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DETERMINING THE SEQUENCE OF ELIMINATION OF IMPURITY IONS FROM THE SURFACE OF HISTORICAL COLD IRON WEAPONS

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Confirming the authenticity of historical cold weapons and determining their age is an urgent problem in practical examination. One of the promising directions for its solution is the experimental study of the process of elimination of impurity ions from iron, which occurs throughout the long history of life.

This paper describes a model that explains the sequence of elimination of impurity ions from near-surface parts of the metal. Deformation indicators of the crystal lattice of iron were calculated and sorted in order of decreasing ionic radius of the impurity chemical element. A diagram of the deformation effect of impurity chemical elements on the volume-centered crystal lattice of iron was constructed. Ions that are larger in diameter are more actively eliminated from the surface layers of the metal, while ions that are smaller are removed to a lesser extent.

With the help of the authors' methodology, a study of the chemical composition of the surface of collection samples of iron cold weapons of the 20th, 19th and 18th centuries was carried out. It has been established that a metal alloy made in the recent past – up to 100 years – is characterized by a very active release of impurity chemical elements on the surface when it is heated. Iron weapons made up to 200 years ago have a significantly lower ability to release chemical impurities because most of the latter have already been eliminated. At the same time, samples of cold weapons of this age already have microdefects in the form of cleavage cracks and caverns, so their surface contains a significant number of compounds of eliminated chemical elements that have accumulated during the long history of their use. Older cold weapons, made 300 years ago or earlier, have impurity ions that are smaller than ferric ions, particularly silicon.

The results of the research are important for the identification and authentication of historical iron cold weapons

Keywords: historical cold weapons, chemical composition, impurity ions, X-ray fluorescence analysis, identification, examination, authenticity

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1. Introduction

Historical melee weapons are a source of objective and important information for reproducing the history of technological development of humankind, studying the military traditions of the peoples of the world. Historical melee weapons are an integral part of prestigious museum exhibits, they are a ceremonial symbol of prestige, social status, and a popular object for collecting. Cold weapons are also a commodity that is widely represented on the world markets of antiquities. Some samples are valued very expensively and are sold at auctions or in elite antique shops.

At the same time, historical cold weapons have always been an object for copying and forgery, and the available methods of examination, which have been constantly improved, do not make it possible to fully solve the complex of questions related to their authenticity. Examination methods, in the vast majority, are based only on visual observations of typological and structural features, decoding of brands and trust in accompanying documents.

Therefore, the problem of confirming the authenticity of historical cold weapons is relevant in museum practice, collecting, and the field of practical expertise.

2. Literature review and problem statement

Many fundamental studies consider the recrystallization of metals and the elimination of impurity ions from the surface. In particular, work [1] analyzed the development of refining technologies in the process of steel production during the last 60 years. A separate research issue is the prospects of the industry with the aim of reducing processing costs and improving the quality of steel. However, this paper does not consider the issue of elimination of impurity ions from the surface of metal cultural monuments.

In work [2], the main issues of X-ray fluorescence analysis for both metals and food products are considered. The work also describes a method of non-destructive testing using a portable X-ray detector for museum artifacts made of wood and fabrics. However, the author does not consider X-ray fluorescence analysis for metal artifacts from different periods of history.

In [3], the characteristics and properties of cast, cut, and forged silver jewelry are considered. The authors have developed proprietary methods of determining the authenticity of jewelry. The methods are universal, show the peculiarities of the products of the studied region, but can be adapted to any region of the world. However, this analysis does not consider historical monuments made of iron, in particular cold weapons.

In work [4], the properties of cast and forged steel products are given, the composition contains impurity elements that reduce the quality of the final product. In order to reduce the content of impurity elements, the authors have developed several methods of refining molten metal.

However, historical melee weapons differ from objects manufactured in recent decades by the features of the production technology, which causes the release of various chemical elements on its surface over time and the influence of the environment. The experimental method can prove that impurity ions are eliminated on the surface during the process of use and storage. In addition, the condition of the surface and the number of chemical elements on the surface can be a criterion for the age of the sample and its authenticity.

Work [5] investigated the process of vacuum casting of steel products, in which a patina is formed due to the contact of the steel with the spray limiter. Patina is a source of impurity ions that can affect the quality of finished products. However, this work does not mention the importance of impurity inclusions for determining the authenticity of historical metal artifacts and their age.

