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DEVISING CRITERIA FOR THE AUTHENTICITY OF HISTORICAL COLD WEAPONS BASED ON X-RAY FLUORESCENCE ANALYSIS OF THEIR SURFACE

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This paper reports the results of studying the chemical composition of the surface of 4 objects of cold weapons of the 19th and early 20th centuries, made of iron – bayonet knives and sabers. This makes it possible to establish the signs of authenticity of cold weapon samples made of iron in that chronological period.

An authentic procedure has been proposed for examining the chemical composition of the surface of historical objects of cold weapons by rubbing the samples with cotton wool swabs and their subsequent investigation. This makes it possible to explore objects of cold weapons, whose size is large, as well as simplify the very procedure for studying objects of historical and cultural value.

Using the X-ray fluorescent chemical analyzer Expert Mobile, chemical elements were found at the surface of samples of cold weapons made of iron. The presence of such elements is the result of the process of re-crystallization and self-purification of metal during a long history of its life. Elements found in almost every rubbing sample were identified: calcium, ferrum, zinc, cuprum, and chlorine.

The studies of cold weapons samples testify to the heterogeneity of the composition of patina formations on their surface, which confirms the authenticity of ancient objects. In addition, the studies have shown a difference in the chemical composition of surface layers of different parts of individual samples of antique cold weapons, which may indicate different times or different technology for their manufacture.

The fluorescence spectra of the obtained rubbing of individual samples of cold weapons were compared with "pure" material, which made it possible to identify elements removed from the surface of objects. The study results are important indicators to confirm the authenticity of cultural monuments and the technology of their manufacture in the past

Keywords: cold weapons, metal affinity, metal crystallization, impurity chemical elements, X-ray fluorescence analysis

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1. Introduction

Fundamental research in the field of materials science, carried out during the last century, allows us to assert that the physicochemical properties of metals and their alloys have been fully studied. Relevant knowledge contributes to the active development of modern technologies and is now widely used to solve numerous practical tasks [1]. It should be noted that at that time special attention was paid to devising the technologies for metal refining – methods for obtaining pure and ultra-pure metals, which are devoid of the content of chemical and mechanical impurities. At the same time, the leading role in the development of such technologies belonged to the results of experimental studies on the recrystallization of metals. The energy of the metal crystalline lattice during the growth time of crystals contributes to pushing out (into thermal solutions or melts) of impurity chemical elements, causing deep purification of the crystalline phase of the metal. These technologies involve melting with the gradual cooling of the melt at temperatures close to eutectics. This makes it possible to indirectly control the growth rate of pure metal crystals, as well as the transition of impurity elements to a melt or solution with their subsequent elimination.

It is worth noting that such processes of metal refining also occur in a solid state at low temperatures close to ambient [2, 3]. However, in that case, they proceed very slowly – for hundreds, and sometimes thousands of years.

This circumstance makes it possible to formulate several important scientific hypotheses for expert activities regarding the possibility of using the results of studying the chemical composition of the surface of cultural monuments made of metals. The main goal is to establish authenticity – determining the age, identifying traces of interference with restoration work, diagnosing the traces of applying certain ancient processing technologies.

In the work of an expert of cultural values, this information is extremely important; mathematical models are also important as they make it possible to define chronometric parameters. Therefore, it is a relevant task to devise criteria for the authenticity of historical artifacts made from metals based on the study of the chemical composition of the surface.

2. Literature review and problem statement

There are many fundamental studies that consider metallurgical processes. Thus, paper [4] analyzed the development of refining technologies in the steel production process over the past 60 years and their prospects for the future, with the aim of reducing the cost of processing and improving the quality of steel.

In paper [5], the authors give the characteristics and properties of cast and forged steel articles, which can be dangerous if there are impurity elements in their composition that radically reduce quality. In order to reduce the content of impurity elements that can affect the properties of the product, several methods of refining molten metal have been developed.

However, historical and cultural items made from metals differ from modern objects in the peculiarities of manufacturing technology, which causes the release of various chemical elements on their surface over time.

Studies of the chemical composition and microstructure of cultural values made of various metals were carried out. In particular, the study of the natural patina on the surface of bronze artifacts [6] is important; the classification and characteristics of patina structures for a deeper understanding of the mechanism of their formation are given.

