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METHODS OF NATURAL SCIENCES IN THE STUDY OF CULTURAL HERITAGE OBJECTS

Electron Microscopy Studies of the Composition and Microstructure of the Niello of Objects of Personal Piety of the 11th–13th Centuries from Suzdal'skoe Opol'e

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Abstract—The results of studying the following three types of crosses with niello decor are given: encolpions decorated with the Crucifixion and the Orant Mother of God, encolpions with a simple cross in the center, and crosses worn next to the skin. All the items are finds discovered in the ploughed layer of rural settlements in the vicinity of Suzdal'. Variations in the composition of the metal of products correlate with their classification into morphological types. The main group of niello masses observed in most crosses (Cu–Pb–S) and its variation with an admixture of zinc (Cu–Pb–S–Zn) are distinguished according to the elemental composition of the niello. A variant of a similar composition with the addition of tin and zinc (Cu–Pb–Sn–S–Zn) is revealed in one composition, and one niello composition is unique in that it contains a large amount of zinc and a small amount of lead (Cu–S–Zn–Pb). Niello samples in which the zinc content is associated with the influence of the metal of the base are identified. There is no correlation between the types of crosses and the compositions of the niello. Based on the microstructures of the niello masses, samples that have been subjected to intense short-term heating during blackening or, conversely, exposed to insufficiently high temperatures for a long time are identified.

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INTRODUCTION

Encolpion crosses and crosses worn next to the skin are the most numerous and expressive categories of material antiquities associated with the spread of Christianity in Eastern Europe in the 10th–13th centuries. From the huge number of these kinds of objects from the Old Russian period, specimens decorated with niello decor stand out. Dark niello looked spectacular against a golden metallic background and attracted attention. To date, the typology and chronology of various groups of crosses have been studied in sufficient detail [1], and a series of analyses of the metal composition have been performed [2]. Topics related to the composition and the technology of applying niello decor to Old Russian items of personal piety began to be developed only in recent years [3–5]. In addition to the importance of studying the technological aspects, studying the niello at these sites is of great historical and cultural importance. Encolpion crosses are the earliest Old Russian items made of copper-based alloys that have been subjected to blackening, so the determination of all the parameters of this process is a great contribution to the study of both the niello art of Old Russia as a whole and world historical technologies.

A number of encolpions that had been studied earlier at the National Research Center "Kurchatov Institute" and crosses worn next to the skin from finds of the Suzdal' archaeological expedition of the Institute of Archaeology, Russian Academy of Sciences, headed by N.A. Makarov, made it possible to determine that multicomponent alloys based on copper with inclusions of tin, lead, and nearly always small amounts of zinc and sulfur (measurements were carried out by the method of scanning electron microscopy with energy-dispersive X-ray analysis (SEM/EDX method)) were used to produce niello. Silver, commonly used in the blackening of archaeological silver items, was not part of the niello mass. The sulfur content in the decoration of the encolpion crosses varies from 11.5 to 21 wt %. A structural study of the niello masses was performed using the X-ray diffraction method on a synchrotron source, and the phase compositions of ten specimens were recorded. It was revealed that the niello masses were mainly composed of copper sulfide (chalcosine, jarleite, anilite, yarrowite, digenite, and covellite) and small amounts of lead (galena) and tin (berndite) sulfides with inclusions of corrosion products, such as lead carbonate (cerussite) and copper oxides (tenorite and cuprite), formed over time.

Scanning-electron-microscope images in the secondary-electron mode were obtained from the blackened regions of the decoration of several encolpions, which indicate the presence of numerous pores due to the release of gas bubbles. Niello microsections of thirteen encolpion panels were investigated using the SEM method and energy-dispersive X-ray microanalysis of the inclusions was performed. The analysis results showed that the niello contains large regions enriched mainly with copper and sulfur, small regions with a predominance of lead and tin with sulfur, and individual inclusions of copper and zinc oxides in the form of a few separate micrograins. As was determined from the results of all the studies, the Old Russian masters did not make niello by alloying individual pure metals with sulfur, but used ready-made alloys based on copper with additives of tin and lead without silver [4].

To accurately determine the technology of melting and applying a niello coating to the panels of the encolpion crosses, the process of manufacturing and applying the niello mass with a composition close to historical samples to a copper alloy was simulated to study structural changes during niello melting, in particular, to identify the sequence of formation of the niello-mass phases observed in the finished product. As was concluded based on the study results, the niello coating on the encolpions was created by melting the niello mass. The melting point and fluidity of the niello alloys were regulated by the concentrations of tin and lead and the use of fluxes [6]. The process of experimental simulation of the manufacture and application of the niello coating showed that the metal of the base affects the final elemental composition of the niello mass in most cases and the melting conditions have an effect on its microstructure [6]. This necessitates the joint analysis of the metal composition of the base, and the composition and microstructure of the niello coating.

OBJECTS UNDER STUDY

The primary task of this study was to answer the question whether there are differences in the formulation and the technology of applying the niello composition to crosses with different types of decoration. To accomplish this task, the following three types of crosses were selected from the Suzdal' collection of the Institute of Archeology, Russian Academy of Sciences (Fig. 1): encolpion crosses with a thin (almost superficial) linear pattern of the Crucifixion and the Orant Mother of God (seven specimens); encolpion crosses with a central cross pattern, the black decoration on which is placed in deep grooves (three specimens); and crosses worn close to the skin with niello that fills sufficiently deep spot cavities around the central convex cross (three specimens). All the crosses were found in the upper plowed layer of rural settlements in the district of Suzdal'. New circumstances described below were revealed during the experiment.