In paper [6], the authors suggest using an X-ray fluorescence analyzer (XRF) to study gold jewelry of ancient Egypt and Mesopotamia. The authors proposed dividing weapons and jewelry into groups according to the chemical composition of the metal. However, this study did not study the specifics of the chemical composition of cold weapons made of steel and other metal alloys.

The chemical composition and microstructure of cultural values made of various metals were studied. In particular, studies of natural patina on the surface of bronze artifacts are important [7]. The classification and characteristics of patina structures are also given for a deeper understanding of the mechanism of their formation. But the authors did not investigate the effect of temperature on patina and changes in the chemical composition of artifacts when they are heated.

The compositional and microstructural study of joining methods in archaeological gold objects of the pre-Roman era was studied by analytical methods [8]. The main goal of the study was to investigate their characteristics both at the compositional and microstructural levels (SEM–EDS, metallography, μ-XRF and μ-PIXE). However, historical items of cold weapons made of iron differ in the course of crystal-chemical transformation, so they require in-depth study.

One of the directions of the study of historical cold weapons is the study of the phenomenon of elimination of ions of impurity chemical elements from the near-surface layers of metal with the help of specially developed methods of testing and studying the chemical composition with the help of an X-ray fluorescence analyzer [9]. At the same time, not only the chemical composition of impurity elements can be used as a criterion of authenticity. Information about the sequence of elimination of these ions in the process of heating the surface is also of practical value.

All this allows us to state that it is appropriate to conduct a study on determining the sequence of the process of elimination of impurity ions, which occurs during the long history of living or during the heating of historical cold weapons made of iron.

3. The aim and objectives of the study

The purpose of this work is to determine the sequence of elimination of impurity ions from the surface of historical iron cold weapons. This will improve the methods of confirming the authenticity of cold weapons.

To achieve the goal, the following tasks should be solved:

– to build a theoretical model that explains the sequence of elimination of impurity ions from the near-surface parts of the metal when it is heated;

– to present the results obtained during the experimental study of a number of collection samples of cold weapons, which differ significantly in age.

4. The study materials and methods

Collection samples of cold steel weapons of the 20^{th}, 19^{th}, and 18^{th} centuries were selected for research. They were not restored or treated with special solutions for their preservation. Considering their different ages, it was assumed that as a result of the natural recrystallization of the metal in the near-surface layers, natural processes of extraction of impurity ions, different in size and properties, take place. In addition, the process of self-cleaning of the metal as a result of the removal of impurity ions to the surface can be accelerated by heating the samples under investigation. The results of determining the chemical composition of the metal surface before and after heating are used to confirm the authenticity of samples of historical cold weapons.

The authors' research method involves making three samples for chemical analysis by rubbing the metal surface. The first sample is made by rubbing the raw surface of the metal with an ashless swab, thereby removing mineral and organometallic substances from it. The second sample is made by rubbing the already cleaned metal surface with an ashless swab. It makes it possible to record the chemical composition of a cleaned surface or a partially cleaned surface. The third sample is made by rubbing the same metal surface with an ashless swab after heating it with a technical hair dryer at an air temperature of 550–600 °C.

The three tampons obtained in this way were burned, and the chemical composition of the ash was determined using an X-ray fluorescence analyzer Expert Mobile (manufactured by INAM LLC, Kyiv). The device is equipped with an X-ray tube with direction/current parameters – 50 kV/0.1 mA, anode – titanium. Photon energy detector of fluorescence (secondary) extraction from the image is SDD. In air, it allows the analysis of elements ranging from the 12^{th} element of the periodic table of magnesium to the 92nd element of the uranium. The accuracy of the device in terms of percentage of chemical element content is 0.05 %.

When making samples, the material is collected from a large surface, the area of which is at least 20,000 times larger than the area analyzed by the X-ray fluorescence device in the standard testing mode. Therefore, it becomes possible to identify the ions eliminated from the metal, present in the metal in very small concentrations.