Work [2] reports a study of the chemical composition and microstructure of the golden object of the XIV–XV centuries that identified signs of its authenticity. Determining patterns of crystal-chemical transformations in the artifacts of history made from metals [3] was also considered but the samples of cold weapons were not studied in the cited paper.

The compositional and microstructural studies of connecting methods in archaeological gold objects of the pre-Rome era were reported in [7]; analytical methods were used in order to characterize them at both the compositional and microstructural levels (SEM-EDS, metallography, μ-XRF, and μ-PIXE).

Egypt's ancient gold jewelry was investigated by X-ray fluorescent analysis in [8]; gold jewelry dating back to the 17^{th} century was also studied.

In addition to gold, silver jewelry that had direct contact with the human body [10] was also investigated by X-ray fluorescent analysis. In the cited study, a nondestructive method of sample removal was used.

However, historical items of cold weapons made of iron are distinguished by the peculiarities of crystal-chemical transformation, so they require in-depth study.

3. The aim and objectives of the study

The purpose of this study is to devise criteria for the authenticity of historical cold weapons made of iron, based on the X-ray fluorescence analysis of surface examination. This would make it possible to establish authenticity and identify historical cold weapons. Thus, expert activity on the assessment of historical cold weapons could be unified.

To accomplish the aim, the following tasks have been set:

– to prepare samples and conduct a study of the chemical composition of ash obtained by rubbing the samples of cold weapons;

– to analyze the chemical composition of rubbing samples of cold weapons without burning them.

4. The study materials and methods

Our authentic research methodology implies that the metal surface of the examined sample was rubbed with a cotton wool swab at its different points (a blade, guards, handles, scabbard and metal trim, if available). Rubbing was carried out by two or three point frictions, with a movement diameter of up to 1 cm, as a result of which separate chemical compounds remained on the cotton swabs. Such elements at their time were eliminated from the primary alloy and could not be brought from the external environment. To improve the reliability of our experiment, up to 20 consecutive rubbing operations were performed on the surface of each object. Cotton swabs were burned with the resulting ash examined by the XFA method (X-ray fluorescent analysis). The XFA method is based on the acquisition and subsequent analysis of the spectrum arising from the irradiation of the examined material by X-rays.

Fluorescence spectra were acquired at the X-ray fluorescence spectrometer (analyzer) Expert Mobile (manufactured by TOV INAM, Kyiv). The device is equipped with an X-ray tube with the parameters of direction/current of 50 kV/0.1 mA; the anode is titanium. The energy detector of photons of the fluorescent (secondary) reflection from the image is SDD, which makes it possible to analyze the range elements from element 12 of the periodic table, magnesium, to element 92, uranium.

X-ray spectra of fluorescence (the spectra of energies of photons), which are obtained as a result of the measurement of samples, are processed using the software for the Expert Mobile spectrometer. Preliminary calibration of the scale of energies (*X*-axis) of X-ray spectra allows for mutual comparison by normalizing based on the background intensity (diffused radiation). Thus, we detect the elemental composition of the rubbing material, excluding the elemental composition of the "pure sample" (cotton swab).

5. Results of studying the chemical composition of the surface of historical cold weapons

5. 1. Results of studying the chemical composition of the ash obtained by rubbing the samples of cold weapons

The presence of the results of natural recrystallization processes can be objectively observed when experimentally studying the chemical composition of the surfaces of metal cultural monuments that were made in the distant past [3, 11].

Thus, repeatedly, there were studies into the chemical composition of iron archaeological sites (Fig. 1), as well as the chemical composition of hydroxides on their surfaces with the help of X-ray fluorescent analyzers. In addition, when studying samples of the corresponding metal with the help of an electron microscope, ultra-pure iron was found in the complete absence of impurities characteristic of iron ores – manganese, chromium, sulfur, and other chemical elements.

It should also be noted that certain chemical elements such as manganese, chromium, and nickel can, under certain conditions, enter the crystalline lattices of iron. While others – potassium, magnesium, aluminum, zinc, lead, and others – can be present only in the composition of microscopic mineral impurities, mainly sulfides and oxides.

