Metallographic Study of XIX Century Oklads Belonging to Russian Icons

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Abstract. Many icons from the XIX and XX centuries can be found on the territory of Romania, with oklads made of Cu, Ag or Cu alloys. This paper analyzes by means of optical and electronic microscopy the samples taken from two oklads belonging to Russian icons of the XIX century: one dated and the other undated but attributed to the XIX century by Florin Colonas - an expert in handicraft of artistic significance. Based on the pins on the surface of one of the oklad and the scientific literature, we tried to identify the manufacturer, the verification mark, with the date of manufacture, the Ag title mark, the mark with the city icon in which the oklad was made, and identifying the technique of realization. The chemical compositions of the oklads were determined by EDX and found to be made of Ag alloys of different chemical composition: the dated oklad is made of Ag-Cu alloy, while the undated one is made of Ag-Cu-Zn alloy.

1. Introduction
In the whole of Romanian art a special place is owned by objects in precious metals mostly hammered in silver and gilded and the Romanian collections include numerous works by both local artists and foreign artists from silverware centers in Russia or other European countries [1].

In the culture of the Thracians at the end of the Bronze Age and the beginning of Hallstatt, during which silver objects replaced the gold ones, the development of silverware and local style with its own features was influenced by Greek art in the cities near the Black Sea [1].

Until the seventh century, in Dobrogea and in the Danube area, both under the domination of Eastern Roman Empire, the gilded silver, gold or bronze fine art objects, made in Byzantine style, were very popular, and the churches in these areas were decorated with Byzantine silverware imported from Constantinople [1].

In the Danubian settlements of Capidava, Garvan, Păcuiul lui Soare, silver and gold adornments, amulets, reliquary crosses dating back to the X-XII centuries, some of local origin, and others brought from the Kievan, Byzantine or Oriental workshops [2].

In the XII-XIV centuries, the centers in the Danubian cities, directly related to Byzantine civilization and art, through political, economic and administrative relations with Byzantium, played a special role in the distribution and production of precious metal objects such as the engolpion crosses from Ibanești and Trifești, the thesaurus from Oțelani, Cotnari and Voinesti. Under the forms of
technique and ornamentation, these objects are related to the Kievan art, which was also of Byzantine origin. In terms of art forms and ornamentation, these objects are related to the Kievan art, which was also of Byzantine origin [1].

The first documentary mentions and the oldest preserved objects that confirm the work of the Romanian silver and gold craftsmen date back to the XIV century. In the XV century the goldsmiths are organized in guilds, with statute-bound rules, and since the 16th century an obligation has been implemented for them to stamp the recognition signs of the city and craftsman on the objects. Silver had to be 14-15 carats and gold 18-20 carats [2].

At the end of the XV century - the beginning of the XVI century, the processing of precious metals was widely spread to monasteries. The richness of silverware in the inventories of Moldovan churches and monasteries confirms, based on inscriptions on objects, the existence of local workshops of a real technical value [3].

The silverware of Russian origin was frequently used in the XVIII century, especially in Moldova [1]. Works of Russian silverware, oklads and objects of worship from the XVIII and XIX centuries can be found in many monasteries in Moldova, especially in Neamț, Secu, Putna [4]. The Russian icons, covered with silver and gilded oklads (garnets) that have spread in large numbers in Romania in the XVIII-XIX centuries, were made in the usual technique of hammering, chiseling and engraving, as well as in the technique of painted enamel, watermark or cloisonné [5].

It is noteworthy that in the XIX century, the Russian silverware retained superior quality of execution, although the traditional manufacturing techniques were replaced with mechanical techniques (lamination / punching) for the processing of precious metals [5, 6].

2. Experimental procedures
2.1. Materials
Two oklads of the XIX century which belong to Russian painted icons were analyzed. Both icons in Figures 1 and 2 present the same subject (Virgin Mary with Child Jesus).

![Figure 1. Oklad of an icon with markings, Russia, 1867, 26.50 x 21.50 cm.](image1)

![Figure 2. Undated oklad, Russia, 19.50 x 14.00 cm.](image2)

The oklad dating back to 1876 is complete, but the undated oklad is incomplete (missing the Virgin Mary's aureole).
Applying the silver window on icons is done for two reasons:
- as a token of appreciation for the character painted in the icon;
- the clothing protects the painted surface of the icon from damage caused by awe, smoke and wax.

