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IDENTIFICATION OF PATTERNS OF CRYSTAL-CHEMICAL TRANSFORMATIONS IN HISTORICAL ARTIFACTS MADE OF METALS

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The theoretical substantiation of the process of elimination of individual chemical elements from crystal lattices of metals in the process of the crystal-chemical transformations taking place during the long history of artifact existence was given. To confirm the theoretical conclusions, five ancient gold items from different historical periods (from the IV century B.C. to the XVIII century A.D.) with approximately the same contents of gold, silver, copper, and iron in the alloy body were studied. The conducted studies will promote more exact attribution of historical artifacts made of metals and revealing the signs of forgery or restoration.

The chemical composition of items was determined immediately under patina and in the alloy body using a scanning electron microscope equipped with an energy dispersion spectrometer. The results have shown a much lower gold content inside the alloy than in the item surface. At the same time, the undamaged surface cleansed of mineral crusts contained significantly fewer impurities than the polished surface which did not have contact with the environment. Therefore, the study of the chemical composition of gold artifacts cannot be conducted solely based on surface studies.

The studies have resulted in establishing a dependence of the concentration of the main component (gold) of the alloy in the artifact surface on the item age in thousands of years. Equations for predicting the age of the items that are chemically belonging to the described item group were also presented.

Studies of peculiarities of crystal-chemical processes are very important in practice to prove the historical artifact authenticity, adjust artifact dating, identify signs of forgery or profound changes caused by restoration

Keywords: metal artifacts, crystal-chemical transformations, chemical composition, gold content

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1. Introduction

Experience in conducting analytical studies of the chemical composition of historical artifacts made of metals indicates the presence of traces of complex material transformations at the aggregate level and at the level of structure of individual crystals [1]. The traces of material transformations are well identified by means of electron microscopes and X-ray fluorescence analyzers. Besides, they represent special recrystallization structures and are accompanied by precipitation of impurity elements, so-called patina, which form mineral crusts on the artifact surface.

The changes continue for long periods, sometimes thousands of years of an item's existence, and are explained by two reasons. The first of them is the chemical interaction of metals with the environment which results in the formation of mineral crusts (aggregates) in the artifact surface. The processes of formation of mineral aggregates which largely depend on the chemical composition of the environment will not be considered in this study.

The second reason is the processes of internal recrystallization of metals as a consequence of gradual balancing of mechanical stresses in lattices of individual crystals of metal aggregates formed in the process of item making. Balancing of mechanical stresses takes place inside the crystal lattice in the presence of foreign chemical elements and foreign mineral inclusions. In addition, the processes of internal recrystallization of metals occur because of size changes in the ions that form the crystal lattice and in the impurity ions brought about by radioactive decay. Also, these processes result from the influence of macroscopic flaws and ion packing flaws with decompaction of crystal lattices and also from the processes of natural crystal growth.

Studies of peculiarities of the abovementioned processes are of great practical importance and become relevant in numerous expert tasks, namely when it comes to the need to prove the authenticity of historical items, identify signs of forgery or profound changes that have occurred as a result of restoration. In addition, the ability to accumulate harmful substances on the surface makes it important to develop recommendations concerning the safety of handling metal artifacts in museums and private collections.

2. Literature review and problem statement

In recent years, scientists have conducted many archaeological and historical studies of historical artifacts made of metals, however, few analytical results were published. The studies devoted to the elucidation of chemical composition and analysis of the techniques used when making antique items of metals can be distinguished among the publications. For example, a silver jewelry item dated by the IV century B.C. found in Israel was studied in [2]. Scientists have studied gold jewelry of the VII century B.C. found in Italy [3] and those found in Spain and dated by the VIII–VI centuries B.C. [4]. These studies paid much attention to the analysis of the chemical composition of small parts of artifacts and their joints to establish manufacturing techniques. However, there is still a need to study the metal artifacts made in other historical periods.

