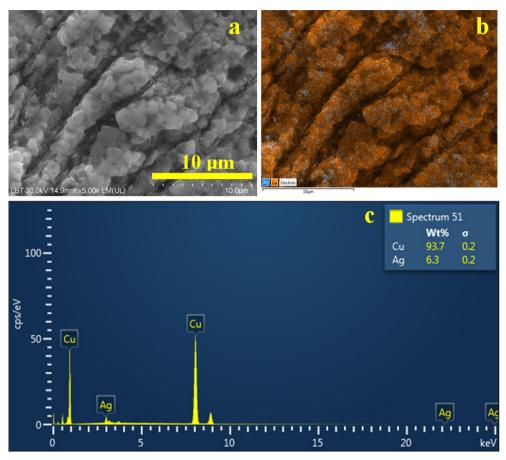
SEI image in Figure 6a reveal the typical hypereutectic microstructure elongated under the rolling direction interlocked with a compact area having a more refined microstructure. BSE image (Figure 6b) featuring the elemental map clearly reveals that the interlocked microstructural constituent is a large copper segregation which confirms the metallographic observation. The microstructure beside the copper segregation has a composition of 65.6 wt.% Ag and 34.4 wt.% Cu as observed in Spectrum 48 (Figure 6c) in good agreement with the worn area observed on the Madonna's head.

It is about a hypereutectic alloy situated in a close proximity of the eutectic composition. Of course, the liquid alloy cooling generates the precipitation of  $\beta$  grains enriching the melt in silver until the eutectic composition is achieved when it solidifies as eutectic grains. Unfortunately large ingots like ones used for coins minting causes an uneven distribution of the temperature under cooling allowing the coalescence of  $\beta$  grains which tends to extract excessively the copper from the remnant melt alloy generating large segregations.

The fact is proved by spectrum 49 indicating an appreciation of the copper content at 73.6 wt. % for the marked area. The shape of segregation is elongated under the rolling direction having a width of about 200  $\mu$ m and the length exceeds the image frame on the lower right corner. So far, it looks similar to the scratches microstructural aspect.

A closer look to the copper segregation microstructure is necessary. A specific area without silver intercalation was chosen at higher magnification (x5000) in Figure 7. While the general aspect of the copper segregation is elongated under the rolling direction the microstructural details reveal small grains of about 5  $\mu m$  having a cold hardened aspect with broken sub-grains of about 1 - 2  $\mu m$  split by parallel cracks oriented perpendicularly on the rolling direction dealing with literature observations [16].

Since silver is more ductile than copper, thus Cu segregation induces rolling defect as observed. The micro-fissures have identical length with the segregation width and a width of about 1 µm ensuring enough space for water and corrosive agents' penetration beside the broken sub grains promoting corrosion. The elemental analysis reveal a composition of 93.7 wt.% copper with minor silver intercalation appearing as blue spots in the elemental map. Although copper does corrode (oxidized by oxygen and by hydrogen sulphide) at the surface, it can form a stable corrosion film or a passivation layer, which prevents it against further corrosion in most environments [20]. The non segregated alloy areas within Figure 6b looks well preserved most likely due to the passivation layer formed in contact with the coin resting ground.



**Figure 7.** SEM microstructural details on the copper segregation: a) SEI image, b) BSE image displaying elemental map and c) EDS spectrum taken overall image.

The micro-fissures within the copper segregation along with the advanced internal fracture of the grains structure facilitate the penetration in depth of the oxidizing agents generating an advanced microstructural corrosion that prevent formation of passivation layer. It is difficult to discuss about the resting soil influence on the copper segregation corrosion while the coin discovery conditions are not known.