5. Results of investigating the sequence of elimination of impurity ions from the surface of historical cold weapons made of iron

5. 1. Construction of a model that explains the sequence of elimination of impurity ions from near-surface parts of the metal during its heating

In the course of experimental studies of a representative number of artifacts, it was established that as a result of recrystallization, the surface of metals, and iron alloys in particular, self-cleanses by eliminating impurity chemical elements [10, 11]. The presence of impurity elements leads to deformation and even destruction of crystal lattices of metals. Moreover, the greater the difference in the sizes of impurity ions from the sizes of iron ions, the greater is the deformation of the crystal lattice, and the higher is the probability of their elimination during the long-term use of the metal product.

The level of local deformation of the crystal lattice caused by the presence of ions of different sizes can be estimated using the dimensionless indicator "*D*" [12], which takes values from zero to one:

$$D = \left| 1 - \frac{\left(R_m + R_j\right)}{d} \right|, \tag{1}$$

where D is the local deformation index of the crystal lattice; R_m and R_i, respectively: radii of iron ions and impurity chemical element according to Polling [13–15]; d is the interionic distance characteristic of the undeformed crystal lattice, i.e., the distance equal to $2R_m$.

It is clear that the greater the concentration of impurity chemical elements in the metal, the greater is the overall deformation index of the crystal lattice. Also, the more ions will be removed from the metal to its surface during natural recrystallization or during heating. At the same time, it is important to note that in ancient iron products, ions with large sizes are not fixed due to the fact that they are removed during a fairly short period of time.

The corresponding "*D*" indicators are calculated using a list of chemical elements (mainly cations), which:

– are available for detection using an X-ray fluorescence analyzer;

– are nherent in iron alloys due to their mandatory presence in the composition of minerals of primary ores (Table 1).

Of course, the above calculations cannot be considered highly accurate and depend on the selected method of calculating ion radii. However, they accurately reflect the ratio of ion diameters, are indicative and sufficient for formulating tasks in experimental studies. The indicator of the minimum deformation of the crystal lattice is associated with trivalent iron ions, the outer shells of which play the role of "electron gas".

Table 1

Calculated parameters of the deformation of the crystal lattice of iron "*D*", sorted in order of decreasing ionic radius of the impurity chemical element. The basis of the calculation is the ion of trivalent iron Fe^{+3}

The name of the cation and its valence	Ion sizes according to Polling, R_i	Deformation index of the crystal lattice "*D*"
Ba^{+2}	0.138	0.52985
K	0.133	0.49254
Pb^{+2}	0.126	0.4403
Hg^{+2}	0.112	0.33582
Ca^{+2}	0.104	0.27612
Cd^{+2}	0.099	0.23881
Na	0.098	0.23134
Cu^{+}	0.098	0.23134
Mn^{+2}	0.091	0.1791
Zn^{+2}	0.083	0.1194
Cu^{+2}	0.08	0.09701
Fe^{+2}	0.08	0.09701
Pb^{+4}	0.076	0.06716
Mg^{+2}	0.074	0.05224
Mn^{+3}	0.07	0.02239
Fe^{+3}	0.067	0
Al^{+3}	0.057	0.074627
Mn^{+4}	0.052	0.11194
Mn^{+7}	0.046	0.156716
Si^{+4}	0.039	0.208955
S^{+6}	0.029	0.283582

Fig. 1 shows a diagram where the calculated value of the deformation index of the iron crystal lattice "*D*" is described by the ordinate axis, and the impurity chemical elements are in the order given in Table 1, described on the abscissa axis. The vertical dashed line separates chemical elements that have larger ion sizes than ferric ions (left) and have a greater deformation effect on the crystal lattice. To the right of the vertical dashed line are chemical elements that have smaller sizes and, accordingly, have less influence on the deformation of the crystal lattice of iron and, therefore, are removed from the metal more slowly. Chemical elements united by red lines indicate a significant age of the samples of cold weapons. The elements connected by a blue line indicate the recent manufacture of cold weapons.

It is clear that all ions that are significantly different in size from the trivalent iron ion cause large deformations of the crystal lattice [12]. It can also be assumed that ions that are larger in diameter are more actively eliminated from the surface layers of the metal, and ions that are smaller are removed to a lesser extent. A corresponding conclusion should be made in relation to the indicators of the speed of their release.