The two oklads were made by mechanical lamination and stamping, techniques that developed in the XIX century [7]. Stamping is a technique that provides the possibility of obtaining a repousse work by means of pressing between two forms - a matrix and a punch. Stamped products have smooth, rounded lines, with no changes in thickness of the metal plate used and no sudden crossings of height [8].

The oklad of the icon dated in 1876 in the control mark presents two series of four similar punches. The first set of markings is in the aureole area (Figure 3) and has the following order:
- the marking with the master monogram - И.С.К. (I.S.K.), for the identification of the craftsman was used the catalog of markings from the book written in 1995 (catalog position 945, page 174) in Russian [M.M. Post]. In the aforementioned book, the ИСК (ISK) monogram appears without any points between the initials and belongs to the craftsman Иван Семенов Комаров (ИванСеменовКомаров) who worked in 1808 in the Russian village Podol'skoye (Подольское) [7]. The difference between the monogram on the oklad shown in this article and the one used by the above mentioned craftsman consists in the existence of the points between the initials of the name [7].
- the monogram of the controller in the control mark, which also includes the date of the verification - АС / ... (А.C./1867), for the identification of the controller was used the catalog of markings from the book written in 1995 (catalog position 2113, page 205) in Russian [7]. In the aforementioned book, the AC / ... monogram belongs to A. Svechin (А. Свечин), who worked in Moscow from 1862 to 1875 [7].
- title mark silver – 84, for the identification of the title mark was used the catalog of markings from the book written in 1995 (catalog positions 12 and 13, page 184) in Russian [7]. The title of silver 84, although it has been met since the middle of the XVIII century, became obligatory starting with May 1, 1798 [7].
- the marking with the coat of arms of Moscow - Saint George on horseback slaying the Dragon. For the identification of marking was used the catalog of markings from the book written in 1995 (catalog positions 2014 and 2015, page 203) in Russian [7].

The second series of four punches is in the clothing area (Figure 4), in this case the three grouped markings (А.C./1867, 84 and the coat of arms of Moscow) are followed by the fourth mark - И.С.К. (I.S.K.).

The undated oklad was attributed to the XIX century Russian workshops by Florin Colonaş - an expert in handicraft of artistic significance.

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Figure 3. Icon oklad with markings, left upper part – aureole.
2.2. Characterization methods
The comparative study of two XIX century Russian icons made of silver alloys was based on literature research and metallographic analysis (optical and electron microscopy).

The metallographic analysis was performed on an optical microscope and the images were taken on the OMNIMET Buehler analyzer. The samples were 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 resolution at MnKα. EDX analyzes were performed for each of the two samples analyzed.

3. Results and discussions
The two oklads were made by mechanical lamination and stamping, techniques that developed greatly in the XIX century [7]. Stamping is a technique that provides the possibility of obtaining a repousse by means of pressing between two forms - a matrix and a punch. Stamped products have smooth, rounded lines, with no changes in thickness of the metal plate used and no sudden crossings of height [8].

It is possible that monogram ИСК appears without any points between the initials and belongs to the craftsman Ivan Semenov Komarov (Иван Семенов Комаров) who worked in 1808 in the Russian village Podol'skoye (Подольское) [7] although the difference between the monogram on the oklad shown in this article and the one used by the above mentioned craftsman consists in the existence of the points between the initials of the name [7]. As regards the controller's monogram in the verification mark – A.C./1867, it probably belongs to A. Svechin (А. Свечин), who worked in Moscow from 1862 to 1875 [7]. The silver title mark - 84 and the city mark Saint George on horseback slaying the Dragon (coat of arms of Moscow) are specific to the XVIII-XIX centuries [7]. We must consider the existence of a significant gap between the manufacturing and verification periods, as well as between the manufacturing site of craftsman Ivan Semenov Komarov (Podol'skoye) and that of controller A. Svechin (Moscow).

The experimental investigations were carried out in the laboratories of Faculty of Materials Science and Engineering from University Politehnica of Bucharest.

From the oklad-holding area on the wood of the icon samples of 1-2 mm² were taken on which metallographic analyzes were carried out to identify the metallographic structure and the chemical composition of the silver alloys.

Before the metallographic analysis performed on an optical microscope (OMNIMET Buehler) the samples were reacted with a solution of: 1 g Cr₂O₃; 1 ml H₂SO₄; 500 ml H₂O₂ (established procedures for highlighting the grain size in the case of Ag-Cu alloys). The silver foil was very heavily deformed (due to the processing technique) by lamination and punching and therefore the size of the grain could not be observed.

