ANALYSIS BY OPTICAL AND ELECTRONIC MICROSCOPY ON THE SILVER OKLAD OF ST. ANDREW ICON (ROMANIAN ART, 19th CENTURY)

Lăcrămioara-Raluca BIVOL[1], Eugeniu VASILE[2] *, Dan GHEORGHE[3] ,Valeriu-Gabriel GHICA[4], Mihai BUZATU[5], Mircea-Ionuț PETRESCU[6], Tünde Anna KOVÁCS[7], Gheorghe IACOB[8]

The oklad of St. Andrew's icon is composed of two parts: the oklad on which are stamped in the center-right, one below the other, two hallmarks (monogram "EF", respectively number "12"), and the riza (halo) which is detachable and has no stamped hallmark on the surface. The analysis of St. Andrew's silver oklad was based on references from the literature and on a complex metallographic analysis (optical and electronic microscopy). Following the examination under the Reichert Univar metallographic microscope, it was observed that the icon oklad was processed by cold deformation. In order to determine the chemical composition investigations were carried out by X-ray spectroscopy (EDX), and scanning electron microscopy (SEM), as a result of which it has been established that the oklad was made of a ternary alloy of silver-copper-zinc.

Keywords: oklad, silver title 12, Ag-Cu-Zn alloy, EDX, SEM.

1. Introduction

The first documentary references on the activity of the master silversmiths from the Romanian territory date back to the 14th century [1]. In Sibiu, Brașov, Cluj and Sighișoara, the craft of precious arts developed strongly, so that in the

[1] PhD Student, Faculty of Materials Science and Engineering, University POLITEHNICA of Bucharest, Romania, e-mail: lrbivol@yahoo.com;
[2] Researcher grade I, Faculty of Applied Chemistry and Materials Science, University POLITEHNICA of Bucharest, Romania, * - corresponding author, eugeniuvasile@yahoo.com;
[3] Prof., Faculty of Materials Science and Engineering, University POLITEHNICA of Bucharest, Romania, e-mail: ghe58dan@yahoo.com;
[4] Prof., Faculty of Materials Science and Engineering, University POLITEHNICA of Bucharest, Romania, e-mail: gvghica@yahoo.com;
[5] Prof., Faculty of Materials Science and Engineering, University POLITEHNICA of Bucharest, Romania, e-mail: buzatu.mihai@yahoo.com;
[6] Prof., Faculty of Materials Science and Engineering, University POLITEHNICA of Bucharest, Romania, e-mail: ipetrescu@yahoo.com;
[7] Assoc. Faculty of Mechanical and Safety Engineering, ÓBUDA University, 1081 Budapest, Hungary, e-mail: kovacs.tunde@bgk.uni-obuda.hu;
[8] Lecturer, Faculty of Materials Science and Engineering, University POLITEHNICA of Bucharest, Romania, e-mail: iacob_gh@yahoo.com

second half of the 16th century in the biggest silverware center in Brașov was working at the same time about 40 master silversmiths [1].

At the beginning of the 16th century, a master silversmith originate from Brașov was active in Câmpulung [1], and the Silversmiths Guild of Moldova was formed in the 17th century in Iași [1]. The saxon master silversmiths from the 16th century who worked in Transylvania provided silverware objects to Moldova and Wallachia [1].

Examples of oklads of silver alloy icons in church collections in Romania that have on their surface the number “12”: “Bunăvestire” (Annunciation), ¼ of 19th century - Cocoş Monastery [2]; “Maica Domnului Îndurerată” (Mother of the Lord Suffering), ¾ of 19th century - St. Teodor Tiron Church [3]; “Adormirea Precistii” (The Dormition of the Virgin), ¾ of 19th century - Celic-Dere Monastery [2].