Mineral products of corrosion activity found in the surface of bronze artifacts and composition of layers, types of patina structures were studied in [5] and models of the ion exchange processes occurring in the alloy-patina-soil system were developed. However, ancient gold artifact items have certain features of the crystal-chemical transformations, so they need further studies.

A number of studies addressing the chemical composition of gold items and gold origin were published. For example, scientists have studied gold artifacts made in ancient Mesopotamia in the III century B.C. [6] and gold Egyptian antiquities of the XVI century B.C. [7]. The origin of gold in Romanian archeological artifacts of various periods was established in [8]. It was shown that when determining the origin of gold in historical artifacts, the content of impurities is essential rather than that of the main components. It is necessary to expand the information base of analytical studies of ancient gold items made in various periods and in various world regions.

Studies of bronze jewelry dated by 1500–1100 B.C. [9] showed a difference in the chemical composition of the base alloy and that in the item surface are of high importance. However, crystal-chemical transformations depending on the age of the items were not analyzed which necessitates further studies in this direction.

3. The aim and objectives of the study

The study objective implied the theoretical substantiation and experimental confirmation of the process of eliminating individual chemical elements from crystal lattices with ionic bonds during crystal-chemical transformations in metal artifacts. This will make it possible to establish the authenticity of historical artifacts, adjust the dating of items, detect signs of forgery or profound changes caused by restoration.

To achieve this objective, the following tasks were set:

– study the chemical composition of gold artifacts in their surface and the alloy body;

– establish probable dependence of gold concentration in the artifact surface on the item age on a condition that the initial concentration of gold was the same during the item manufacture.

4. Materials and methods used in the studies of signs of crystal-chemical transformations occurred in gold artifacts

A scanning electron microscope equipped with a REM-106 energy dispersion spectrometer (SEM-EDS REM-106, Ukraine) was used in the studies. The studies were carried out on five samples of gold alloy artifacts of different ages. Nine to ten measurements were made in three to five points of the artifact surface. Microanalysis was performed for elements from Na to U. The procedure of quantitative calculation of content of chemical elements was based on calibration using samples of pure Ag, Au, Cu, and other metals as well as the study of intensities of spectral lines of elements using the method of ZAF-corrections. The lower limit of determination (LOD) of the content of chemical elements was 0.1 %. The resolution (locality) of the analysis was 5–10 μm. Digital images of the metal surface were obtained in secondary electrons.

5. The results obtained in the study of signs of crystal-chemical transformations in gold artifacts

5. 1. The results obtained in the study of the chemical composition of historical artifacts made of gold

To elucidate mechanisms of natural recrystallization, it should be mentioned that crystal lattices of metals (gold, iron, silver, copper, and lead) are formed by ionic chemical bonds. In an ideal condition, they are close-packed (face-centered or body-centered hexagonal and cubic lattices). These metals and alloys are most commonly found in ancient and medieval historical artifacts. Bonds between ions in metals are provided by compensatory interaction and a combination of outer shell electrons (so-called electron gas). The whole system is quite strong, has significant deformability, and can exist for a long time in a stressed state. In addition, the electron gas makes it possible to restore and maintain a certain structure of the crystal lattice, i.e. optimally close-packed. It is clear that any reduction of packing density creates a radially oriented stress in chemical bonds of a significant number of ions and not only those in the immediate vicinity of the flaw center but also the ions of the second and third-order of layering.

Fig. 1 shows an idealized model of flaw formation in the structure of crystals where the inclusion of an ion or atom of larger or smaller size causes deformation of the crystal lattice. The picture was created in the Word software package.

Fig. 1 demonstrates that any ion of inappropriate dimensions and chemical properties tends to be pushed off the crystal lattice. In this case, the crystal lattice shows the ability to restore its equilibrium state thanks to the properties of the electron gas. Foreign ions are eliminated from the metal surface through interaction with environmental anions or by the direct ejection of ions into the intercrystalline space to the induction surface of individual crystals in the aggregate. In both cases, a dislocation is formed which reduces the density and regularity of the crystal lattice and leads to a decrease in the force of attraction between ions which, in turn, helps remove the impurity ion from the lattice.