The six cross panels under study belong to the type of miniature smooth encolpions with straight branches or branches slightly expanding to the ends with the image of the Crucifixion on the front panel and the Orant Mother of God on the reverse panel: specimen 1, Suvorotskoe 8, 2013, No. 451/15; specimen 2, Suvorotskoe 8, 2015, No. 491/10; specimen 3, Poganoe Ozero, 2006, No. 206; specimen 4, Kleshchino, 2016, No. 205/40; specimen 5, Fedosino 1, 2018, No. 867/6; and specimen 6, Karel'skaya Slobodka 5, 2011, No. 14/12. The cross panels are cast accurately in accordance with the melt models without gaseous impurities and other defects. Traces of grinding are visible on the sides. The front surfaces of the flaps are dense and smooth. They have a shallow traced pattern obtained during casting. The decoration on the encolpion panels is given in two variants. On one variant, the figures of Christ with a headband and the Mother of God are made in a somewhat sloppy manner. They are accentuated by thin strips of niello (Fig. 1, specimens 2 and 4–6) (type IV.6.1 from ([1], pp. 165–170)). On the second variant, the patterns are finer and more detailed: the edge zones of the panels are decorated with a ribbed design and the niello mass fills small areas of the surface (Fig. 1, specimens 1 and 3) (type IV.5.5 from ([1], pp. 171–173)). These variants of encolpions are standard products found throughout almost the entire territory of Old Russia, but largely in the northern part. They are among the earliest in Old Russia. Their appearance is recorded at sites from the end of the 11th century. The crosses existed until the end of the 12th century [3].

One specimen is an encolpion with straight branches and rounded ends in the form of tears (specimen 7, Chernizh 2, 2014, Nos. 7/6, 9/8, and 12/11). The panels are decorated with figures of Christ and the Orant Mother of God with bystanders (Fig. 1, specimen 7) (type IV.2.1 or IV.2.2 [1]). The thin lines of the pattern were drawn onto the metal before it had cooled down (the sides of the displaced metal are visible when magnified) and partially emphasized by niello strips placed on the surface of the panels. Encolpions of this type date back to the XII century by Peskova ([1], pp. 142–145).

Crosses of the second type are three miniature smooth encolpions with branches slightly expanding

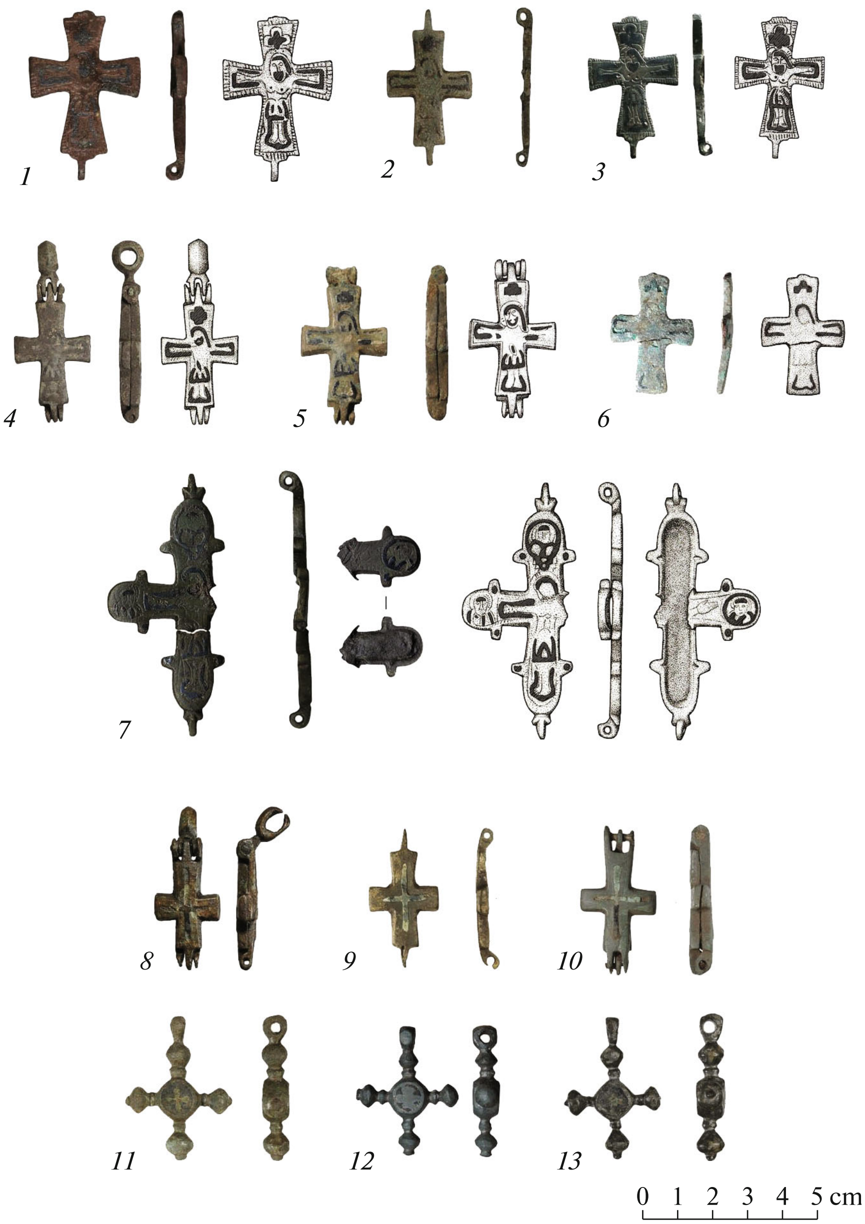

Fig. 1. Crosses from the villages of Suzdal'skoe Opol'e. Type 1: (*1*) Suvorotskoe 8, 2013, no. 451/15; (*2*) Suvorotskoe 8, 2015, No. 491/10; (*3*) Poganoe Ozero, 2006, No. 206; (*4*) Kleshchino, 2016, No. 205/40; (*5*) Fedosino 1, 2018, No. 867/6; (*6*) Karel'skaya Slobodka 5, 2011, No. 14/12; (*7*) Chernizh 2, 2014, nos. 7/6, 9/8, and 12/11. Type 2: (*8*) Grigorovo 2, 2018, no. 12/12; (*9*) Grigorovo 1, 2015, Nos. 13/2 and 74/63; (*10*) Suvorotskoe 8, 2016, No. 380/48. Type 3: (*11*) Suvorotskoe 8, 2015, No. 589/107; (*12*) Vasil'kovo 4, 2012, No. 168/25; (*13*) Veska 2, 2016, No. 54/2.

toward the ends, both panels of which are decorated with a central black image of a simple cross (specimen 8, Grigorovo 2, 2018, No. 12/12; specimen 9, Grigorovo 1, 2015, Nos. 13/2 and 74/63; and specimen 10, Suvorotskoe 8, 2016, No. 380/48). The niello is applied in deep grooves obtained during casting or pressed in metal that has not yet been cooled (Fig. 1, specimens 8–10) (type IV.6.2 [1]). This type was widely distributed throughout the territory of Old Russia in the 12th–13th centuries ([1], p. 136). Akin to the encolpions with the Crucifixion and the Orant, these crosses have a high degree of standardization.