In the case of this icon oklad, which has the inscription in Romanian "SF. AP. ANDREI" (St. Andrew the Apostle), two hallmarks are stamped: the number “12” which should represent the silver title used for the work, namely the “EF” mark – the monogram of master silversmith (maker’s mark) or assay master (assayer’s mark). Usually, the verification of the metal purity and the execution of objects from an artistic and technical point of view were carried out by the most talented and experienced silversmiths, who also had the quality of assay masters [1].

Type of mark 12 was part of the German silver standardization system, “löthige” (löthig) which is based on the number of parts out of a total of 16 [4]. Basically, for the mark 12 löthige, the amount of pure silver is calculated by dividing 12 to 16 (12/16), the result being .750 (750/1000 parts pure silver). The title of silver 12 has been used in Germany since the 1600s to the early 1800s [5].

Based on the law of 1809, the löthige system for measuring purity of silver was also used in one of the three districts (Scavonia, Lombardo Venetian and Hungarian) of Austria, respectively the Hungarian District [6].

The stamping of the number “12” (and one letter) on the silver objects was also used in the context of the Habsburg House's political measures from 1 September 1806 - 31 July 1807 and 1809-1810, with the aim of enriching the state budget by confiscating and melting precious metals from churches and private collections [7]. The seized pieces of silver could be redeemed by the owners by paying the tax of 12 kreutzers/loth of silver, which was certified by the application of the remark stamp – “repunzierungsstempel” [7]. This mark was one of the three variants of the existing stamps at that time. Number “12” was the proof that the ransom fee of 12 kreutzers/loth of silver (in no case the purity of silver in the löthige system) was paid, and the letter near the number “12” signified the city where the piece was remarked [7].

On the territory of our country, “the silver mark *12* appears between 1750-1850 in Brașov, around 1760 in Sibiu, and in Oradea, during the 18th century until 1810 [8].”

2. Materials and methods

The analysis on the oklad of St. Andrew's icon was based on metallographic analysis (optical and electronic microscopy) and on literature references.

The oklad of St. Andrew's icon is composed of two parts: the oklad (Figs. 1a and 2a) on which are stamped two hallmarks: monogram “EF”, respectively number “12" (Fig. 2b) and the riza (Fig. 1b) which is detachable and has no stamped mark on the surface.

Fig. 1. The oklad (a) and riza (b) – detail

Fig. 2. Reverse image overview (a) and hallmarks (b) – detail

Silver objects may be affected by silver corrosion products, such as silver sulfide (black), silver chloride (white) and chlorargyrite (gray-like substance) [9], but it is also known that sometimes corrosion compounds of less noble metal affect the noble metal surface.

For example, silver alloys containing non-precious metals are coated with a layer of dark oxide (Figure 3) - this corrosion is caused by the formation of the sulfides of the alloying metal [9]. The surface of the lower quality silver objects is covered with corrosion products of copper [9], and “once formed on the surface of the object; the copper compounds can form an adherent, compact and protective layer, masking the actual metallic support of the artifact [10].”

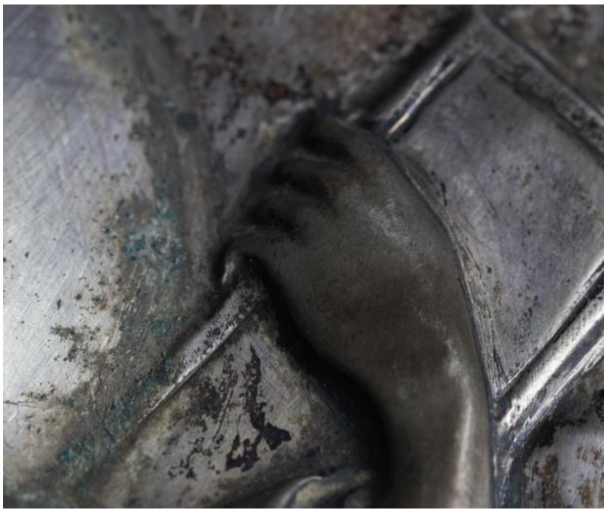

Fig. 3. Corrosion products – detail

2.1. Metallographic analysis

In order to highlight the structure, a sample of 1.5 mm^2 was taken from the edge of the icon, from the area of penetration of the oklad fastening nail on the wooden support of the painting.