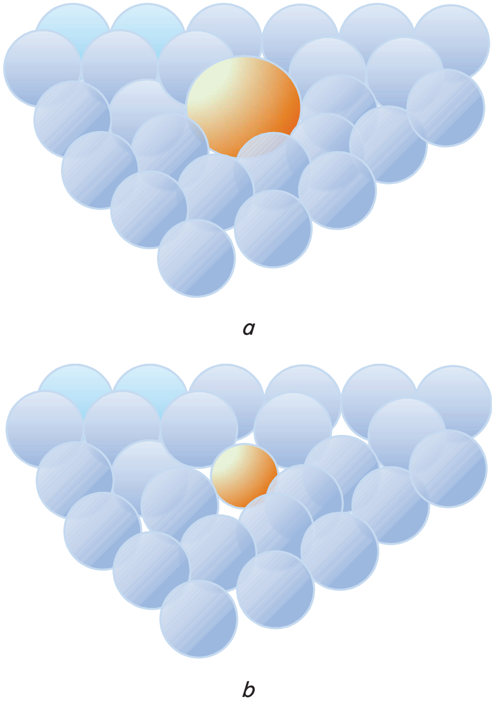

Fig. 1. Two fragments of pseudohexagonal packing of ions in a crystal lattice of iron and the dislocations caused by the presence of: *a* – a larger potassium ion; *b* – a smaller chromium ion

Thus, compounds of those impurity chemical elements that differ from the base alloy ions, most in their size, appear in the artifact surface made of metal alloys in the process of recrystallization and during a long storage time. For example, the process of extraction of zinc, aluminum, calcium, potassium, bismuth, and arsenic is the most active (of course, if these elements were present in the primary melt) for cast iron and iron alloys. Copper, chromium, manganese are released less intensely.

Thus, over time, metals change structurally and chemically and these changes can be considered as indicators when confirming the authenticity of historical artifacts.

The study of features of the described processes makes it possible to model the processes of self-refining (metals self-purification from impurity elements) at the level of ideas of modern crystal chemistry. This makes it possible to theoretically substantiate the results of empirical studies of chemical composition in historical artifact surfaces as well as propose methods for the practical solution of expert problems of establishing the authenticity of the cultural artifacts made of metals. In addition, the results of such studies will contribute to the development of measures for safe handling of antiques as the chemical impurities such as As, Bi, Sb, Pb, Hg, etc. eliminated from the alloys can be dangerous to humans because they cause allergies, chemical damage, or poisoning.

Guided by the ideas of modern crystal chemistry, we can say that the energy of the ions of impurity elements in the crystal lattice of pure metals depends on the electrical interaction and size of ions. In this case, we are talking about covalent chemical bonds between ions. This follows from Max Bourne's formula [10] and can be determined by the attraction-repulsion force:

$$F=-\frac{\left(Z_1 Z_2 e^2\right)}{4\varepsilon\pi R^2}, \tag{1}$$

where F is the force of attraction-repulsion of ions in the crystal lattice; Z_1 and Z_2 are the integers (ion charges); e is the electron charge; $4\varepsilon\pi$ is the constant; R is the distance between ions, i.e. the sum of radii (r_1+r_2).

Formula (1) shows that the strength of interaction of ions in the crystal lattice is directly proportional to the product of charges and inversely proportional to the distance between ions. Therefore, these two parameters play a crucial role in understanding the processes of elimination of impurity elements from the metal alloy which is considered in this study. Structural parameters of the crystal lattice (coordination numbers, packing density, covalent bond strength, and repulsive force) which were once studied and described in [11] are more indirect. When studying the hardness of binary crystals, it was proposed to use valence parameters instead of ion charges:

$$H=\alpha\beta\gamma K\frac{W_1 W_2}{d^2}, \tag{2}$$

where H is the crystal hardness; α is the repulsive force of ions; β is the density factor of crystalline packing associated with the coordination number (β is CN); γ is the coefficient of attenuation of the chemical bond; K is the coefficient of the strength of the chemical bond; W_1 and W_2 are the valences of ions in the crystal lattice; d is the distance between ions, i.e. the sum of radii (r_1+r_2).