Fig. 1. A small Scythian sword found in the northern Black Sea region, with a gold handle and a scabbard (absolutely pure iron) (a private collection)

It should also be noted that the results of such studies are almost not published but the relevant data are widely represented in analytical reports of cultural values experts. However, the experts' reports provide no explanation for the nature of the relevant phenomena that lead to the self-refining of metals. Instead, sometimes there are unreasonable judgments about the presence of special technologies for smelting metals in distant historical times or even the cosmic origin of the relevant artifacts.

The experimental study, the results of which were reported earlier [1, 3], makes it possible to draw the following conclusion. History artifacts that have survived under the conditions of burial and are known as archaeological finds have an extremely high rate of variability in the content of chemical elements in the results of measurement on different surface areas. This is understandable because their surface was in a state of chemical interaction with the environment, and its chemical composition changed significantly. Some elements inherent in metal alloys formed easily soluble compounds and were removed, while others that were in the environment, forming insoluble compounds, remained on the surface. In addition, gradual natural recrystallization contributed to the elimination of individual chemical elements from the composition of the metal to its surface, where there was also a further process of chemical interaction and transfer. It is this feature that is the subject of our special attention.

Authors drew attention to the possibility of taking harmful substances to the surface of metals, which makes up-to-date research in the field of safety of work with history artifacts [1].

So, the chemical composition of the metal surface is investigated, as well as the chemical composition in its deeper parts with the help of an X-ray fluorescent analyzer (at a depth of 3–5 nanometers). For example, within the modern scratch and at the depth under study of 3–5 nanometers, we would observe a significant difference in the chemical composition. This difference would depend on the degree of chemical differentiation of metal on the surface and the resolution of the device [3].

If we are talking about the study of iron articles, then, to confirm their authenticity, it is advisable to investigate the composition of the impurities on their surface and in deeper parts of the metal. Such studies were carried out with the involvement of cold weapons samples stored in the funds of the National Military History Museum of Ukraine.

Indicators determined during the study accurately indicate the use of certain metal processing technologies and features of the manufacture of objects in the past. They also show chemical and physicochemical changes in the structure of samples due to long-term interaction with the environment, the destructive effects of the acidic environment of the soil, and restoration work during recovery and storage.

The results of study [2, 3] indicate the possibility of detecting traces of mass transfer (diffusion) processes. Diffusion implies gradual adaptive changes in the chemical composition and structure of the metal by mutual penetration of molecules or metal atoms the molecules or atoms of an iron alloy over a long time of iron objects existence.

To confirm the scientific hypotheses described above, four samples of cold weapons were chosen. The results of point samples and detected elements are given in Table 1.

The results of studying the chemical composition of the metal surface of the selected samples of cold weapons, given in Table 1, demonstrate a high level of variability in the sets of the detected chemical elements and intensity of the corresponding lines on fluorescence spectra.

According to Table 1, we can pay attention to the fact that some of the chemical elements occur more often than others. For example, calcium, ferrum, zinc, cuprum, and chlorine are found in almost every rubbing sample. And nickel was discovered only once in the rubbing from sample No. 3 (Russian officer's cavalry saber, sample of 1827/1909) and sample No. 4 (Polish saber with the image of the coat of arms "chase" copy of the twentieth century).

The element plumbum was discovered in the rubbing from sample No. 2 (Spanish bayonet knife, a sample of 1913, to the Mauser rifle, 1893/1916 in leather scabbard), and sample No. 4 (Polish saber with the image of the coat of arms "chase" copy of the twentieth century).

Manganese was found in two samples of bayonet knives dating back to the early twentieth century.

Such heterogeneity is direct evidence of the course of the processes of elimination of impurity chemical elements on the metal surface with the formation of areas covered with ultra-thin hydroxide films. On the surface of metal objects made recently, such high discrepancies in the chemical composition are not observed. Therefore, this feature can be used as a criterion for the authenticity of antique and museum samples of cold weapons. In addition, indicator chemical elements that may indicate the age of artifacts are the chemical elements that are isomorphic in the crystalline lattice of iron – manganese, chromium, nickel, and, possibly, silicon and cobalt.

Particular attention should be paid to the results of analytical studies, where the absence of iron is registered. There are two explanations for this phenomenon.