This assumption allows us to say that the surface of older historical cold weapons will be characterized by a lower number of impurity chemical elements. Most of the elements will be represented by ions close to iron ions in size – trivalent aluminum, tetravalent silicon, hexavalent and heptavalent manganese, and possibly hexavalent sulfur or elements with ion sizes much smaller than ferric iron. If the melee weapon is a copy made recently, ions with large dimensions will be detected on its surface. Such elements are lead, potassium, calcium, sodium, phosphorus, and copper, i.e., those that, despite the high rate of elimination from the alloy, did not have time to leave the crystal lattice.

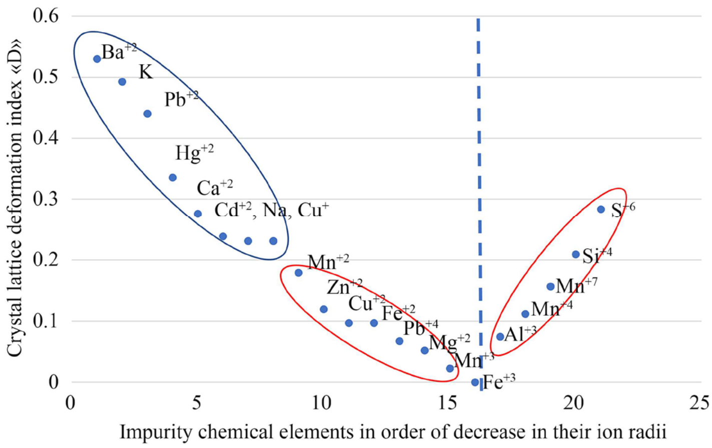

Fig. 1. Diagram of the deformation effect of impurity chemical elements on the volume-centered crystal lattice of iron

Features of the extraction of ions of chemical elements from the crystal lattice of iron, which occur in a certain sequence, help solve the question of the authenticity of historical cold weapons. Thus, historical weapons, which are accompanied by relevant documents indicating their age, can be verified for authenticity. Authenticity is established on the basis of the results of the analysis of the chemical composition of mineral and organometallic accretions on the surface of the artifact using an X-ray fluorescence analyzer.

The graphic formalism of the diagram shown in Fig. 1 is a crystal-chemical model that describes the system of mathematical ratios of ion radii and explains the reasons and sequence of the process of elimination of impurity chemical elements from the surface layers of the metal. It makes it possible to use the "*D*" parameter – the ratio of the size of the impurity ions to the size of the trivalent iron ion – as a criterion for confirming the authenticity of a cold weapon. If there are impurity chemical elements on the surface of the metal, for which $D>0.3$, cold weapons should be classified as modern products, and if $D<0.3$ – as products manufactured in the past – the age of which exceeds 100 years.

The sequence of elimination of impurity chemical elements from the crystal lattice is carried out in order from the largest *D* index and ionic radius to the smallest (from left to right). Moreover, the total concentration of impurity chemical elements on the surface of the metal is higher if there were more of them in its composition from the beginning.

Older melee weapons show a higher level of surface self-cleaning. That is, only impurity ions for which $D<0.2$ can be detected on the surface after heating. Moreover, the total concentration of impurity chemical elements released on the surface of the artifacts after its heating will be much lower.

Using the model described above, the age of historical cold weapons, given the presence of relevant impurity chemical elements on its surface, is determined as follows: with $D>0.3$, modern weapons and weapons of the 20th century; at $0.15<D<0.3$ – a weapon of the 19th century; with $D<0.15$ – weapons manufactured before the 19th century.

Therefore, in order to draw a reasonable conclusion about the authenticity of historical cold weapons, it is enough to conduct sampling according to the method described above, to identify chemical elements that are eliminated from the surface of the metal when heated, as well as their total number and their *D* coefficients.

5. 2. The results of an experimental study of a number of collectible samples of cold weapons, which differ significantly in age

To confirm the model, samples of cold weapons were selected, which were provided by the National Military Historical Museum (Ukraine) and are described in Table 2.

It is important to note that the samples of cold weapons selected for the study were not restored or treated with special solutions for their preservation. This should be considered a prerequisite to ensure the purity of the experiment.

As a result of the study of a steel knife made in the 20th century, it was established at the first stage that chemical compounds of phosphorus, zinc, and sulfur have accumulated on its surface. Their presence should be associated with interaction with the environment. Repeated rubbing (second stage) confirms the partial cleaning of the surface (Table 3).