Hardness should be considered as an integrated indicator of the strength of chemical bonds between ions in the crystal lattice. An attempt was made in [11] to find a correspondence between the hardness of minerals which is measured in practice using a microhardness tester and Max Bourne's physical model. Studies and mathematical modeling have confirmed this relationship. At the same time, as can be seen from formula (2), the relation provided for the use of a large number of correction factors with their nature not unambiguously explained.

Attempts have been made to model the relationship of other physical properties of minerals with peculiarities of their crystal lattice structures and chemical composition [12]. The results of mathematical modeling of the relationship between the magnitude of the optical refractive index of transparent minerals with a simple chemical composition (binary minerals) and the structure of the crystal lattice have been quite successful. It was established that the light refraction index largely depends on the mass of the ions, the distance between ions, and the existing types of chemical bonds in the crystal lattice [13]:

$$n=\frac{\left(M_1+M_2\right)R_{ok}}{d^3 Cn\Delta EO}4.18\cdot 10^3, \tag{3}$$

where n is the index of light refraction; M_1, M_2 are the masses of ions (cation and anion, respectively); R_{ok} is the size of the main cation; d is the distance between the cation and the anion; Cn is the coordination number of the cation; ΔEO is the difference between the cation and anion electronegativities.

The above formulas (1) to (3) indicate that all physical properties of crystalline bodies depend on masses of ions, their charges, and the distance between them. At the same time, according to the periodic law, these characteristics are completely interdependent because the ion mass explains the configuration and number of electron shells, nature, and strength of chemical bonds between ions in the crystal lattice, the distance between ions, and the type of packing. Referring to the results of studies in the field of crystal chemistry, it can be argued that a change in one of these parameters, e.g. the ion mass, automatically leads to a change in other parameters.

Therefore, it is expedient to assume that the force of ejection of impurity elements from the crystal lattice of metals is directly proportional to the deformation of the crystal lattice which occurs in the presence of ions of different sizes. The general estimate of such deformation can be described as follows:

$$D = \left| 1 - \frac{(R_{mi} + R_{ii})}{d} \right|, \tag{4}$$

where D is the degree of deformation of the crystal lattice; R_{mi}, R_{ii} are the radii of the metal ion and the ion of the impurity element, respectively; d is the distance between ions in the metal.

The value of D is zero if the sum of R_{mi} and R_{ii} is equal to the distance between ions in the metal. Thus, the more significant the value of D, the more intensely the impurity ions will be eliminated from the metal crystal lattice. The rate of auto refining will also be proportional to the D parameter.

It should also be noted that the nature of the process of elimination of impurity ions is stochastic, i.e. occurs according to the relativistic laws. Thus, during the history of the existence of the artifact, natural self-cleaning of the alloy surface takes place, i.e. concentration of the metal from which the item was made increases, and the quantity of impurity elements decreases. Assuming that temperature of historical artifact storage is close to constant, i.e. 10~20 °C, we can say that the rate of decrease in the concentration of impurity ions dC in time t is directly proportional to the degree of the crystal lattice deformation D:

$$\frac{dC}{dt} = Dk \text{ or } dt = \frac{dC}{Dk}, \tag{5}$$

where k is constant.

Taking into account the fact that the derivative of the product of the constant and the function is the product of this constant and the derivative of the specified function, we come to an important conclusion. The age of a culture artifact made of a metal having a constant concentration of impurity ions can be estimated by measuring the concentration of impurities in the artifact's surface and its body. Measurements on the surface should be made immediately under the patina. The inaccuracy of calculations will relate to the lack of information about the type of chemical bonds of impurity elements, thermodynamic conditions of the process, the influence of the environment, and other factors.