Table 1

Results of examining cold weapons samples from the National Military History Museum

No.	Description and photo of the item	Sample	Cl	P	Ca	Fe	Cu	Zn	K	Ti	Mn	Pb	Ni
1	German bayonet knife sample 1883/98 New type (1933–1945) to the rifle 98K No. 4267R 	1(No. 7) blade	+	+	+	+	+	+	+	+	–	–	–
		2(No. 8) blade	+	–	+	+	+	+	–	+	+	–	–
		3(No. 16) scabbard	+	–	+	+	+	+	+	+	+	–	–
2	Spanish bayonet knife sample 1913 to the Mauser rifle 1893/1916 in leather scabbard No. 70287 	1(No. 1) blade	+	+	+	+	+	+	+	+	+	+	–
		2(No. 3) blade	+	–	+			+	+	+	+	–	–
		3(No. 7) blade	+	–	+	+		+	–	–	–	–	–
3	Russian officer's cavalry saber sample 1827/1909 (no scabbard) 	1(No. 1) blade	–	–	–	–	–	–	–	–	–	–	–
		2(No. 2) blade	–	–	+	+	–	–	–	+	–	–	–
		3(No. 13) blade	–	–	+	+	+	+	+	+	–	–	+
		4(No. 14) blade	–	–	+	+	–	–	–	+	–	–	–
		5(No. 17) handle	–	–	+	+	+	+	+	+	–	–	–
		6(No. 18) handle	–	–	+	+	+	+	–	+	–	–	–
4	Polish saber with the image of the coat of arms "chase" copy of the twentieth century (no scabbard) 	1(No. 1) blade	–	–	+	+	+	+	–	+	–	–	–
		2(No. 2) blade	–	–	+	+	+	+	–	+	–	–	–
		3(No. 6) blade	-	–	+	+		+		+	–	–	–
		4(No. 7) blade (decoration)	-	–	+	+		+		+	–	–	–
		5(No. 11) guard	–	+	+	+	+	+	+	+	–	+	+

The first is the presence of ultra-thin hydroxide films on the surface, in which those chemical elements that have only recently been eliminated from the alloy are concentrated from ultra-small mineral impurities (calcium, potassium, chlorine, phosphorus, copper, zinc). However, iron is a newly formed and well-crystallized substance.

The second is the treatment of the surface with preserving substances in order to remove iron hydroxides.

Thus, observing the peculiarities of sets and the content of chemicals at the surface of iron artifacts, we receive answers to the questions posed in this article about their authenticity and the presence of traces of restoration intervention. It is also possible to conduct refining experiments that would theoretically substantiate the observed features of the chemical composition of the surface.

5. 2. Results of studying the chemical composition of rubbing from the samples of cold weapons without burning them

Of interest for the practical examination of authenticity are the results of studying individual parts of cold weapons. Differences in the chemical composition on different parts of an artifact may indicate different times or different technology for their manufacture. Thus, using an example of sample No. 3 (Russian cavalry officer saber) (Fig. 2), one can see that some elements, such as nickel and potassium, are found in single samples of rubbing.

It is worth noting that chemical elements on different parts of the same sample tend to coincide. Thus, using an example of sample Number 3, we can see that elements such as calcium, iron, and titanium are observed both on blade samples and on the rubbing from the saber handle.

The results of studying the chemical composition of rubbing from 4 cold weapons samples confirm the hypothesis about a different course of the processes of elimination of impurity chemical elements at the metal surface of various parts of antique cold weapons made of metal. Thus, we can conclude that there is a well-formed layer of patina, in which chemical elements are present, eliminated not only from the crystal lattice of iron crystals but also from microscopic mineral particles. The presence of these mineral particles shows the level of metal purity at the time of the creation of the artifact and is also valuable expert information.

Visually, the above-described results of studying the concentration of impurity chemical elements on the surface, as well as the presence of the reported elements, can be seen on the spectrum of fluorescence (Fig. 3).

The comparison of two measurements of cotton wool "with rubbing" from sample No. 2, taken from the saber blade (contour spectrum) and "pure sample" No. 1 (cotton swab), in the form of a solid painted spectrum, indicates that the rubbing material includes titanium and iron. This was taken from the saber blade of a Russian officer.