The third stage of research involves studying the determination of the chemical composition of substances on the surface after its heating. At the same time, a significant number of ions of impurity chemical elements is released, especially those that were not detected in the first two stages of research (Table 3).

Table 2

Samples of cold weapons used in the study

Sample No.	Photograph	Sample summary
1		Twentieth century knife with wooden handle
2		Nineteenth-century sabre (scabbard with metallic trim)
3		Steel dagger of the eighteenth century

Table 3

The results of a study of the chemical composition of the surface of an iron knife made in the 20th century

Experiment phase	Fe, %	P, %	Cu, %	Zn, %	Si, %	S, %	Ag, %	The sum of impurity elements, %
One	93.48	2.37	–	1.32	–	2.83	–	6.52
Two	96.94	–	–	1.33	–	1.73	–	3.06
Three	51.25	2.57	2.19	12.24	8.63	21.62	1.5	48.75

The total number of impurity chemical elements and their compounds, which were released from the metal during its heating, is very high, as evidenced by the indicators of the sum of concentrations shown in Table 3. This indicates a low level of its recrystallization, a large number of ions of extraneous elements that have not yet been eliminated, and, accordingly, the relatively young age of the knife. When the surface of the object is heated, the gloss of its surface becomes cloudy.

Table 4 gives the results of an experimental study of sabers of the 19th century. The long history of use of this object led to the accumulation of a significant amount of patina secretions of mineral and mineral-organic composition on its surface. This was the result of the process of gradual natural recrystallization of the metal with the release of impurity ions on its surface and their interaction with the environment.

At the second stage (second tampon) of the experiment, only insignificant concentrations of zinc were recorded. Therefore, it can be assumed that all the substances that were observed at the first stage were removed earlier.

At the third stage of the experiment, the appearance of a significant number of chemical elements that were not inherent to the surface at the first stage of the study is observed. At the same time, their total number is much smaller than for the subject of the 20th century, described in Table 3. This indicates significant self-cleaning of the metal surface as a result of its natural recrystallization – "aging".

Table 4

The results of a study of the chemical composition of the surface of an iron saber made in the 19th century

Experiment phase	Fe, %	P, %	Cu, %	Zn, %	Si, %	S, %	Au, %	The sum of impurity elements, %
One	82.28	–	3.1	2.1	7.31	5.21	–	17.72
Two	99.18	–	–	0.82	–	–	–	0.82
Three	89.72	0.96	3.95	0.06	3.02	1.18	1.11	10.28

The last item described in Table 5 is up to 300 years old. It is clear that its surface has been repeatedly cleaned and therefore does not contain traces of many long-eliminated chemical elements. The presence of sulfur and phosphorus indicates the presence of organic compounds that at one time accumulated in microcaverns and microcracks associated with the intergranular interaction of iron crystals, which increased in size and became more complex in shape.

Rubbing the metal in the second stage reveals an increase in sulfur on the surface, which can be explained by the release of organic compounds from microdefects with slight heating as a result of friction.

The third stage of the experiment allows diagnosing the process of elimination of a small amount of copper and a very large amount of silicon. This certainly indicates that the main part of impurity chemical elements that were present in the primary alloy has already been released from the near-surface layer of iron into the environment. However, ions approaching the size of ferric iron are still present and continue to be released. Silicon, the ion radius of which is smaller than the radius of trivalent iron, is stored in the near-surface parts of the metal in a significant amount, and its release occurs only under the influence of heating.

It should also be noted that the concentrations given in Table 5 are normalized at the level of 100 %, therefore they do not reflect the indicators of absolute concentrations of chemical elements in the studied samples. If necessary, the effect of normalization can be taken into account. To this end, it is necessary to analyze the emission spectra and reach similar conclusions based on the determination of the altitudes of the corresponding spectral lines.

