Most substances change their chemical composition and structure over time, as well as enter the chemical interaction with the environment. This, of course, applies to alloys of gold, which gradually recrystallize, decompose into different phases and push out impurity elements from their own crystalline lattices [1]. Under normal atmospheric pressure and temperatures, due to climatic factors, this process takes place over the millennia. That is why the detection of attributes of its course is important as they serve the indicators for proving the authenticity of ancient history artifacts, for example.
examining their age, as well as when discovering the traces of later restoration works at their surface.

Diagnosing the natural transformations of the structure and composition of gold alloys is easier with the help of classical methods of metallographic research [2, 3] and, especially with the use of an electron microscope. Under an electron microscope, various substances are well recognized with a possibility for chemical analysis of their content. At the same time, it should be noted that studying historical artifacts has its own characteristics, which are not described in classic works. Particularly, in the study of historical artifacts, there are secondary mineral formations at the surface, related to chemical elements, eliminated from alloys, and converted into new compounds as a result of interaction with the environment. We also register a special structure of the recrystallized metal, which reflects the nature of the spatial distribution of initial mechanically stressed areas, created as a result of applying certain machining techniques that had existed in the past.

Considering the importance of establishing the historical authenticity of historical items made of gold during their identification, it is a relevant task to undertake a research aimed at revealing and substantiating the signs of authenticity in the items dated to various historical periods.

## 2. Literature review and problem statement

In recent years, many studies have been conducted into historical artifacts, but only few analytical results have been published. Scientists undertake research into historical items made from various materials. Thus, papers [4, 5] analyzed the chemical composition and microstructure of ancient silver jewelry made in the bronze and iron days of human history that were found in Israel. Therefore, the issues on the chemical composition and microstructure of golden historical items remain unresolved.

Separate groups of scientists conducted a study into gold jewelry from VIII–VI centuries BC from treasures found at the territory of Italy [6], Spain [7], Cyprus [8], as well as Egyptian ornaments of XIX–XIII centuries BC [9]. They paid special attention to studying the chemical composition of small elements of gold jewelry and their attachment areas to establish the method for manufacturing these objects. However, there is also a necessity to study historical items made of gold, manufactured over other historical periods.

Paper [10] provides an example of the identification of glass mosaics dated to I–IX centuries by determining the chemical composition of golden foil used as a base.

Moreover, scientists discovered several counterfeit objects at the National Museum of Archeology of Florence using the organoleptic and physical-chemical methods [11]. We may note that the study into the chemical composition of alloys at the surface failed to explicitly answer the question on the object authenticity.

Paper [12] presents theoretical information on metallography, as well as gives many examples of studies into the microstructure of historical items made from various metals. Despite the practical significance of such results, the information base of analytical research on cultural property needs further expansion.

Work [13] presents results of a study into the microstructure of jewelry items made from silver from various chronological periods and experimentally confirms the diversity of the antique alloy structure. More reliable research results are given in [14], which describes the main chemical and structural features of the natural redistribution process of matter. In addition, the authors studied the traces of recrystallization of metals in historical items made of gold, silver, copper, iron from various historical periods. However, cultural values from other historical periods have not been considered, which necessitates a further research in this area.

## 3. The aim and objects of the study

The aim of this work is to present and describe the main features of the gold artifacts authenticity, examined using an electron microscope and an X-ray fluorescence analyzer, as an example of the historical artifact of the XIV–XV centuries. The object of research is the golden element of the Mongolian warrior’s armor.

To achieve this goal, the following tasks were solved:
- to study the microstructure of the Mongolian warrior’s armor golden element at different magnifications and to identify signs of its authenticity;
- to investigate the chemical composition of the golden element of the Mongolian warrior’s armor at the surface and in places of current scratches and to establish the signs of its authenticity.

## 4. Materials and methods to study the authenticity of the golden element of the Mongolian warrior’s armor

An analytical study into the metal surface (gold) was performed by means of a raster electron microscopy and an X-ray spectral microprobe analysis; X-ray fluorescence chemical analyses were carried out separately for the examined metal particles.