The third type of crosses includes the following three double-sided crosses worn next to the skin with a rounded crossing and ornately shaped branches with spheres at the ends (Fig. 1, specimens 11–13): specimen 11, Suvorotskoe 8, 2015, No. 589/107; specimen 12, Vasil'kovo 4, 2012, No. 168/25; and specimen 13, Veska 2, 2016, No. 54/2. In the middle crossing of each of the crosses worn next to the skin, there

Table 1. Elemental compositions of specimens according to SEM/EDX data (wt %)

	1	2	3	4	5	6	7	8	9	10	11	12	13
C	2.1	1.9	0.1	1.7	2	0.2	2.8	2	1.6	4.1	1.2	0.2	1.3
O	0.1	0.2	0.1	0	1.2	0.1	0.6	2.8	1.5	2.2	0.3	0.6	0.2
Al	0.3	0.3	0.4	0.1	0.2	0.1	0.1	0.2	0.1	0.1	0.5	0.4	0.3
Si	0.1	0.2	0	0.1	0.1	0.1	0.2	1.4	0.1	0.2	0.1	0.1	0.1
S	9.2	10.5	15.4	12.5	15.2	14.2	7.3	6.2	12.5	12.7	14.8	10.5	7.8
Sn	0.6	1.7	2.7	0.7	0.1	2	2	16.4	2.1	1.8	0.1	1.7	0.8
Fe	0.3	0.4	0.5	0.5	0.5	0.7	0.5	2.1	0.6	0.6	0.4	0.4	0.5
Ni	0.2	0.1	0.3	0.2	0.1	0.2	0.2	0.2	0.2	0.3	0.2	0.2	0.1
Cu	65.5	67.6	57.8	59.1	57.5	55.5	58.4	32.5	48.5	46.5	66.9	69.5	62.4
Zn	4.6	1.1	2.2	0.9	0.4	7	2	4.8	6.9	0.7	10.5	1.3	2.9
Pb	17	16.1	20.6	24.4	22.9	20	26	31	26	31.1	5.2	15.2	23.8
P								0.4					

Specimen nos. are the same as in Fig. 1.

is a convex relief image of a small cross with expanding branches on both sides of the cross. The circle of the crossing is contoured by a convex smooth border. The remaining recessed area is filled with niello. As with encolpions, crosses of this type have a high degree of standardization. They are found throughout the territory of Old Russia and date back to the 12th–13th centuries ([7], p. 413).

METHODS

The elemental composition of the metal of the crosses was investigated by the SEM/EDX method using a Helios Nanolab 600i double-beam scanning electron–ion microscope (Thermo Fisher Scientific, USA) equipped with an EDX system (EDAX, USA) at an accelerating voltage of 30 kV in the high vacuum mode (10^{-4} Pa).

The morphology (microstructure) and elemental composition of the samples were studied using a Versa 3D double-beam scanning electron–ion microscope with a focused ion beam (Thermo Fisher Scientific, USA) with an EDX system (EDAX, USA) at an accelerating voltage of 30 kV in the low vacuum mode (30 Pa). SEM images showing elemental contrast were obtained using a concentric backscatter (CBS) detector.

The EDX spectra and element-distribution maps were processed using the TEAM software package (EDAX, USA). All data on the compositions are given in weight percentages. Data on the elemental contents are adjusted to 100%.

For electron-microscopic studies, microfragments of the niello mass were selected from the regions of blackening on the crosses. They were finished with epoxy resin by cold pouring and polished. The metal of the crosses was investigated without taking samples from the cleaned surfaces.

RESULTS AND DISCUSSION

Composition of the Niello Mass

All niello compositions contain sulfur, copper, and lead (Table 1). Tin and zinc are present only in some cases. As noted in [4], impurities enter the composition of the niello mass during its manufacture from copper alloys of various compositions.

In all cases, the content of copper ranges from 55 to 67 wt %, the content of sulfur ranges from 7 to 15 wt %, and the content of lead ranges from 16 to 26 wt %. The content of tin does not exceed 2.7 wt %. In five samples, the zinc content ranges from 0.4 to 2.2 wt %; two items are distinguished, namely, specimens 1 and 6, in which the zinc contents are 4.6 and 7.0 wt %, respectively (Fig. 2a).

The niello masses of the three crosses belonging to type 2 (specimens 8–10) are very different in composition (Fig. 2a). The copper content in all three samples is not very high and drops to 32.5 wt % in specimen 8 (in specimens 9 and 10, 48.5 and 46.5 wt %, respectively). Specimens 9 and 10 are close in elemental composition to the items of the first group (specimen 9 is close in composition to items 1 and 6 with increased zinc contents, and specimen 10 is close to items 2, 3, 4, 5, and 7), but with a slightly higher lead content (26 wt % in specimen 9 and 31 wt % in specimen 10). The niello mass of specimen 8 stands out among all the studied compositions in terms of a large amount of tin (16.4 wt %) against a background of a high lead content (31 wt %) and the presence of small