Sample preparation was performed by grinding and polishing on the Buehler Alpha machine as follows:

- The grinding was done in four steps, using abrasive papers with granulations of 75, 45, 25, 15 μm, with the following parameters: 4 N/mm^2 pressing force; 300rot / min turntable speed; 3min/stage grinding time;
- The polishing was done on a "Buehler-Microflok" textile support in five steps using diamond suspensions as abrasive materials with granulations of 9, 6, 3, 1 μm with the following parameters: 4 N/mm^2 pressing force; 200 rpm turntable speed; 3 min/step polishing time;

- The final polishing step was carried out on a "Buehler-Vibromet" vibration polishing device, using as abrasive an aqueous suspension of colloidal silica with granulation of 0.02 μm for 6 hours.

After final polishing, the sample was attacked with 2% NITAL by immersion for 15 seconds.

2.2. Analysis by scanning electron microscopy

The sample was also analyzed by Scanning Electron Microscopy using a Quanta Inspect F50, with a field emission gun (FEG) with 1.2 nm resolution and an Energy Dispersive X-ray Spectrometer (EDXS) having 133 eV resolutions at MnKα. Electron microscopy analyzes were performed on the sample before and after the metallographic polishing.

3. Results and discussions

Metallographic examination of the sample showed that it was worked up by deformation. The structure of the material has an appearance of elongated and interstitial particles, typical of cold deformation structures (Fig. 4).

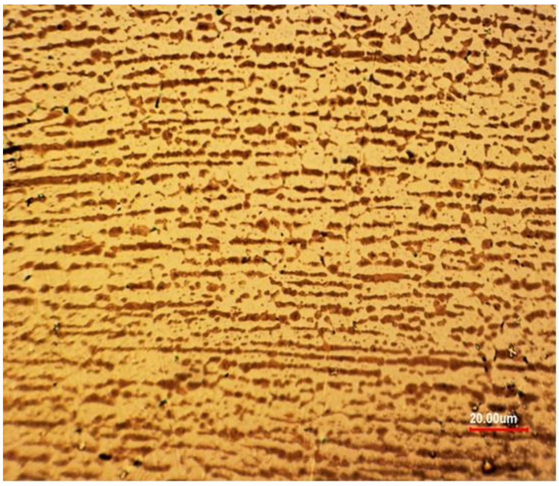

Fig. 4. Metallographic analysis of the surface attacked with 2% NITAL

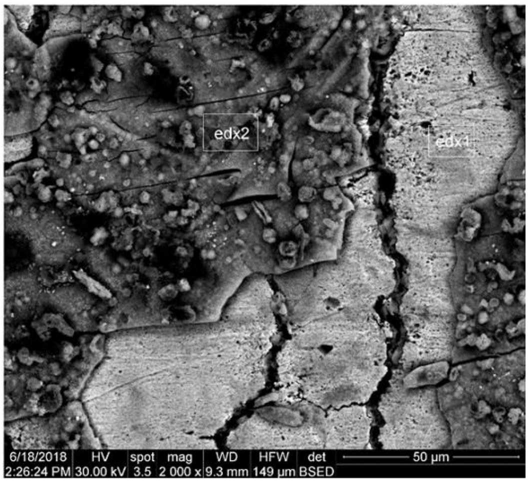

Fig. 5. SEI image with the two analyzed micro-areas on the oklad surface (EDX1 and EDX2); non-polished sample

The EDX analysis on the non-polished surface (Fig. 5) revealed that a film of oxides and carbonates based on silver and copper was formed on the surface of the oklad. Two representative micro-areas were captured and analyzed:

- Micro-area 1 (EDX 1) on which the thick oxide layer detaches from the oklad surface; following the EDAX ZAF Quantification (Standardless) analysis, it can be seen that the concentration of Ag is about 80% on the analyzed surface, the Cu concentration is 3% and the Zn concentration is 1.25% (Fig. 6).