Table 5

The results of investigating the chemical composition of the surface of an iron dagger made in the 18th century

Experiment phase	Fe, %	P, %	Cu, %	Si, %	S, %	The sum of impurity elements, %
One	85.86	3.37	–	–	10.77	14.14
Two	96.27	–	–	–	3.73	3.73
Three	67.68	3.43	3.42	16.94	8.53	32.32

6. Discussion of the results of investigating the sequence of elimination of impurity ions from the surface of historical cold weapons made of iron

It should be noted that the iron alloys used to create cold weapons in the past and in the present differ not only in that they have different levels of purity and different chemical impurities. The difference is that their surface is in a different physical state, which is described by the phenomenon of gradual natural recrystallization (or "aging"). This process is characterized by an increase in the size of crystalline grains (or the transformation of individual individuals into so-called mosaic aggregates), the destruction of grain boundaries, and the release of chemical elements and impurities.

In contrast to [9], where there were no studies with the effect of different temperatures, this study is based on the temperature effect on the surface of samples of historical cold weapons of different ages.

Comparing the results of the research on the chemical composition of the ash residue of tampons for the above-mentioned samples of cold weapons, it is important to note that the metal alloy produced in the recent past – up to 100 years ago – is characterized by a very active release of impurity chemical elements (Table 3). This is well diagnosed when it is heated on emission spectra and in the results of recalculation of relative concentrations.

Iron weapons manufactured up to 200 years ago are characterized by a significantly lower ability to extract impurity chemical elements because most of the latter have already been eliminated (Table 4). At the same time, samples of cold weapons of this age already have microdefects in the form of cleavage cracks and caverns. Therefore, their surface (if it has not been intensively cleaned) contains a significant number of compounds of eliminated chemical elements that have accumulated during the long history of their life. Moreover, the corresponding chemical elements – zinc, gold, and others – are contrasting in relation to iron, that is, they have much larger ion sizes.

For older cold weapons, manufactured 300 years ago or earlier, impurity ions are characteristic, the sizes of which are smaller than the sizes of trivalent iron ions, in particular silicon (Table 5). The absence of chemical elements with ionic radii significantly larger than the size of trivalent iron, as well as the presence of active elimination of silicon ions, is a sign of the manufacture of the object in the distant past.

The results of the research are important for the identification and authentication of historical iron cold weapons.

The study of artifacts of different ages allows us to divide the time of the manufacture of cold weapons into three periods. The first is a weapon manufactured within a period of up to 100 years. The second is a weapon manufactured within the framework of a two-hundred-year history. The third is a melee weapon made more than 300 years ago.

A limitation of this study may be that the tests were conducted on samples not older than 300 years.

The prospect of future research may be the use of more powerful equipment (industrial dryer and RFA) and the implementation of a larger number of surface rubs. This will make it possible to observe the process of elimination of impurity ions from the surface of historical cold weapons in dynamics.

In the case of using newer equipment, for example with a wave converter, the results will be even more thorough due to the potential possibility of determining the valence of the corresponding ions.

7. Conclusions

1. A model was built that explains the sequence of elimination of impurity ions from the near-surface parts of the metal when it is heated or during the long history of the object's existence. The model makes it possible to use parameter "*D*" – the ratio of the size of impurity ions to the size of the trivalent iron ion as a criterion for confirming the authenticity of a cold weapon. If there are impurity chemical elements on the surface of the metal, for which $D>0.3$, cold weapons should be classified as modern products, and if $D<0.3$ – as products manufactured in the past – the age of which exceeds 100 years.

2. With the help of the authors' methodology, a study of the chemical composition of the surface of collection samples of iron cold weapons of the 20^{th}, 19^{th}, and 18^{th} centuries was carried out. The results confirm that the rate of release of impurity chemical elements depends on their ionic sizes and, accordingly, on the level of deformation of the crystal lattices of iron in which they are located. Verification of the model on real objects of historical cold weapons made it possible to determine their age based on the criterion of the presence of relevant impurity chemical elements on its surface: with $D>0.3$, the weapon was assigned to modern and 20^{th} century; at $0.15<D<0.3$ – to the 19^{th} century; with $D<0.15$ – to the 19^{th} century.

Conflicts of interest

The authors declare that they have no conflicts of interest in relation to the current study, including financial, personal, authorship, or any other, that could affect the study and the results reported in this paper.

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Data availability

All data are available in the main text of the manuscript.