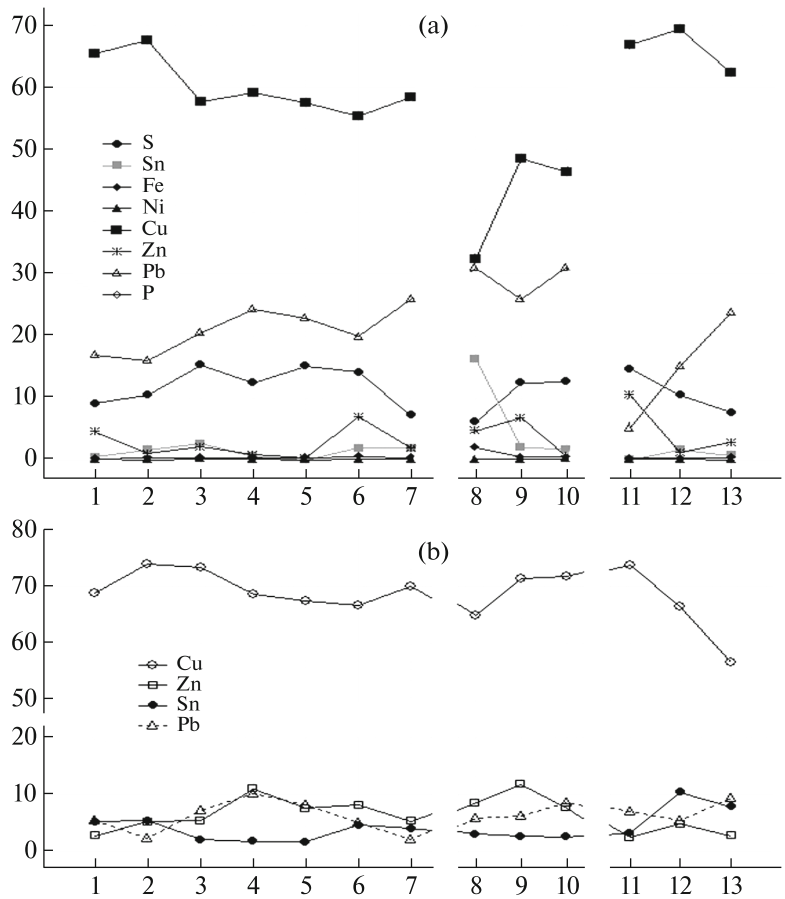

Fig. 2. Elemental compositions of (a) the niello mass and (b) the metal of crosses according to the SEM/EDX data.

amounts of sulfur (6.2 wt %) and zinc (4.8 wt %). In addition, the microinclusion of phosphorus (0.4 wt %) is present in sample 8.

The niello masses of two crosses of the third type (Fig. 2a) are also close in composition to the most widespread composition among the studied types, namely: the niello masses of specimens 12 and 13 predominantly contain copper (62.4 and 69.5 wt %, respectively), and impurities of lead (15.2 and 23.8 wt %, respectively) and sulfur (10.5 and 7.8 wt %, respectively). The third cross of this group, i.e., specimen 11, is unique in the composition of its niello mass; the lead content in it is substantially reduced (5.2 wt %) and the zinc content is increased (10.5 wt %) (Fig. 2a).

Thus, analysis of the elemental composition of niello made it possible to distinguish the main types of the niello-mass compositions among the studied crosses, namely: group 1 (Cu–Pb–S) that includes eight items (specimens 2, 3, 4, 5, 7, 10, 12, and 13) and group 2 (Cu–Pb–S–Zn), which is a variation that includes three items (specimens 1, 6, and 9) with a higher zinc content. Two samples, namely, specimens 8 and 11 stand out. In the composition of the niello mass of specimen 8, the tin content is substantially increased and zinc is present (Cu–Pb–Sn–S–Zn). Specimen 11 has a reduced lead content and an increased amount of zinc (Cu–S–Zn–Pb).

SEM/EDX Studies of the Morphology of Polished Sections of the Specimens

Earlier experiments on the creation of niello made it possible to conclude that the morphology found on the polished sections of niello microsamples is influenced by a number of factors, such as the temperature and time of heating, the degree of melting of the niello mass, and, first and foremost, the elemental composition [6]. Therefore, the morphology of polished sections of niello microsamples from Suzdal'skoe Opol'e was analyzed within the following groups, into which the samples were classified when studying the elemental composition of the niello masses: group 1 of the Cu–Pb–S compositions (Fig. 4, specimens 2, 3, 4, 5, 7, 10, 12, and 13), group 2 of the Cu–Pb–S–Zn compositions (Fig. 5, specimens 1, 6, and 9), and two unique niello masses of the Cu–Pb–Sn–S–Zn and Cu–S–Zn–Pb compositions (Fig. 5, specimens 8 and 11, respectively).