- Micro-area 2 (EDX 2) located on the layer of oxides, sulphates and carbonates that formed over time on the oklad surface. On this section the concentration of Ag drops to 55%, the concentration of Cu rises to 13% and the Zn concentration is around 1% (Fig. 7).

High percentage of Ca, Si, Al, Mg, O, C, and especially S (8.13% wt) have been identified, which signifies a strong concentration of sulphates, oxides and carbonates characteristic of corrosion processes. This confirms that corrosion compounds of less noble metal over time cover the noble metal surface (see Fig. 4).

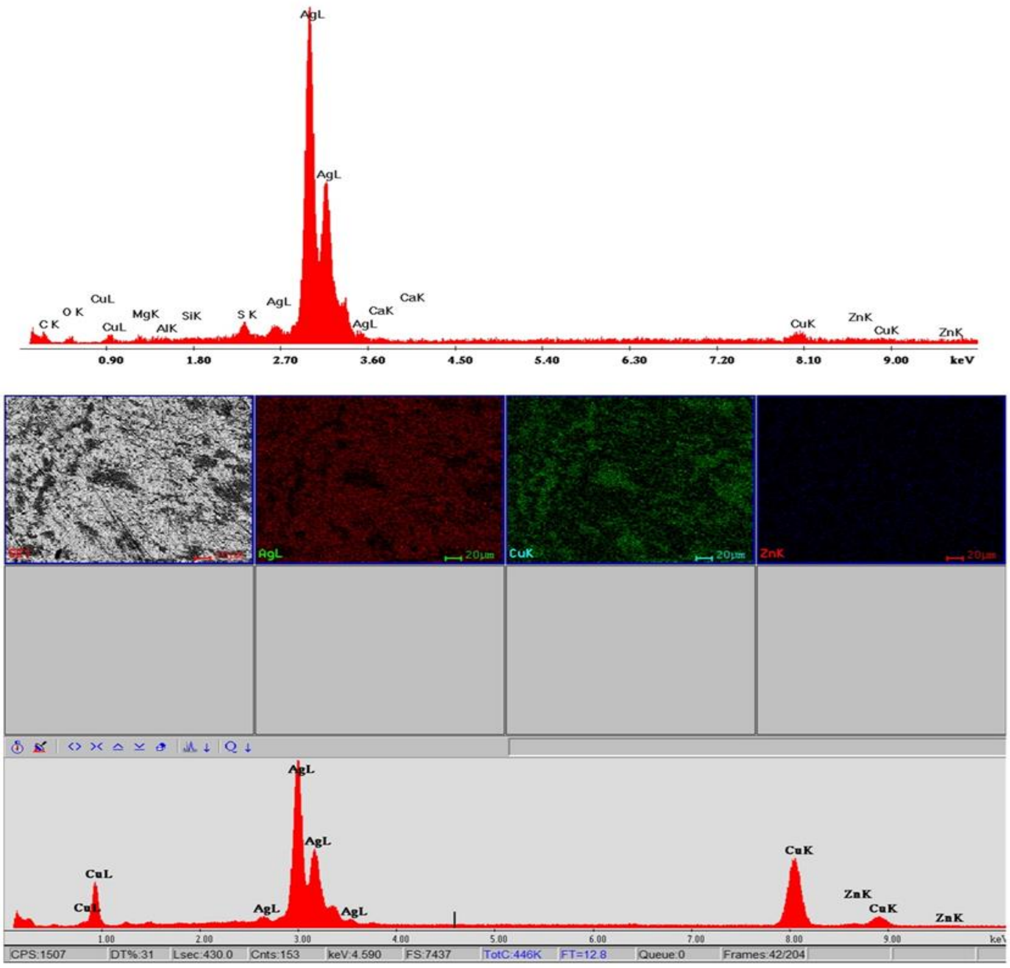

Fig. 6. Micro-area 1 (EDX 1) - analysis on the surface from which the oxides / sulphates / carbonates layer has been removed