To test our hypothesis, it is necessary to conduct a series of studies of well-attributed items of different ages, i.e. experimentally investigate the type of function of change in concentration of impurity elements on concrete examples of artifacts of different ages. The results of such studies have been partially published [1], however, it is clear that further studies will further clarify the nature of many currently unknown phenomena.

It has been established that the items made of gold in the distant past are characterized by the fact that their undamaged surface contains significantly fewer impurities than the ground-in surface which had no contact with the environment. The surface should be cleaned of mineral crusts, but without leaving signs of rough cleaning.

Studies of the gold overlay on the ancient Greek shield dated by the IV century B.C. were conducted by ArtAnalytics LLC (Expert Opinion dated 25.05.2017, No. 00105), Fig. 2. Age of the item: more than 2,400 years. The results indicate a significant difference in the chemical composition of the metal on the overlay surface and in its body.

Fig. 2. The view of the gold overlay on the ancient Greek shield with the image of Medusa Gorgon from a private collection (with the permission of the owner). Diameter: 53 cm

Fig. 3 shows a photo of a surface fragment of the sample taken from the artifact in the secondary electron image (SEI) at a ×150 magnification. The numbers indicate the points where the chemical composition was examined. The results are presented in Table 1.

To make the obtained results more convincing, the study was carried out in five points of the artifact surface where new scratches were found. These data showed affinity both in terms of the lowest and highest concentrations of gold in the artifact surface. It should be noted that measurement of gold concentration within the scratch also indicates that some part of patina precipitates was rubbed from the surface into the scratch metal, so great variability in results was observed. Such errors can be avoided by using modern methods of material evaporation from the surface in a vacuum (laser ablation). However, no such hardware capabilities were available for the studies.

Table 1 shows that the largest difference between gold concentrations in this artifact surface and its deeper metal layers was more than 20 %. We suppose that this phenomenon is connected with the process of gradual natural recrystallization of the gold alloy and the elimination of impurity elements.

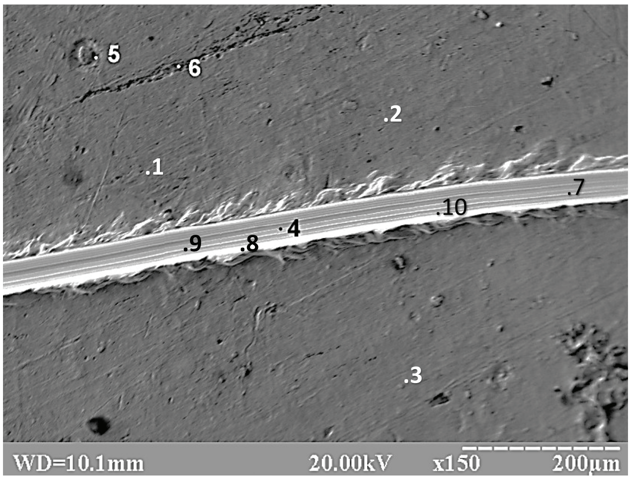

Fig. 3. A fragment of the image of the examined metal surface (in a secondary electron image) where there is a new scratch which makes it possible to study chemical composition in deeper layers of the metal. Numbers 1, 2, 3, 4, … indicate the points where the chemical composition of the gold alloy was studied

Table 1

Results of the study of chemical composition in the surface of the gold overlay on the ancient Greek shield

Point number	Study location	Au	Ag	Cu	Fe	Sum
1	surface	95.3	1.1	3.6	~ 0	100
2	surface	91.4	1.1	4.1	3.4	100
3	surface	99.0	~ 0	0.5	0.5	100
4	scratch	87.13	10.2	2.4	0.27	100
5	surface	84.57	11.93	2.38	1.12	100
6	surface	89.18	9.5	0.63	0.69	100
7	scratch	80.1	11.3	8.3	0.3	100
8	scratch	80.3	5.4	10.2	4.1	100
9	scratch	79.0	11.3	8.1	1.6	100
10	scratch	85.2	10.1	4.7	~ 0	100

Next, consider the results of analytical studies of the item shown in Fig. 4. It is a Byzantine gold ring dated by the XIII–XIV centuries (private collection). The age of this item was determined to be within 600–700 years (Expert Opinion by ArtAnalytics LLC dated July 1, 2016, No. 00088).