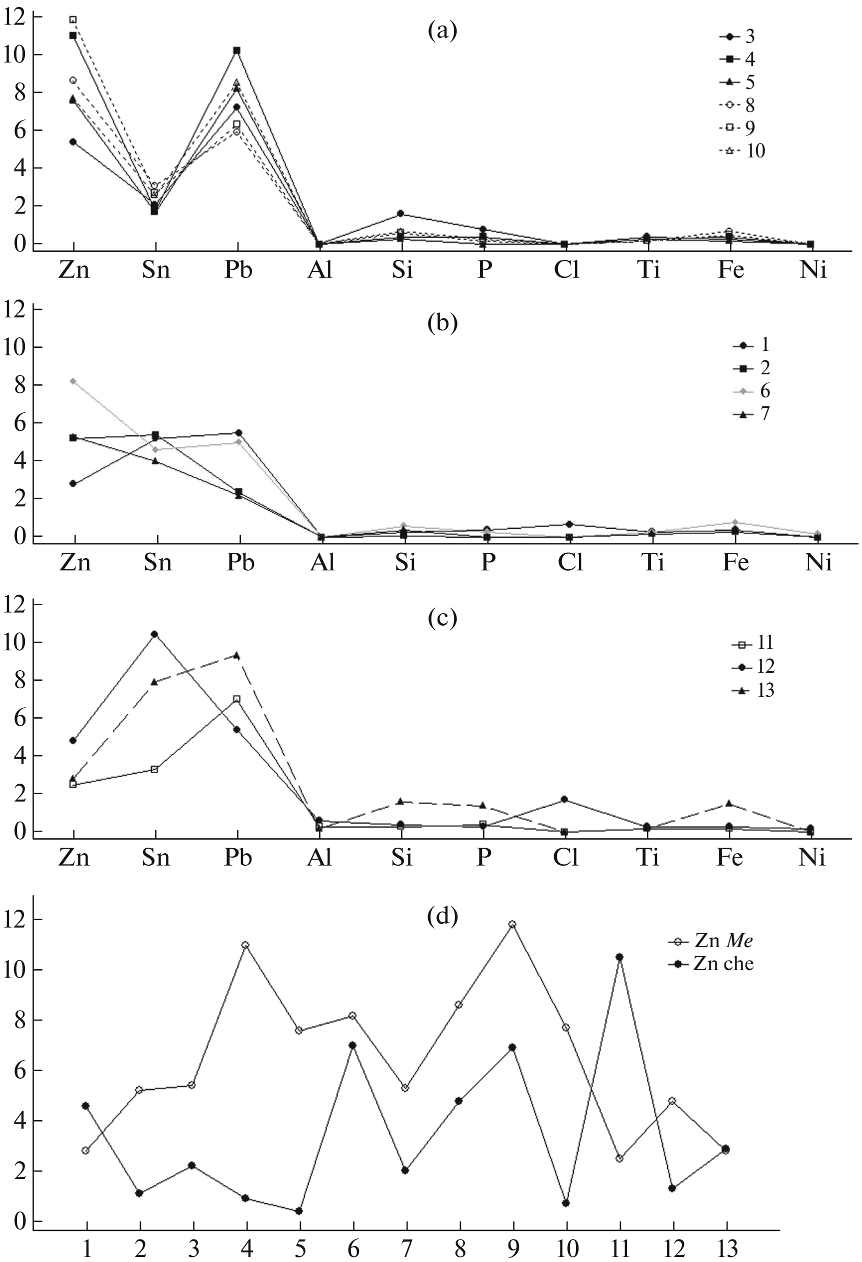

Fig. 3. Elemental compositions according to REM/ERM data: of the metals of crosses of groups (a) 1, (b) 2, and (c) 3, and (d) the contents of zinc in the metal (Zn *Me*) and niello (Zn *ni*) of the crosses.

Maps of the distribution of chemical elements obtained by SEM/EDX methods (Fig. 6) were used to study the elemental composition of the niello-mass regions together with analysis of the morphological features of the polished sections of the specimens. The morphology of the polished sections of the studied crosses was compared with the experimental simulation data [6].

The niello mass of specimens from the largest group of niello compositions, i.e., Cu–Pb–S, is quite diverse in morphology. Specimen 13 whose niello mass is slightly molten stands out among other specimens. Lead precipitates are visible (Fig. 6a), but there are no dendritic structures. Specimens 2, 3, and 4 are distinguished by a large number of formed phases (Fig. 6b). Experimental simulation showed similar results with the fairly rapid intensive melting of niello masses. For specimen 3, this process probably took a little longer, since small dendritic structures had formed (Fig. 6b), but the extremely high nonuniformity of the sample morphology also indicates short-term intensive heating. In turn, specimens 7 and 12