Table 1

Oklad - average composition (EDX1)

Elem	Wt %	At %	K-Ratio	Z	A	F
CK	5.85	27.92	0.0236	1.2010	0.3355	1.0001
OK	4.16	14.89	0.0047	1.1836	0.0947	1.0002
MgK	1.47	3.46	0.0034	1.1396	0.2011	1.0042
AlK	0.84	1.79	0.0025	1.1068	0.2686	1.0078
SiK	0.75	1.52	0.0031	1.1397	0.3573	1.0141
SK	1.96	3.50	0.0132	1.1315	0.5725	1.0403
AgL	80.43	42.72	0.7597	0.9489	0.9954	1.0001
CaK	0.25	0.35	0.0013	1.1471	0.4423	1.0005
CuK	3.05	2.75	0.0278	1.0169	0.8956	1.0000
ZnK	1.25	1.10	0.0117	1.0220	0.9174	1.0000
Total	100.00	100.00				

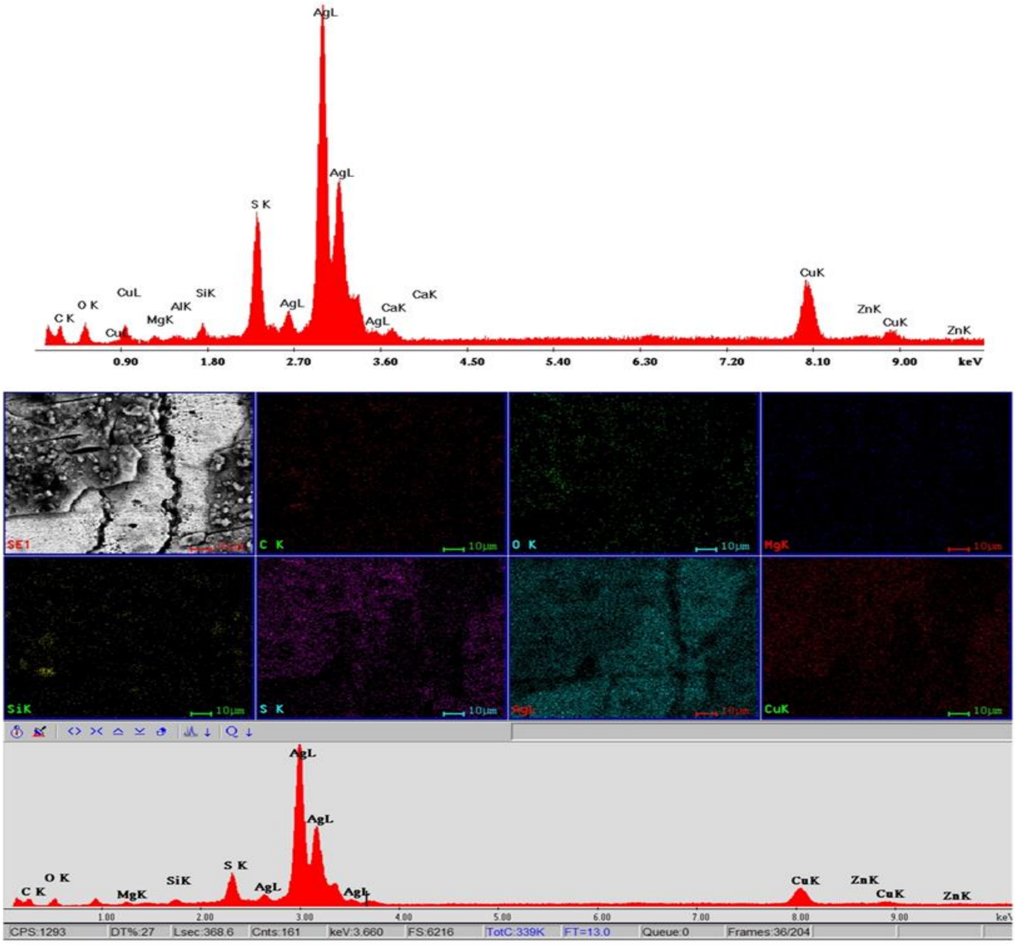

Fig. 7. Micro-area 2 (EDX 2) - analysis on the surface covered with the oxides / sulphates / carbonates layer