Fig. 4. The view of the golden Byzantine ring. Outer diameter: 23.7 mm; overlay dimensions: 13.2×10.7 mm; weight: 14.8 g

Fig. 5 shows an electronic image of the ring surface with a new scratch. The results of measuring the content of gold and other chemical elements applying the energy-dispersion method are given in Table 2.

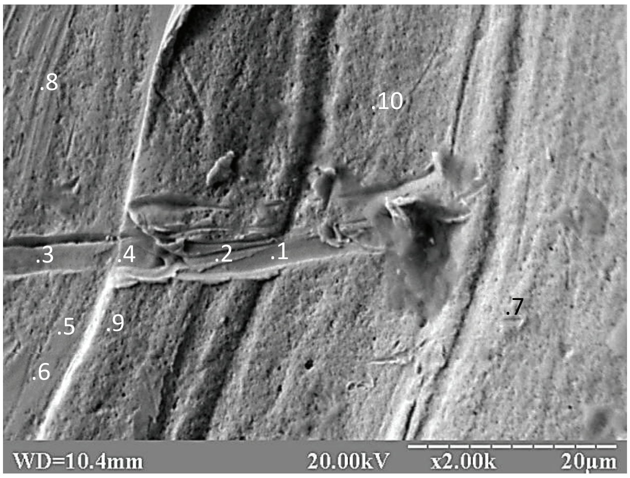

Fig. 5. Secondary electron image of the ring surface where the scratch was found. Numbers indicate the points of study of chemical composition

Table 2

The results of the study of chemical composition in the surface of the gold alloy from which the ring was made

Point number	Study location	Au	Ag	Cu	Fe	Sum
1	scratch	92.51	4.72	2.58	0.19	100
2	scratch	93.96	4.76	1.18	0.1	100
3	scratch	95.71	3.26	0.55	0.48	100
4	scratch	90.6	6.72	2.29	0.39	100
5	scratch	92.65	5.66	1.49	0.2	100
6	scratch	94.84	3.88	0.63	0.65	100
7	surface	97.5	1.81	0.29	0.4	100
8	surface	96.47	3.43	0.09	0.01	100
9	surface	96.97	2.68	0.35	0	100
10	surface	96.31	3.35	0.34	0	100

As the third example, consider the results of a study of the gold coin which was used in the Russian empire in 1712 (at the time of emperor Peter I ruling) [14], Fig. 6. Diameter: 21.5 mm, weight: 3.44 g. (Expert Opinion by ArtAnalytics LLC dated July 31, 2014, No. 00059).

Fig. 6. The view of the gold coin of emperor Peter 1 ruling period

When studying the coin surface under an electron microscope, we had the opportunity to examine the chemical composition of the gold alloy including the areas with micro scratches (Fig. 7).

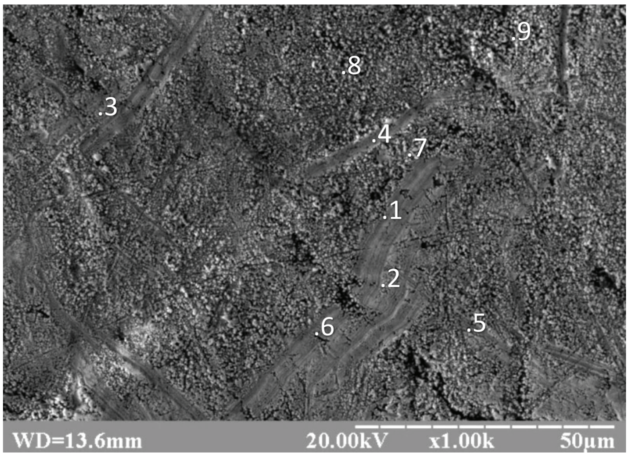

Fig. 7. Microsection of the gold coin surface with a shallow micro scratch. Secondary electron image (SEI)

The results of the study of the chemical composition of the gold alloy in the test points are presented in Table 3.