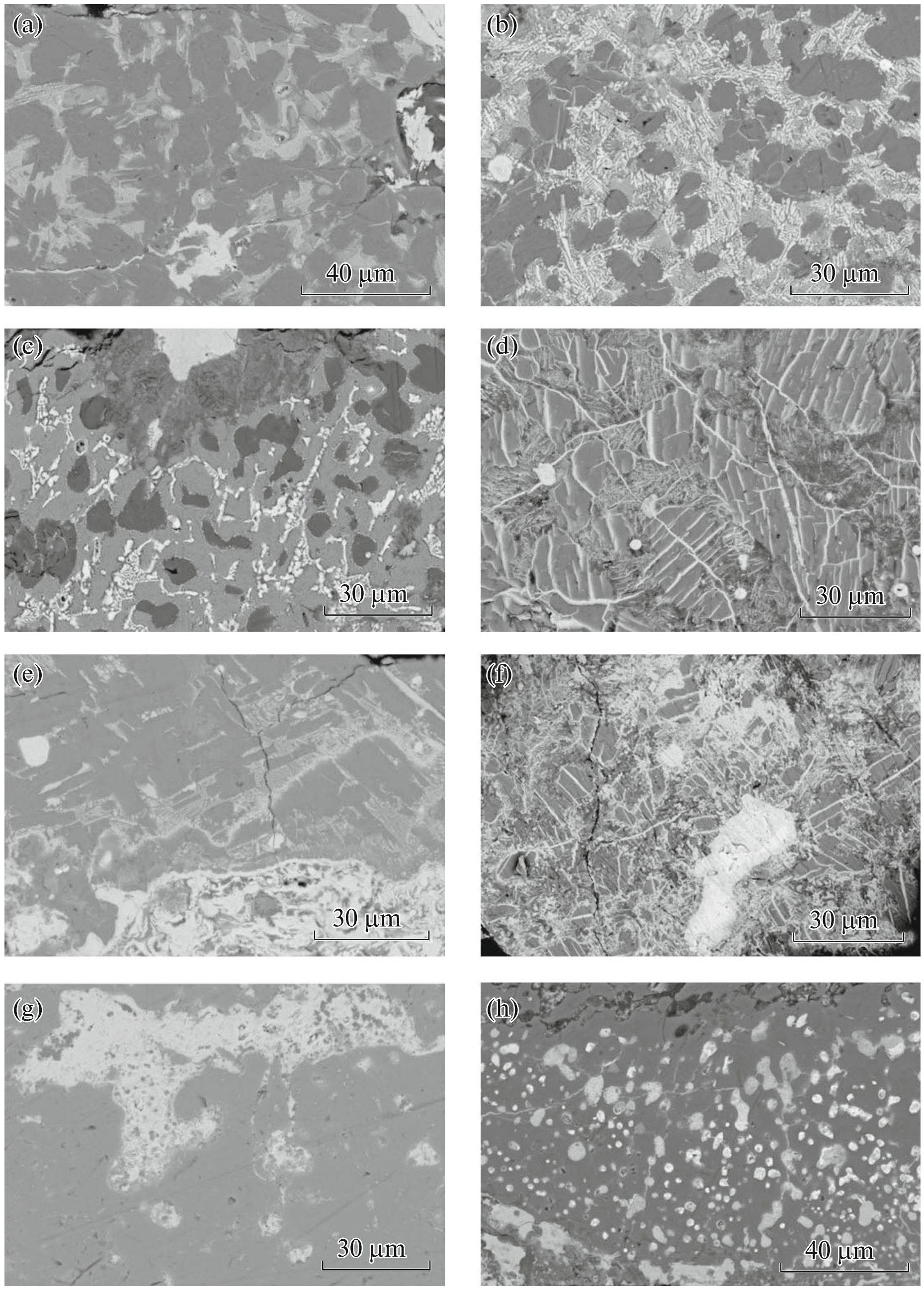

Fig. 4. SEM images obtained in the backscattered electron mode for the morphology of niello compositions of the Cu–Pb–S group of specimens (a) 2, (b) 3, (c) 4, (d) 5, (e) 7, (f) 10, (g) 12, and (h) 13.

have a smaller variety of formed phases on the contrary. The weak dissolution of large lead and lead–tin precipitates and a small number of predominantly large dendritic structures indicate the slow melting of these niello masses under insufficiently intense temperature regimes. Specimens 5 and 10 are distinguished by an extremely high number of heterogeneous dendritic structures, as well as by a small variety of phases. In both specimens, the presence of lead precipitates that retained their rounded shapes was recorded (Fig. 6c). Thus, lead precipitates that have not lost their rounded shape suggest that the temperature of niello remelting was insufficient despite the fact that a large number of dendritic structures indicate a rather long process of melting of niello compositions.

Among the specimens belonging to the group of Cu–Pb–S–Zn compositions, two specimens that are very similar in morphological features stand out. A small variety of recorded phases, the weak formation of dendritic structures, and the presence of incom-

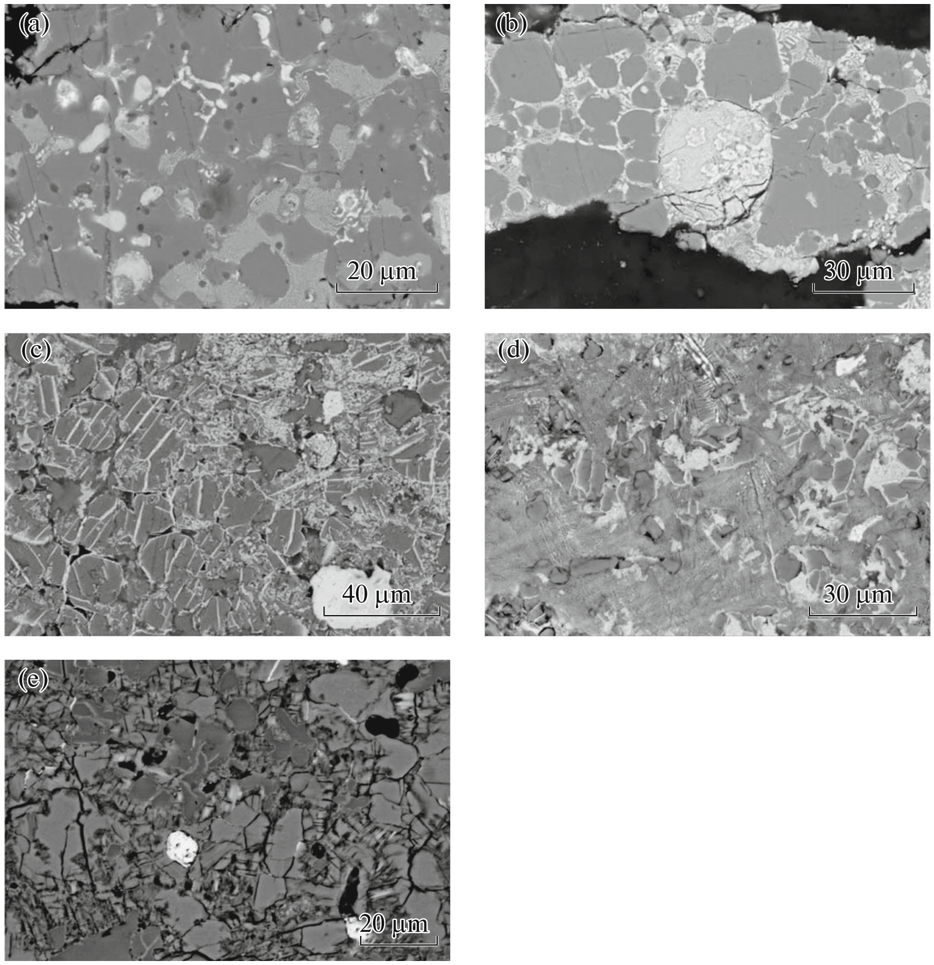

Fig. 5. SEM images obtained in the backscattered electron mode for the morphology of niello compositions of the Cu–Pb–S–Zn group of niello samples and unique specimens 8 and 11 for specimens (a) 1, (b) 6, (c) 9, (d) 8, and (e) 11.

pletely melted lead precipitates that retained their rounded shape are indicative of an insufficient temperature of melting with rather long heating of niello masses in specimens 1 and 6 (Fig. 6d). Specimen 9 is very similar in morphological features to specimens 5 and 10 and is probably manufactured under similar conditions.

Specimens 8 and 11 which are unique in the compositions of the niello mass were analyzed separately. The morphology of specimen 8 with the Cu–Pb–Sn–S–Zn composition was quite close to the morphology of specimens 5, 9, and 10, and was probably manufactured under similar conditions, but the precipitates of specimen 8 were melted to an even lower degree. The morphology of specimen 11 (Fig. 6e) cannot be compared with the data of experimental studies because of the uniquely high content of zinc, as well as the extremely small amount of lead in the composition (Cu–S–Zn–Pb composition), and no clues can be made for this reason about the melting conditions of this niello mass.