Table 2

Oklad - average composition (EDX2)

Elem	Wt %	At %	K-Ratio	Z	A	F
CK	11.13	36.74	0.0280	1.1544	0.2179	1.0001
OK	8.01	19.85	0.0099	1.1378	0.1083	1.0003
MgK	0.68	1.11	0.0015	1.0958	0.2024	1.0036
AlK	0.46	0.68	0.0014	1.0644	0.2755	1.0067
SiK	1.13	1.60	0.0047	1.0962	0.3701	1.0118
SK	8.13	10.05	0.0534	1.0887	0.5880	1.0272
AgL	55.70	20.48	0.4782	0.9041	0.9492	1.0004
CaK	0.84	0.83	0.0048	1.0925	0.5161	1.0018
CuK	12.86	8.03	0.1158	0.9720	0.9264	1.0000
ZnK	1.06	0.64	0.0098	0.9760	0.9434	1.0000
Total	100.00	100.00				

After the metallographic preparation, the sample was re-analyzed by EDX analysis (Fig. 8) and Scanning Electron Microscopy (Fig. 9a, b).

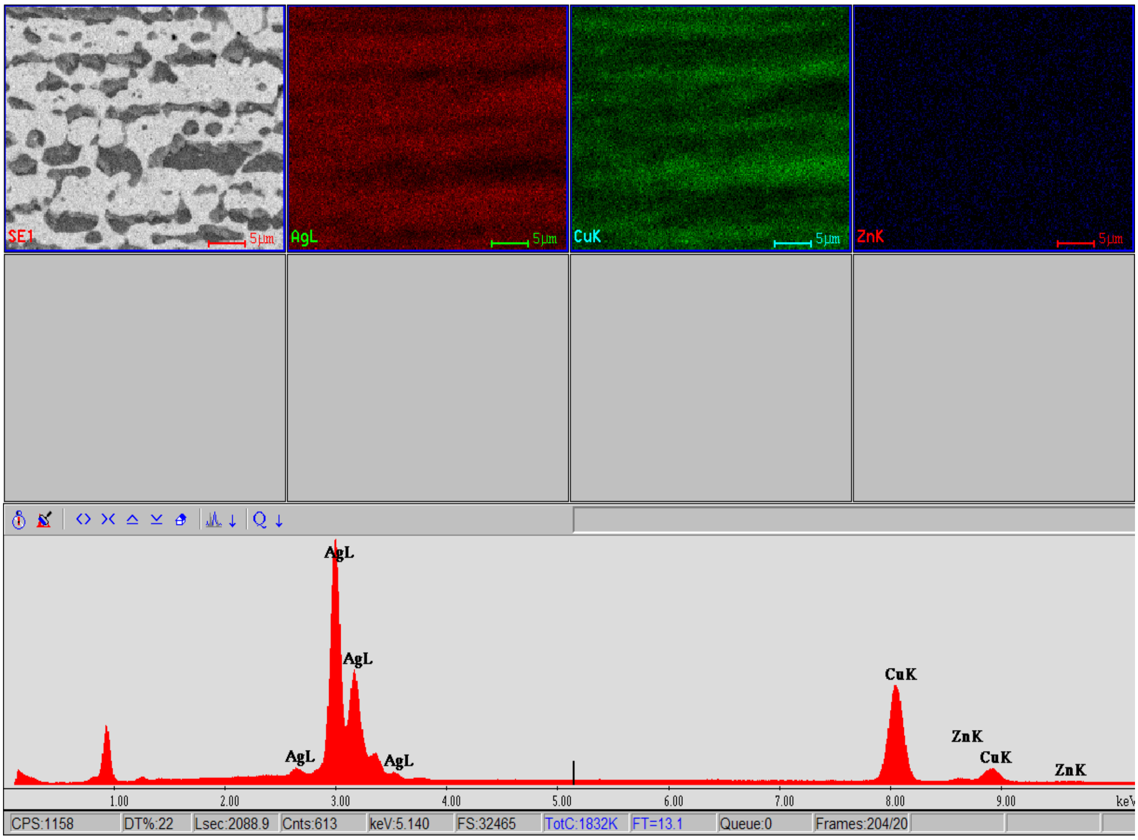

Fig. 9. EDX analysis of St. Andrew oklad - Mapp all