References

1. Kikuchi, N. (2020). Development and Prospects of Refining Techniques in Steelmaking Process. ISIJ International, 60 (12), 2731–2744. doi: https://doi.org/10.2355/isijinternational.isijint-2020-186
2. Palmer, P. Introduction to Energy-Dispersive X-ray Fluorescence (XRF) – an Analytical Chemistry Perspective. Available at: https://www.asdlib.org/onlineArticles/ecourseware/Palmer/ASDL%20Intro%20to%20XRF.pdf
3. Ashkenazi, D., Gitler, H., Stern, A., Tal, O. (2017). Metallurgical investigation on fourth century BCE silver jewellery of two hoards from Samaria. Scientific Reports, 7 (1). doi: https://doi.org/10.1038/srep40659
4. Mincu, V., Constantin, N. (2013). Refining Steels Produced in Electric Arc Furnace. U.P.B. Sci. Bull., Series B., 75 (2), 109–116. Available at: https://www.scientificbulletin.upb.ro/rev_docs_arhiva/full80c_761668.pdf
5. Mincu, V., Negru, M., Constantin, N. (2012). Increase the Ingots Quality Cast in Vacuum. Solid State Phenomena, 188, 339–345. doi: https://doi.org/10.4028/www.scientific.net/ssp.188.339
6. Guerra, M. F., Pagès-Camagna, S. (2019). On the way to the New Kingdom. Analytical study of Queen Ahhotep's gold jewellery (17th Dynasty of Egypt). Journal of Cultural Heritage, 36, 143–152. doi: https://doi.org/10.1016/j.culher.2018.09.004
7. Robbiola, L., Blengino, J.-M., Fiaud, C. (1998). Morphology and mechanisms of formation of natural patinas on archaeological Cu–Sn alloys. Corrosion Science, 40 (12), 2083–2111. doi: https://doi.org/10.1016/s0010-938x(98)00096-1
8. Scrivano, S., Gómez Tubío, B., Ortega-Feliu, I., Ager, F. J., Paul, A., Respaldiza, M. A. (2017). Compositional and microstructural study of joining methods in archaeological gold objects. X-Ray Spectrometry, 46 (2), 123–130. doi: https://doi.org/10.1002/xrs.2738
9. Merezhko, N., Vovk, Y., Indutnyi, V., Pirkovich, K., Davydiuk, V., Andreiev, O. (2021). Devising criteria for the authenticity of historical cold weapons based on X-ray fluorescence analysis of their surface. Eastern-European Journal of Enterprise Technologies, 6 (12 (114)), 6–11. doi: https://doi.org/10.15587/1729-4061.2021.247624
10. Indutnyi, V., Merezhko, N., Pirkovich, K. (2019). Studying the authenticity of the golden element from a Mongolian warrior's armor by physical-chemical methods. Eastern-European Journal of Enterprise Technologies, 1 (12 (97)), 34–40. doi: https://doi.org/10.15587/1729-4061.2019.157156
11. Vovk, Y., Merezhko, N., Indutnyi, V., Pirkovich, K., Lytvynenko, Y. (2022). Determining dangerous chemicals on the surface of metallic historical artefacts. Eastern-European Journal of Enterprise Technologies, 6 (12 (120)), 6–12. doi: https://doi.org/10.15587/1729-4061.2022.268175
12. Indutnyi, V., Merezhko, N., Pirkovich, K., Andreiev, O. (2021). Identification of patterns of crystal-chemical transformations in historical artifacts made of metals. Eastern-European Journal of Enterprise Technologies, 1 (12 (109)), 44–51. doi: https://doi.org/10.15587/1729-4061.2021.225418
13. Hlosariy terminiv z khimiyi (2008). Donetsk, 738. Available at: https://upload.wikimedia.org/wikipedia/commons/7/79/Opeida_Shvaika_Glossary_of_chemistry_terms.pdf
14. Periodychnist zminy radiusiv atomiv khimichnykh elementiv. Available at: https://www.miyklas.com.ua/p/himija/8-klas/periodichnii-zakon-i-budova-atomiv-39913/periodichna-tablitcia-i-zakonomirnosti-zmini-vlastivostei-khimichnikh-ele_-39922/re-5bfdbee7-e780-454c-ad37-358b9eec1426
15. Atomni ta yonni radiusy. Shchilna struktura atomnykh krystaliv. Available at: https://chemeducation.pnu.edu.ua/wp-content/uploads/sites/14/2020/02/Лекція_3_радіус.pdf