Composition of the Metal of Crosses

The obtained data on the niello composition were compared with the data on the base alloys, since the metal of the base can affect the composition of the niello masses. All the studied objects of personal piety are made of copper alloys. These alloys are different in terms of the content of impurities (Fig. 2b). A substantial number of metal compositions were allocated to a large group with some variation in the composition components among the items within the group (Fig. 3a). The group included specimens 3, 4, 5, 8, 9, and 10. Alloys of this large group are characterized by a copper content in the range from 65 to 73.3 wt %, a tin content in the range from 1.7 to 3.1 wt %, and a lead content in the range from 5.9 to 10.2 wt %. The zinc content ranges from 5.4 to 11.8 wt %. All these formulations are quaternary copper alloys with a substantial lead content, a smaller content of tin, and a high variability in the zinc content. This group includes all the crosses of the second group, i.e., three miniature smooth encolpions with a niello image of a simple

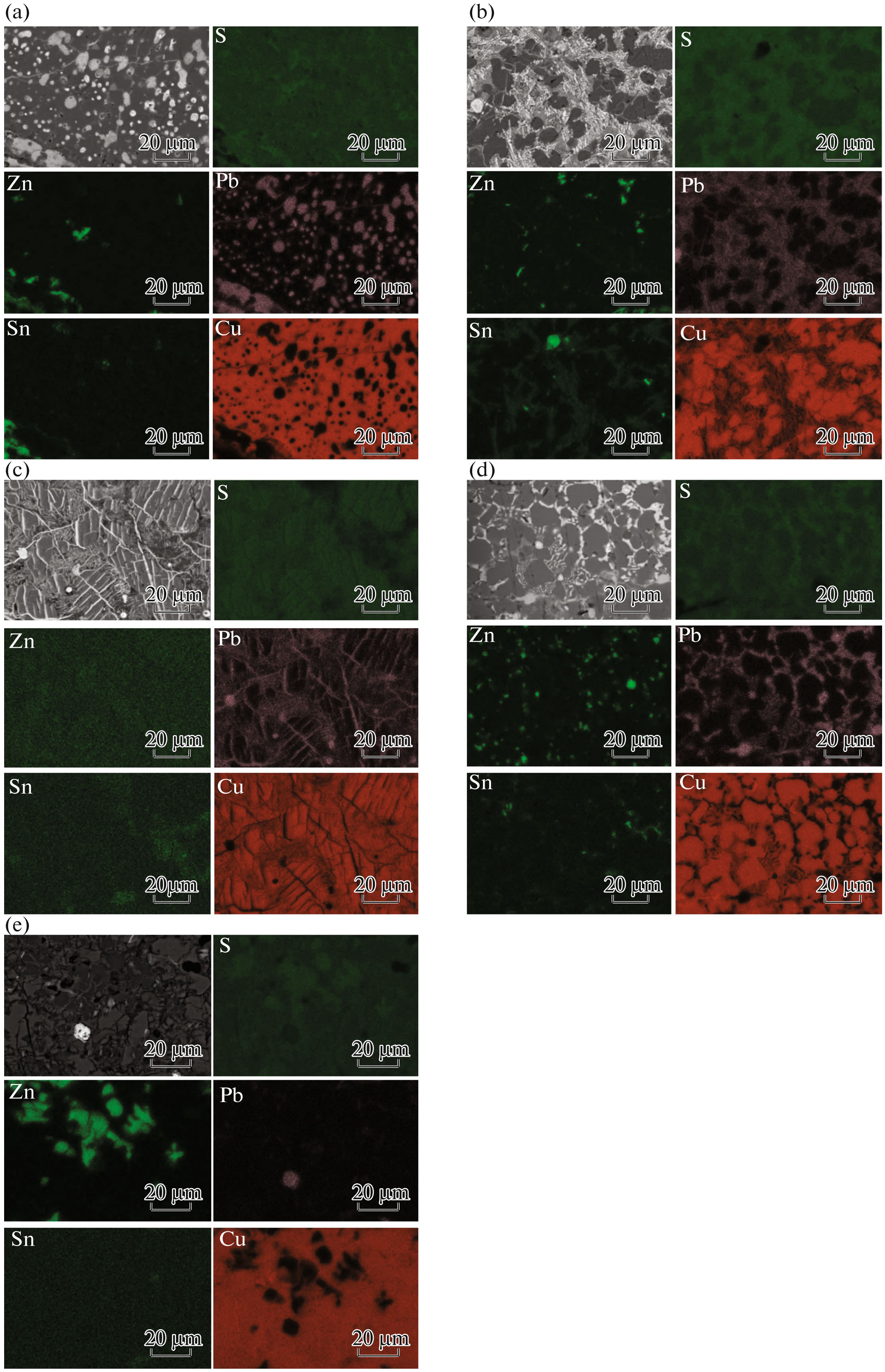

Fig. 6. Maps of the distribution of elements in samples according to the SEM/EDX data for samples from different niello groups for specimens (a) 13, (b) 3, (c) 5, (d) 1, and (e) 11.

Table 2. Elemental compositions of the metal of encolpions according to SEM/EDX data (wt %)

	1	2	3	4	5	6	7	8	9	10	11	12	13
Cu	68.8	73.9	73.3	68.7	67.5	66.7	70	65	71.3	71.8	73.7	66.5	56.6
Zn	2.8	5.2	5.4	11	7.6	8.2	5.3	8.6	11.8	7.7	2.5	4.8	2.8
Sn	5.2	5.4	2.1	1.8	1.7	4.6	4	3.1	2.7	2.6	3.3	10.4	7.9
Pb	5.5	2.4	7.2	10.2	8.2	5	2.2	5.9	6.3	8.5	7	5.4	9.3
Al											0.3	0.6	0.2
Si	0.3	0.1	1.6	0.4	0.3	0.6	0.4	0.4	0.6	0.7	0.3	0.4	1.6
P	0.4		0.8	0.4		0.3		0.4	0.2	0.3	0.4	0.3	1.4
Cl	0.7											1.7	
Ti	0.3	0.2	0.4	0.3	0.3	0.3	0.2	0.2	0.2	0.3	0.2	0.3	0.2
Fe	0.4	0.3	0.3	0.4	0.2	0.8	0.3	0.7	0.5	0.4	0.2	0.3	1.5
Ni						0.2						0.2	

Specimen nos. are the same as in Fig. 1.

cross, and their elemental composition is quite uniform (Table 2 and Fig. 3a, specimens 8, 9, and 10). In addition, this group includes three items from the first group of crosses, which also have a very close elemental composition (Table 2 and Fig. 3a, specimens 3, 4, and 5).