However, it is about the conjugated effect of water infiltration into the soil layers which mostly contains granular matter as quartz and calcite mixed with fine clay mixture based on kaolinite and muscovite [21, 22]. These minerals are able to release ions that might facilitate corrosion processes. The basic oxidation reactions use the oxygen present in the resting ground according to the following equations:

$$2Cu + O_2 \rightarrow 2CuO \tag{1}$$

$$4Cu + O_2 \rightarrow 2Cu_2O \tag{2}$$

Taking into consideration the potential presence of sulfur within the resting ground there is a more complex of oxidation to cuprite according to the equation (3):

$$2\text{CuS} + 3\text{O}_2 \rightarrow 2\text{Cu}_2\text{O} + 2\text{SO}_2.$$
 (3)

The soil's organic matter or the decomposing of organic remains beside the coin (e.g. vegetal fiber or leather bag containing a coin pile, or underground human body decay in case of graves discoveries) might release significant amounts of hydrogen sulphide [23, 24]. The well preserved state of the silver grains indicate low influence of sulfides that also attack silver (giving a black tarnish) and most likely oxidative corrosion facilitated by the mineral species within soil. The fact highlights the importance of archeological findings to be made by specialists with care for the information regarding the resting ground and its stratigraphy.

The current study limitation resides in the investigation of a single coin having the pseudo-scratches pattern oriented on the rolling direction. The random finding without knowing the characteristics of the resting environment for over 300 years also limits the physicochemical investigations. Literature data clearly indicate the importance of the finding place on the archeological discussions [25, 26].

The further analysis should be focused on larger coins number discovered in the precise archeological context which allows additional investigations of the resting ground. The detailed mineralogical investigations (X ray diffraction coupled with Mineralogical optical microscopy) of the resting ground might evidence some specific aspects regarding the coins corrosion and preservation state.

#### NUMISMATIC SIGNIFICANCE

Current physicochemical investigation reveal that copper segregation would have been difficult to be detected below of the good silver layer deposited during minting process ensuring a very nice appearance of the

coin. Hence, the core is made of a silver of about 65 wt.% the contemporary weighing would have been all right maintaining good silvery aspect if clipped. The intensive circulation causes intense friction over the coin surface erasing the good silver from the high relief details revealing the debased alloy. The repeated contact of debased silver with the hands induces oxidation of the copper  $\beta$  grains and segregations forming a passivated dark patina layer based on Cu<sub>2</sub>O and CuO which appear natural beside the shiny good silver on the lower areas of the coin's topography. The problem occur after about 400 years after the minting because of different corrosion of  $\beta$  grains and copper segregations which further appear as pseudo-scratches on the coin surface.

Unfortunately, the present study is focused on a single random find coin which is a limitation. Further research should be conducted on similar coins belonging to well known archeological finds to reveal if the copper segregation and its corrosion is confirmed and could be appreciated as a typical sign for debased small denominations. Local Transylvanian hoards are abundant in such monetary type but it worth to see its spread on the other countries circulation through the commerce [12, 27].

As the findings show, Gabriel Bethlen groats reached central Europe, for example Poland. But we have only four finds of such so far: Gdańsk – Łagiewniki, Jarosław, Dabrowa Chełmińska, Mieścisko. From which only the one from Gdansk-Łagiewniki is available. However, these are much rarer finds than the most common gold coins of this ruler in deposits from Poland and Silesia. Gabriel Bethlen's wide groat occurred during archaeological research in the Łagiewniki district of Gdańsk. It can be found in a publication by Professor Borys Paszkiewicz [6].

Parallel scratches are also visible on this specimen, which probably became apparent after the coin was cleaned. Similar damage to that seen on the Gabriel Bethlen groat in question can also be seen on other copies of the same type. For example on one found on the website, where the damages are smaller but clearly [28]. In addition, such damages are common on 24-kreuzer coins minted by Gabriel Bethlen in the Duchy of Opole and Racibórz [8]. Interestingly, the inflationary 24-kreuzer coins were registered only in the territory of historical Silesia (where they were minted), while the groat coins were kept in deposits from Greater Poland, probably recognized as full-value Transylvanian coins, despite Bethen's mints producing using worse money than the reform envisaged.

Visible, after conservation, damages on Bethlen coins reveal both the limits of seventeenth-century coin production technology and the economic urgency of minting. The incomplete homogenization of the Ag–Cu alloy caused copper micro-segregations that served as future corrosion nuclei.