The samples were analyzed by Scanning Electron Microscopy using a Quanta Inspect F50 (Figures 9 to 12), and in terms of chemical composition. The results of the EDX analysis performed in three points for each of the two samples analyzed are shown in Tables 1 (for the marked sample) and Table 2 (for the unmarked sample).
Figure 5. Optical Microscopy (Marked oklad).

Figure 6. Optical Microscopy (Unmarked oklad).

Table 1. Marked oklad - average composition (EDX).

| Elem | Wt %  | At %  | K-Ratio | Z   | A  | F    | Net Inte. | Backgrd Inte. | Error | P/B   |
|------|-------|-------|---------|-----|----|------|-----------|--------------|-------|-------|
| Ag   | 88.54 | 81.99 | 0.85    | 0.99| 0.97| 1.0000| 442.56    | 8.92         | 0.67  | 50.57 |
| Cu   | 11.45 | 18    | 0.10    | 1.05| 0.88| 1.0000| 56.6      | 7.37         | 2.09  | 7.73  |

The result obtained for the marked oklad: 87-88% silver, copper (11.06-12.12%) corresponds to the silver quantity specific to the silver title 84.

Table 2. Unmarked oklad - average composition (EDX).

| Elem | Wt %  | At %  | K-Ratio | Z   | A  | F    | Net Inte. | Backgrd Inte. | Error | P/B   |
|------|-------|-------|---------|-----|----|------|-----------|--------------|-------|-------|
| Ag   | 82.7  | 73.97 | 0.77    | 0.98| 0.95| 1.0000| 400.04    | 9.46         | 0.53  | 43.39 |
| Cu   | 15.48 | 23.49 | 0.14    | 1.05| 0.89| 1.0000| 75.70     | 7.05         | 1.3   | 10.84 |
| Zn   | 3.47  | 2.54  | 0.01    | 1.06| 0.91| 1.0000| 7.56      | 6.55         | 6.16  | 1.19  |

The result obtained for the unmarked oklad: 82.2-82.7% silver, copper (15.48-16.22%), zinc (1.58-3.47%).

Figure 7. EDX analysis on the marked oklad.
The electron microscopy analysis (scanning + EDX) on the marked oklad allowed the identification in the eutectic Ag-Cu alloy (87-88% Ag, 11.06-12.12% Cu) of the two present phases: silver-rich beta phase (etches light) and cooper-rich alpha phase (etches dark). From the electron-probe analysis of one of the dendritic arms that appear here as dark globules, resulted a composition of 83% Ag 17% Cu (Figure 9 and Figure 10).

The electron microscopy analysis (scanning + EDX) on the unmarked oklad allowed the identification of the ternary alloy Ag-Cu-Zn: 82.2-82.7% Ag, 15.48-16.22% Cu, 1.58-3.47% Zn.
There is a possibility that it has been used in alloy development silver and a Cu-Zn brass with up to 20% Zn given that the Cu / Zn ratio is 5:1.

According to the Cu-Zn equilibrium diagram, the alpha phase formed at this concentration of Zn in Cu has the same structure as copper (cubic with centered faces) and is a typical solid substitution solution, some of the copper atoms being replaced by zinc atoms \[^9\]. Therefore, the same two phases will be present: silver-rich beta phase (etches light) and cooper-zinc rich alpha phase (etches dark). From the electron-probe analysis of one of the dendritic arms that appear here as dark globules, resulted a composition of 15.54-30.73% Cu, 2.06-2.42% Zn, bal. Ag (Figure 11 and Figure 12).

Because the pure silver was too soft to create silver work objects, it was alloyed with copper, or with copper and zinc to improve the mechanical and machinability characteristics.

4. Conclusions

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

Marked oklad allowed identification of: the craftsman Ivan Semenov Komarov (ИванСеменовКомаров) who worked in 1808 in the Russian village Podol'skoye (Подольское); the quality controller A. Svechin (А. Свечин), who worked in Moscow from 1862 to 1875; the silver title mark - 84; the coat of arms of Moscow - Saint George on horseback slaying the Dragon.

The undated oklad was attributed to the XIX century Russian workshops by Florin Colonaş - an expert in handicraft of artistic significance.

The marked oklad is produced from the Ag-Cu alloy: 87-88% silver, copper (11.06-12.12%) and corresponds to the silver quantity specific to the silver title 84.

The unmarked oklad is produced from the Ag-Cu-Zn alloy: 82.2-82.7% silver, 15.48-16.22% copper, 1.58-3.47% zinc.

The metallographic structure is typical of eutectic alloys.

5. References

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