Table 3

The results of the study of chemical composition in the surface of the gold alloy from which the coin was made

Point number	Study location	Au	Ag	Cu	Fe	Sum
1	scratch	92.88	6.18	0.93	0.01	100
2	scratch	94.79	4.75	0.46	~ 0	100
3	surface	95.9	2.44	1.39	0.27	100
4	scratch	94.35	4.83	0.56	0.26	100
5	surface	95.01	3.98	0.65	0.36	100
6	scratch	94.52	3.5	1.33	0.65	100
7	scratch	94.04	5.13	0.58	0.25	100
8	surface	96.5	3.3	0.19	0.01	100
9	surface	95.9	2.44	1.39	0.27	100

Similar studies of chemical composition in the surface were conducted with a sample of the ancient Greek jewelry item which is more than 1,500 years old (Fig. 8).

Fig. 8. The gold bracelet with an oval medallion decorated with a grenade insert faceted in the form of a cabochon. Brackets are made hollow in the form of lion figures. Weight: 94 grams. (Scientific Report by ArtAnalytics LLC dated 04.01.2017, No. 00102)

Areas with a gold content of up to 98.5 % were found in the surface of this artifact in locations where the patina was chipped-off while this metal content did not exceed 96.7 % in the micro scratches.

5. 2. The results of establishing the dependence of gold concentration in the surface of artifacts on the item age

When analyzing the results of the study of the chemical composition of historical artifacts made of gold, maximum, minimum, and average values of gold content in the studied artifacts were calculated (Table 4).

Table 4

Maximum, minimum, and average values of gold content in the studied artifacts

Item name	Average content of cleaned gold under the patina	Average content of gold in the alloy body	Maximum content of cleaned gold under patina	Minimum content of gold in the alloy body	Difference between gold content in the surface and the alloy body
Overlay on the old Greek shield	91.89	82.35	99.0	79.0	20.0
Bracelet with an oval medallion	97.78	95.45	98.5	83.7	14.8
Byzantine ring	96.81	93.38	97.5	90.6	6.9
Peter I gold piece	95.83	94.12	96.5	92.88	3.62

Data in Table 4 show an increase in the difference between the gold content in the surface and in the deep item parts with the age of the artifact demonstrated by the result of crystal-chemical transformations in metal artifacts. As a result of this process, natural refining of the gold alloy in the artifact surface occurs resulting in an increase in the main component (gold) content.

Fig. 9 visually shows the increase in the difference between gold content in the surface and the alloy body with the item age. The blue ball denotes a figurative point that describes Peter I gold coin; the red ball denotes the Byzantine ring; the green ball denotes the ancient Greek gold bracelet; the blue ball denotes the gold overlay on the ancient Greek shield with an image of Medusa Gorgon.

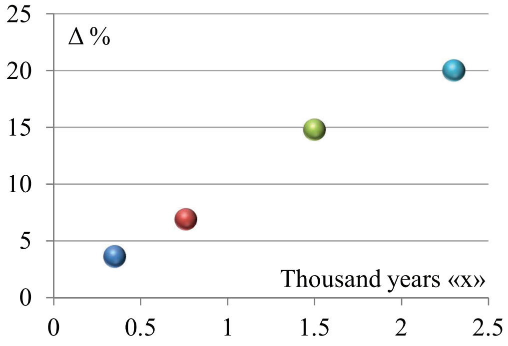

Fig. 9. Dependence of the difference Δ between gold content in the surface and the body of the artifact (ordinate axis) on the item age in thousands of years (abscissa axis)

Fig. 10 shows the dependence of the maximum concentration of the main component (gold) of the alloy in the artifact surface on the age of the item in thousands of years. The color of the figurative points corresponds to that indicated in Fig. 9. The violet ball denotes the armor ornaments described in a previously published study [1].