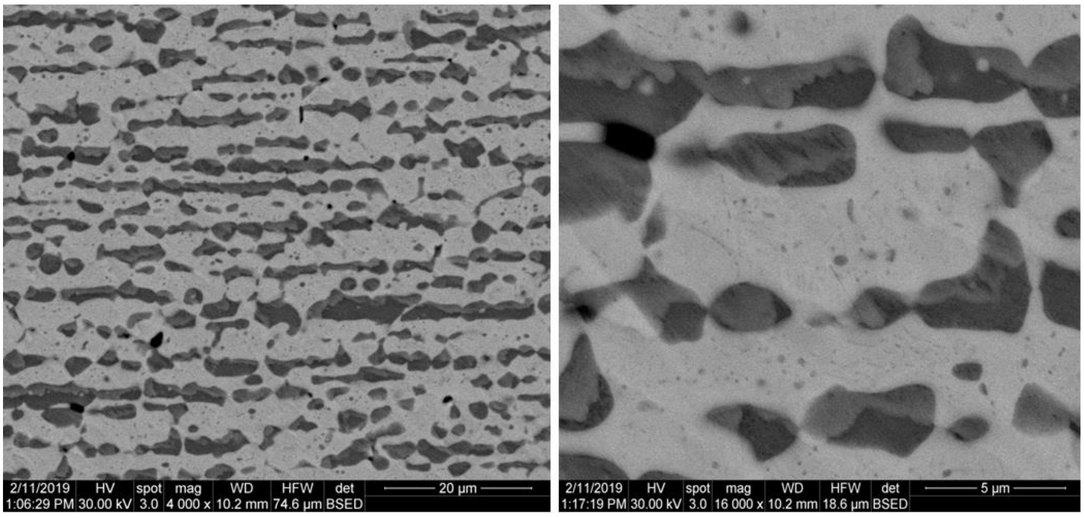

Fig. 8. SEI image of the sample; magnification x4.000 (a) and x16.000 (b)

We can observe the silver matrix in which are embedded elongated, lined up, tougher particles of Ag-Cu eutectic with Zn addition. Following metallographic preparation, after polishing, the softer silver matrix sometimes covers the eutectic Ag-Cu (Zn). The addition of zinc to silver and copper alloys lowers the eutectic temperature and increases the ratio of silver to copper in eutectic, according to the phase equilibrium diagram.

Several EDX analyzes were performed in several positions to determine the chemical composition of the alloy - EDX 1, EDX 2, EDX 3 and the overall EDX 4 and the results are centralized in Table 3.