Iron and titanium are indicator chemical elements that may indicate the age of the saber under study, as well as become an indicator of the authenticity of the sample.

Thus, when storing metal objects, there are gradual adaptive changes in the chemical composition and structure over a long time of exhibiting and storage in the museum funds.

Fig. 2. Russian officer's cavalry saber, sample 1827/1909 (without scabbard) from the archives of the Fund of the National Military History Museum of Ukraine

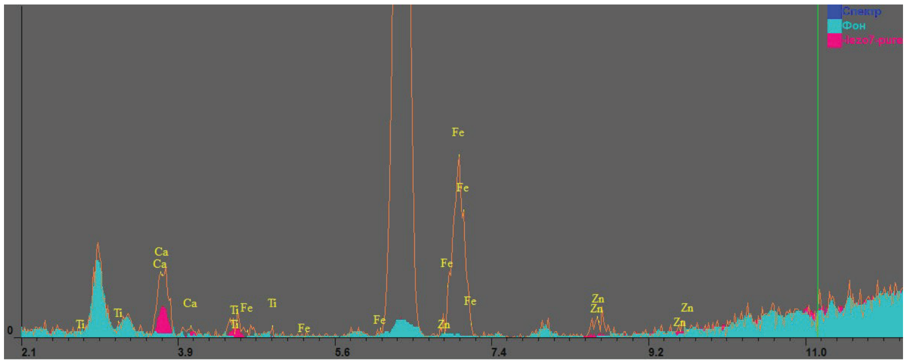

Fig. 5. The spectrum from the rubbing of sample No. 3 "Polish saber with the image of the coat of arms "chase", sample No. 7

Due to the long-term storage of cold weapons and interaction with them, the surfaces of samples host the new easily soluble compounds that cannot always be safe for humans. The impurity elements that were found on the surface of the sample are confirmation that complex processes of differentiation of substances and their recrystallization are under way. It is this process that leads to pushing out the impurity chemical elements from the balanced structures of the crystalline lattices of metal. These elements accumulate in the intracrystalline space, interact with the environment, form various chemical compounds, and accumulate on the surface of metal artifacts in the form of patina minerals.

Consequently, our study confirms that the main signs for the construction of unambiguous statements regarding the authenticity of historical artifacts may be the XFA of samples taken by using a method that does not destroy the surface.

To confirm the hypothesis described in this paper, consider the fluorescence of the spectrum using an example of sample No. 4 "Polish saber with the image of the coat of arms "chase" (Fig. 4 – sample image, Fig. 5 – its fluorescence spectrum).

Fig. 5 shows that the comparison of two measurements of the cotton swab "with rubbing" (contour spectrum) and "pure" cotton swab (solid painted spectrum) indicates that the material of "rubbing" includes iron, calcium, zinc, titanium.

The impurity elements that were found on the surface of the sample can be identified as the confirmation of the process of mass exchange of substances on the surface.

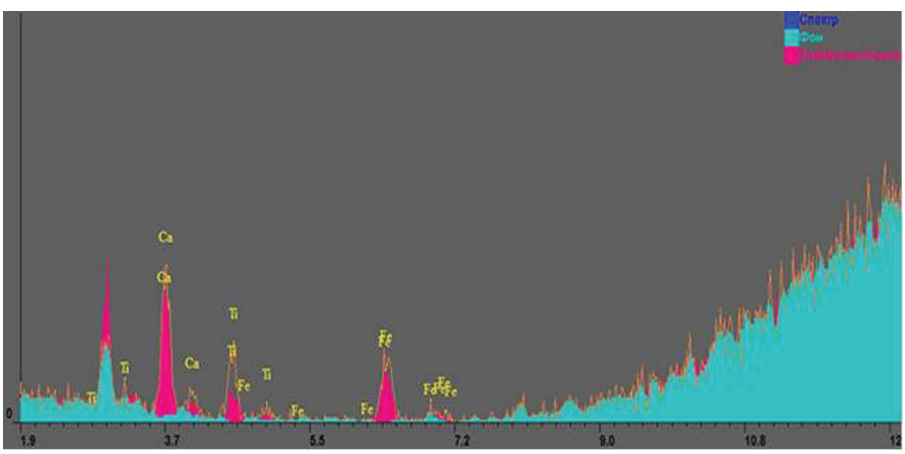

Fig. 3. The spectrum of the examined rubbing from sample No. 3 "Russian officer's cavalry saber", sample No. 2

Fig. 4. Polish saber with the image of the coat of arms "chase" copy of the twentieth century (without scabbard) from the archives of the National Military History Museum of Ukraine

The described process led to pushing out the impurity chemical elements of iron, calcium, zinc, and titanium from the crystalline lattices of metal.