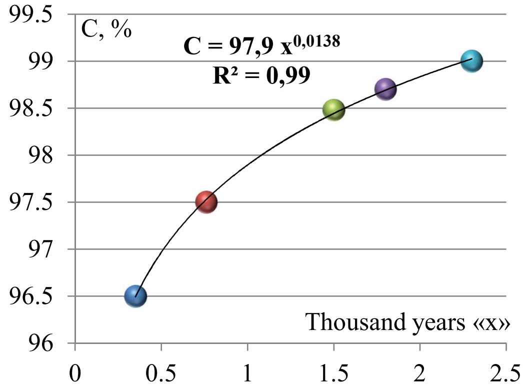

Fig. 10. Dependence of maximum concentration of the main component (gold) *C* of the alloy in the artifact surface (ordinate axis) on the item age in thousands of years (abscissa axis) as well as the equation describing this dependence and the quality index of approximation by K. Pearson

As can be seen from Fig. 10, the tendency to eliminate impurities from gold alloys is quite good. The exponential equation presented in Fig. 10 describes the saturation function with an asymptotic approximation of the concentration index *C* from 95.66 to 100 %. This means that the best results in predicting the artifact age based on the study of change in gold concentration in the item surface and in the body should be expected when the initial concentration of gold (during the item manufacture) is about 95 %. Separate studies should be performed for items with other initial concentrations of this metal.

Proceeding from the results of polynomial approximation of the observed dependence of gold concentration in the surface on the artifact age *T*, the following equation for predicting the item age was obtained:

$$T = 0.28C^2 - 53.7C + 2588.9. \qquad (6)$$

Of course, the equation should only be used when the item under study is chemically related to the group of items described above.

6. Discussion of the results obtained in the study of historical artifacts made of gold

The study results convincingly show the course of crystal-chemical transformations in metals that took place during the long history of storage.

At the same time, it should also be noted that only the items of different ages in which contents of gold, silver, copper, and iron in their bodies were approximately the same were involved in the study. Variability of the obtained results is explained by inhomogeneities in the structure of crystalline aggregates in the metal, elimination of impurity elements, and the index of resolution of the emission probe.

In particular, gold concentration was mostly above 90 % in the body and up to 99 % on the surface depending on the item age. The choice of items for the studies described above is explained by the fact that alloys should form crystals of approximately the same size during the long process of natural recrystallization and the surface should not be oversaturated with small defects filled with patina and interfere with the natural self-cleaning. We consider that the items in which the initial concentration of gold is low, not higher than 90 %, need a separate study.

The results indicate the need for the studies with sets of items having approximately the same base chemical composition differing from each in their gold contents within 10 %. In addition, it is desirable that the items were made using the same technology, such as casting, smithery, or bending.

Further studies are aimed at collecting small reference sets (up to 10 samples) of well-attributed artifacts for which numeric measurements sufficient to establish the laws of distribution of original data will be made as well and deeper studies will be conducted using the methods of dissolving surface microsections (chemical ablation). Particular attention will be paid to the elaboration of criteria for proving the authenticity of gold artifacts and algorithms of age calculation.

7. Conclusions

1. Chemical composition of gold artifacts was determined immediately under patina and in the alloy body using a scanning electron microscope equipped with an energy dispersion spectrometer. The results have shown gold content in the alloy body much lower than in the item surface. At the same time, the undamaged surface cleaned from mineral crusts contained significantly fewer impurities than the polished surface which was not contacting with the environment. Thus, the study of the chemical composition of gold artifacts cannot be conducted based solely on the surface study. Preparation of metal artifacts for their demonstration in museums must not include the procedure of rough mechanical surface cleaning which destroys traces of crystal-chemical transformations in the metal.

2. Dependence of concentration of the main component (gold) of the alloy in the surface of the studied artifacts on item age in thousands of years was established. An equation for predicting age of the items chemically related to the group of items described in this article was presented. This is an additional mechanism for the attribution of metal artifacts. In particular, the expert activities concerning the estimation of metal artifacts can be standardized.

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