# CONCLUSIONS

The poor elaboration of debased silver alloy combined with less control of temperatures during the specific technological steps generates large copper segregations within its microstructure.

The rolling regime prove to be adequate for the debased alloy respectively to the hypereutectoid composition of eutectic and  $\beta$  grains but induces over cold hardening of the copper segregation becoming elongated in the rolling direction having small intra-crystalline micro-cracks perpendicular on the rolling direction.

The hypereutectic microstructure seems to be well passivated to the corrosion while the copper segregation is affected in depth by the corrosive agents. Thus, the cleaning procedure removes the formed oxides revealing pseudo-scratches.

Over centuries, these zones oxidized preferentially, producing linear reddish "scratches" observable on cleaned specimens—misleadingly interpreted as post-mint damage. In reality, they constitute tangible metallographic evidence of hidden inflationary stress in the early-modern Transylvanian economy.

## **EXPERIMENTAL SECTION**

The object of current research is a wide groat issued by Gabriel Bethlen in 1626 at Baia Mare mint (N.B. Nagy Banya) presented in Figure 1. It is a random finding without archeological background and less information about the resting ground. The coin was cleaned using the standard procedure [29] as follows:

- The coins were subjected to ultrasound treatment for 10 minutes in aqueous environment;
  - Immersed in EDTA solution 5 % for 15 minutes;
  - Final ultrasound cleaning in water for 4 minutes.

Reflected light microscopy was effectuated using a Ulefone uSmart C01 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). The chemical etching was effectuated 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.

X ray diffraction (XRD) was performed with a Bruker D8 Advance diffractometer with Cu k $\alpha$  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 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 a 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.

# REFERENCES

- 1. I. Petean, G.A. Paltinean, A.C. Taut, S.E. Avram, E. Pripon, L. Barbu Tudoran, G. Borodi, *Materials*, **2023**, 16, 5809. https://doi.org/10.3390/ma16175809
- 2. I. Petean, L. Barbu Tudoran, G. Borodi, E. Pripon, *Acta Mvsei Porolissensis*, **2025**, 47, 387-395.
- 3. I. Petean, G.A. Paltinean, E. Pripon, G. Borodi, L. Barbu Tudoran, *Materials*, **2022**, *15*, 7514. https://doi.org/10.3390/ma15217514
- 4. K.K. Karaman, S Pamuk, S. Yıldırım-Karaman, *J. Monet. Econ.*, **2020**, 115, 279–300. https://doi.org/10.1016/j.jmoneco.2019.07.007
- H. Boubaker, J. Cunado, L.A. Gil-Alana, R. Gupta, R. *Phys. A Stat. Mech. Its Appl.*, **2020**, 540, 123093. https://doi.org/10.1016/j.physa.2019.123093
- 6. B. Paszkiewicz, Coin in old Gdańsk Archaeological research in 1997-2009 (in Polish: Moneta w dawnym Gdańsku badania archeologiczne w latach 1997-2009), Gdańsk, **2013**.
- 7. M. Grochowska-Jasnos, *Acta Musei Porolisensis*, **2025**, *Acta Mvsei Porolissensis*, **2025**, 47, 397-438.
- 8. Ł. Sroka, P. Milejski, *The Hoard of Prague Groschen and Seventeenth-century Coins from Osieczów, Bolesławiec District*, Bibliotheca Nummaria Leopoldina 2. Wrocław. **2020**.
- 9. F. Ciulavu, Studii si Cercetari Numismatice Serie noua, 2013, 4(16), 127-143.
- 10. F. Ciulavu, *Activitatea monetăriei de la Alba Iulia. Studiu numisamtic, istoric și arheologic*, Editura Mega, Cluj-Napoca, **2020**.
- 11. E. Pripon, *Tezaure monetare medievale și premoderne descoperite pe teritoriul orașului Zalău (I)*, Editura Mega, Cluj-Napoca, **2018**.
- 12. Corina Toma, *Tezaure monetare și tezaurizare în Transilvania secolelor XV/XVI-XVII*, Editura Muzeului Tării Crisurilor Oradea, Oradea, **2016**, 148, 132-148.
- 13. M. Grochowska-Jasnos, *Graffiti on post-medieval coins: practical, symbolic, and alchemical messages*, Book of abstracts, Numismatica Centroeuropea Conference, Legnica, Poland, **2025**, 61-63.