On the surface of metals, the ions of those chemical elements that have dimensions much larger or smaller than the size of iron ions that make up the crystal lattices are concentrated. The ions of chemical elements smaller than iron are less intensively released from the metal. Chemical elements are also concentrated on the surface of iron products.

Thus, historical and cultural monuments have a special property – to be constantly covered with new mineral layers with slight changes in the temperature and humidity in storage areas.

6. Discussion of results of studying the chemical composition of the surface of historical cold weapons

The results of our research, given in Table 1 (ash investigation) and illustrated in Fig. 3, 5 (studies of rubbing without incineration), convincingly indicate the progress of crystal-chemical transformations in the objects of historical cold weapons, occurring during their long-term storage.

The study reported here (Table 1) may also indicate that harmful substances cannot be completely removed from the surface of artifacts because most of them are in the microcrack system and are inaccessible for mechanical treatment [12].

Thus, the hypothesis is confirmed that patina crusts are a source of information about impurities that were inherent in metals at the time of their manufacture, made from ferrous metals in particular.

Note that the study of samples of cold weapons made from metals was carried out by point-rubbing the surfaces with cotton wool swabs, followed by examination using X-ray fluorescent analysis. This method of obtaining rubbing from the surface does not destroy or damage objects of cold weapons that have historical and cultural value.

However, this method is not ideal because cotton wool also contains residues of chemical elements that require the processing of the resulting spectra.

Unlike work [3], where the metal surface was mainly carried out using raster electron microscopy and X-ray spectral microprobe analysis, only the X-ray fluorescent research method was used in this paper. This method does not make it possible to detect carbon residues but we understand that the different carbon content in the composition affects the purity of the metal of the studied cold weapons samples.

The total amount of impurities on the surface of metal artifacts of history cannot be a sign of authenticity but the content of individual complexes of ions in a proportion corresponding to the idea of the speed of their release from metal is an important diagnostic feature.

This makes it possible to establish authenticity and identify historical cold weapons. Thus, expert activity on the assessment of historical cold weapons can be unified.

In-depth study of the processes of "natural recrystallization" [1] of metals in the artifacts of history and the construction of relevant models to explain their nature is an important and relevant scientific and applied task in the modern expert field. It is planned to conduct further research into the chemical composition and microstructure of history artifacts made from metals at different times.

7. Conclusions

1. We have tested our authentic procedure for studying the chemical composition of the surface of historical objects of cold weapons by rubbing the samples with cotton wool swabs and their subsequent examination. This makes it possible to explore the surface layer of cold weapon objects, which are often larger than a working chamber of the X-ray fluorescent analyzer. In addition, this technique simplifies the research procedure itself since it is not necessary to deliver objects of historical and cultural value to a specialized laboratory.

Our study of cold weapons samples testifies to the heterogeneity of the composition of patina formations on their surface, which confirms the authenticity of ancient objects. Elements found in almost every rubbing sample were identified: calcium, ferrum, zinc, cuprum, and chlorine. In addition, the study has revealed a difference in the chemical composition of surface layers of different parts of individual samples of antique cold weapons, which may indicate different times or different technology for their manufacture.

2. We have compared fluorescence spectra from rubbing the individual samples of cold weapons with "pure" material, which made it possible to identify elements removed from the surface of objects: iron, calcium, zinc, titanium. This makes it possible to more accurately determine the chemical composition of the patina of historical items of cold weapons.

Thus, the study reported here confirms the possibility of using X-ray fluorescent analysis to draw conclusions on the authenticity of artifacts made of iron and other metals, as well as, after additional research, to build mathematical models for predicting their age.

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