Two of the remaining three crosses of the first group, namely, specimens 2 and 7, have a similar composition. Their alloys have comparable contents of zinc (from 5.2 to 5.7 wt %) and lead (from 2.2 to 2.4 wt %), and a similar content of tin (from 4 to 5.4 wt %) (see Table 2 and Fig. 3b, specimens 2 and 7). Another cross of the first group is characterized by a lower amount of zinc (2.8 wt %) and a slightly higher lead content (5.5 wt %), and the alloy of specimen 6 with similar contents of tin and lead contains a higher amount of zinc (8.2 wt %) (see Table 2 and Fig. 3b, specimens 1 and 6).

The lead content in copper alloys of the crosses worn close to the skin (third group) is different and ranges from 5.4 to 9.3 wt %. Specimens 12 and 13 are primarily distinguished by a higher tin content (from 7.9 to 10.4 wt %). Specimen 11 contains a smaller amount of tin in the alloy (3.3 wt %) (see Table 2 and Fig. 3c). The compositions of all the crosses worn close to the skin of this study are united by a fairly low content of zinc in the metal, which ranges from 2.5 to 4.8 wt %.

Thus, the elemental composition of the metal of the crosses made it possible to identify a large group of objects similar in the alloy type. All crosses of the second type, i.e., miniature smooth encolpions with a black image of a simple cross, and several encolpions of the first type were classified into this group. Crosses worn close to the skin were also allocated to a separate group with some variations in the content of the main alloy components, but with a general tendency toward a decreasing amount of zinc in the metal.

An analysis of the compositions of niello masses (Fig. 3d) did not reveal correlations between the type of niello and the morphological type of crosses. Probably, a niello composition of some standard formulation was used with some changes in the composition and amount of impurities. Among the studied items, only one composition significantly different from the others in terms of the niello mass, namely, specimen 11 was found.

As was found in the study devoted to experimental simulation of the blackening [6], the niello composition captures zinc vapors that come from the metal when heated during the deposition of the niello to the metal. For comparison, data on the zinc content in the metal of crosses studied in [6] and in the compositions of niello masses applied to these crosses are given in Fig. 3d. A comparison of the obtained data shows that there are three types of composition combinations with respect to the content of zinc in this specimen. In two cases, the zinc content is substantial in both the metal and the niello mass, but it is higher in the base metal in the first case (Fig. 3d, specimens 6, 8, and 9) and in the niello mass in the second case (Fig. 3d, specimens 1, 11, and 13). In the third case, the presence of zinc in the black mass is insignificant with a rather high content in the composition of the metal (shown in rectangles in Fig. 3d, specimens 4, 5, and 10). It is in the third case that it can be assumed that zinc was introduced into the composition of the niello mass by vapor capture in the process of melting on the base metal. For some specimens, it is difficult to determine whether the zinc-containing alloy was used in the niello composition (highlighted in ovals in Fig. 3d, specimens 2, 3, 7, and 12).

CONCLUSIONS

An analysis of the elemental composition of the niello mass of crosses of three types makes it possible to distinguish the main variant of the niello composition among the studied crosses, namely, Cu–Pb–S. Niello of this composition with some variations in the amount of impurities is detected for eight specimens, among which most crosses contain the image of the Crucifixion (specimens 2, 3, 4, 5, and 7), one cross contains a cross image in the central part (specimen 10), and two of them are crosses worn close to the skin (specimens 12 and 13). For three items (specimens 1, 6, and 9), a variant of the niello composition containing zinc (Cu–Pb–S–Zn) is determined. The composition of specimen 8 with the addition of tin (Cu–Pb–Sn–S–Zn) is close to the last variant. The niello composition of specimen 11 is unique in that it contains a large amount of zinc and a low content of lead (Cu–S–Zn–Pb). There is no correlation between the types of crosses and the compositions of the niello.

The elemental composition of the metal of the crosses makes it possible to identify a large group of objects similar in the alloy type. All crosses of the second type, i.e., miniature smooth encolpions with a niello image of a simple cross, and several encolpions with an image (specimens 3, 4, 5, 8, 9, and 10) are allocated to this group. Crosses worn close to the skin are classified into a separate group with some variations in the content of the main components of the alloys, but with a general tendency toward a decreasing amount of zinc in the metal (specimens 11, 12, and 13).

The study of the morphology of the polished sections of niello samples and the comparison of the results with the experimental data of simulated blackening have made it possible to draw a number of conclusions about the temperature regimes of the melting of niello masses. The type of morphology is revealed on some specimens, the formation of which is characteristic of intense short-term heating. The morphology of the others is a result of long-term exposure to insufficiently high temperatures.

A comparison of the obtained data on the elemental composition of the base metal and the niello masses makes it possible to identify items (specimens 4, 5, and 10) in which zinc entered the niello, presumably, as a result of capturing the vapors of zinc from the base.

The obtained results allow us to conclude that the Old Russian masters used a certain standardized niello composition as a rule, which included copper, lead, and sulfur, despite some variations in the compositions of the niello masses. Impurities of tin and zinc that are present in different quantities in the niello and create a number of variants of this formulation are probably associated with the compositions of the initial materials. The differences in the compositions of metal alloys, which were revealed during the study, correlate well with the classification of items into morphological types. However, the studied sampling is not sufficiently indicative at the moment, so the determination of metal alloys that are characteristic of certain typological groups of crosses requires further research.

On the basis of the morphology of encolpions, a hypothesis about the possible presence of several large production workshops at Christian centers that produced standardized products for wide distribution throughout the territory of Old Russia was put forward earlier [3]. The single basic niello formulation revealed in this study and the presence of correlations between the typology of crosses and the metal composition used indirectly confirm the assumption about the production of standardized personal objects of personal piety.

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CONFLICT OF INTEREST

We declare that we have no conflicts of interest.

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