- I.R. Souza Filho, M.J.R. Sandim, D. Ponge, H.R.Z. Sandim, D. Raabe, *Materials Science and Engineering: A*, 2019, 754, 636-649. https://doi.org/10.1016/j.msea.2019.03.116
- S. Semboshi, S. Sato, G. Miyamoto, K. Ito, S. Kasatani, H. Hyodo, *Materials Science and Engineering: A*, 2025, 941, 148638. https://doi.org/10.1016/j.msea.2025.148638
- X. Zhu, Z. Xiao, J. An, H. Jiang, Y. Jiang, Z. Li, *Journal of Alloys and Compounds*, 2021, 883, 160769, https://doi.org/10.1016/j.iallcom.2021.160769
- 17. A.E. Gheribi, J. Rogez, F. Marinelli, J.C. Mathieu, M.C. Record, *Calphad*, **2007**, 31, 380-389. https://doi.org/10.1016/j.calphad.2006.10.005
- B. Bozzini, G. Giovannelli, C. Mele, F. Brunella, S. Goidanich, P. Pedeferri, Corrosion Science, 2006, 48, 193–208, https://doi.org/10.1016/j.corsci.2004.11.024
- 19. M. Di Fazio, F. Di Turo, L. Medeghini, L. Fabrizi, F. Catalli, C. De Vito, *Microchemical Journal*, **2019**, 144, 309-318. https://doi.org/10.1016/j.microc.2018.09.016
- H. Huisman, R. Ackermann, L. Claes, L. van Eijck, T. de Groot, I. Joosten, F. Kemmers, N. Kerkhoven, J-W. de Kort, S. Lo Russo, D. Ngan-Tillard, B. van Os, M. Peter, C. Pümpin, J. Vaars, Z. Zhou, *Journal of Archaeological Science*, 2023, 47, 103799. https://doi.org/10.1016/j.jasrep.2022.103799
- 21. S.E. Avram, L.B. Tudoran, G. Borodi, I. Petean, *Appl. Sci.*, **2025**, 15, 6445. https://doi.org/10.3390/app15126445
- 22. S.E. Avram, L.B. Tudoran, G. Borodi, M.R. Filip, I. Ciotlaus, I. Petean, *Sustainability*, **2025**, 17, 2906. https://doi.org/10.3390/su17072906
- 23. B.S. van der Meulen-van der Veen, *Journal of Archaeological Science: Reports*, 2023, 48, 103839. https://doi.org/10.1016/j.jasrep.2023.103839
- 24. M. Habibzadeh, O. Oudbashi, R. Naseri, S. Bahadori, *Journal of Archaeological Science: Reports*, 2025, 65, 105186. https://doi.org/10.1016/j.jasrep.2025.105186
- 25. M. Grochowska-Jasnos. Numismaticky Sbornik. 2022. 36. 41.
- 26. C.C. Gavrila, M.Y. Lates, G. Grebenisan, Sustainability, 2024, 16, 2322.
- 27. C. Toma, *Un tezaur monetar descoperit în localitatea Chișcău, jud. Bihor (sec. XVII)*, in I. Glodariu, G. Gheorghiu (ed.), Studii de Istorie și Arheologie. Omagiu cercetătorului Dr. Eugen Iaroslavschi, Clui-Napoca, 2010, 292.
- 28. Siedmiogród, Gabriel *Bethlen (1613–1629). Grosz szeroki 1626 CC, Koszyce*, https://archiwum.niemczyk.pl/product/366185/siedmiogrod-gabriel-bethlen-1613-1629-grosz-szeroki-1626-cc-koszyce, accessed on 9 october **2025**.
- 29. W. Mourray, *Metallic antiquities conservation from the archeological excavation to the museum*, Editura Tehnica, Bucuresti, **1998**.