Table 3

Chemical compositions according to EDX analysis

Analysis	Elem	Wt %	At %	K-Ratio	Z	A	F
EDX 1	AgL	74.63	63.44	0.6841	0.9798	0.9355	1.0000
	CuK	24.22	34.95	0.2288	1.0486	0.9007	1.0000
	ZnK	1.15	1.61	0.0111	1.0541	0.9217	1.0000
	Total	100.00	100.00				
EDX 2	AgL	71.10	59.21	0.6437	0.9771	0.9264	1.0000
	CuK	27.11	38.33	0.2566	1.0460	0.9049	1.0000
	ZnK	1.79	2.46	0.0174	1.0514	0.9252	1.0000
	Total	100.00	100.00				
EDX 3	AgL	77.39	66.87	0.7160	0.9819	0.9422	1.0000
	CuK	21.43	31.43	0.2020	1.0506	0.8975	1.0000
	ZnK	1.19	1.70	0.0115	1.0562	0.9189	1.0000
	Total	100.00	100.00				
Overall EDX 4	AgL	70.71	58.74	0.6394	0.9769	0.9258	1.0000
	CuK	28.03	39.52	0.2654	1.0458	0.9054	1.0000
	ZnK	1.27	1.74	0.0124	1.0511	0.9256	1.0000
	Total	100.00	100.00				

4. Conclusions

The results obtained from present work can be summarized as follows.

1. The oklad of “St. Andrew's” icon was probably executed in the 19th century, and the monogram “EF” belonged to a master silversmith or assay master from a local workshop whose name was not identified. The number “12” is the silver title of the löthige silver purity measurement system, equivalent to .750 in the metric system; in any case “12” is not the remark stamp, applied after the payment of the redemption fee of 12 kreutzers.

2. Technical execution of silver oklad is punching, chiseling and engraving (Figs. 1 and 2).

3. Through optical and electronic microscopy analyzes the chemical composition and metallographic structure was determined. The silver matrix was identified in which elongated, lined up (consequent to cold plastic deformation) and harder particles were embedded, formed of Ag-Cu eutectic with Zn addition.

4. The chemical composition indicates the presence of Ag (over 70 wt %) which corresponds to the inscribed mark “12”.

5. According to EDX analyzes, the O. Mureşan's opinion [10] is confirmed that as time goes on, corrosion compounds of less noble metal, “once formed on the surface of the object, can form an adherent, compact and protective layer, masking the real metallic support of the artifact in question” [10].

R E F E R E N C E S

[1]. *C. Nicolescu*, The art of precious metals in Romania (in Romanian), Editura Meridiane, București, 1973.

[2]. *S. S. Duciu*, Testimonies of Orthodox Art and Culture from the Diocese of Tulcea 17th-20th century (in Romanian), Editura Universitaria, Craiova, 2013.

[3]. *S. S. Duciu*, Testimonies of Orthodox Art and Culture from the Diocese of Alexandria and Teleorman 17th-20th century (in Romanian), Editura Universitaria, Craiova, 2014.

[4]. *J. K. Dobney*, Royal Kettledrums from the House of Hanover, in The Galpin Society Journal, **vol. 69**, Apr. 2016.

[5]. *S. L. Smith*, European Silver Quality Markings. The Beer Stein Journal, Nov. 1994. Accesed June 24, 2018 from: https://www.beerstein.net/articles/bsj-2c.chtm.

[6]. *C. A. Markham*, Handbook to foreign hall marks on gold and silver plate: (With the exception of those in French plate) Containing 163 stamps, Gibbings and Co., Limited, London, 1898.

[7]. *D. M. Andrásy*, Mărci de taxă aplicate pe piese de argintărie (Trademarks tax applied to parts of silverware), in Patrimonium Banaticum, vol. III, 2004.

[8]. *L. D. Postolache, I. Darida, A. Floroiu, M. V. Dudu, I. Sburlea, B. Mălinescu* and *A. V. Herăscu*, Methodological landmarks from the conservation and restoration process of six royal icons made by Nicolae Grigorescu at the Zamfira Monastery (in Romanian), in Caietele restaurării, Ed. ACS, București, 2018.

[9]. *O. I. Minzhulin*, Restoration of metal works (in Russian) Спалах, Kiev, 1998.

[10]. *O. Mureșan*, About a rigorous language in researching metal artifacts (in Romanian), in Arheovest I, Arheo Vest, Timișoara, 2013.