For research, we used the raster electron microscope-microanalyzer (REMMA-202, Ukraine) with a large vacuum research chamber, equipped with an energy-spin spectrometer. Microanalysis was performed on elements from 11 Na to 92 U. The method of quantitative calculation is based on standardization using the samples of pure metals Ag, Au, Cu, and others, as well as correction of spectral intensity lines of elements using the ZAF-correction method. The limit of reliable detection of the chemical elements content is up to 0.5 %. The spatial detail (location) of the analyses is 5–10 microns. Digital images of the metal surface were obtained from secondary electrons.

The chemical composition study was performed using the X-ray fluorescence analyzer (ElvaX, Ukraine). Under this method, we determined elements from 11 Na to 92 U with an error not exceeding ±0.05 %. The Elvatech MCA Software was used to control the work of the spectrometer.

## 5. Results of studying the golden element of the Mongolian warrior’s armor’s authenticity

### 5.1. Results of microstructure study into the golden element of the Mongolian warrior’s armor

To determine the sequence of further research, consider Fig. 1 that shows the most important expert signs for the golden alloys schematically. These signs include: superficial cracking, the presence of secondary mineral deposits (pati-
na), the appearance of secondary emissions of the chemical evolution traces and the presence of mineral formations brought from the environment.

The investigated decoration has a loop at the back of the device, which suggests that it was attached to protective clothing (chain mail). Note the transient damage that may have occurred due to the impact of a weapon.

The study was conducted at different parts of the surface, including the areas of mechanical damage. Fig. 3 shows a fragment of the golden disk surface in the zone of mechanical damage. The metal exhibits considerable brittleness and almost no bending deformation. There are well noticeable features of the relief on the metal edges, which indicate a loss of plasticity.

Surface areas shown in Fig. 3, under an electron microscope, even at small magnification (100–350 times), show a system of cracks with triple points characteristic of ancient metals (Fig. 4) – spatial locations of three crystals. Fig. 4 also shows a trace of a modern scratch that extends from the right angle of the upper left quadrant of the image to the lower left quadrant. Within this scratch, we will conduct a study of the chemical composition of the gold alloy (point 29 in Fig. 4).

The metal structure, which is observed under an electron microscope, even at small magnifications (150 times), explains the high fragility of the gold alloy, as well as the presence of small silicon concentrations. We have detected silicon compounds in the study of object fragments by X-ray fluorescence analysis. The electronic photo image also visualizes all the features of the chemical impurity distribution in accordance with the general scheme shown previously in...
In addition, we can see special roughness of the metal surface, the traces of tools used for its cleaning, as well as individual cavities, formed as a result of the extraction of foreign impurity minerals present in the poorly refined alloy.

We paid special attention to studying the old golden objects using an electron microscope into the structure of the metal, which can most easily be explored at a fracture. Thus, Fig. 5 shows an electronic image of the edge of a fresh breakage, which is made using an electron microscope also at low magnification (200 times). It is well known that the points “9” and “10” made it possible to investigate the chemical composition of the gold alloy in the deeper parts of the item. It is obvious that the chemical composition of the metal in these areas will correspond to the original chemical composition of the metal from which the item was made.

At magnification of the electronic image of the surface up to 2,000 times, we observe extremely complex morphology of the metal, which can most easily be explored at a fracture. Note: color indicates the results of studying the chemical composition research within modern scratches, where the metal detects the primary chemical glass.

By analyzing Table 1, we also notice that in the deepened parts of the metal, where the concentration of gold is much smaller, the concentrations of silver are elevated. That relates to the fact that the silver compounds are more soluble in the range of 81–98 %.

Table 1

| Test point trial number | Fe  | Cu  | Ag  | Au  | Sum |
|-------------------------|-----|-----|-----|-----|-----|
| 1                       | 0.59| 0.7 | 4.48| 94.23| 100 |
| 2                       | 0.51| 0.72| 13.08| 85.69| 100 |
| 3                       | –   | 0.76| 7.26| 91.98| 100 |
| 4                       | 0.57| 0.88| 11.52| 87.03| 100 |
| 5                       | 0.49| 1.46| 2.64| 95.41| 100 |
| 6                       | 0.49| 0.45| 0.71| 98.35| 100 |
| 7                       | –   | 0.47| 2.14| 97.39| 100 |
| 8                       | 0.37| 1.17| 5.47| 92.99| 100 |
| 9                       | –   | 0.99| 34.69| 64.32| 100 |
| 10                      | 0.52| 1.11| 35.76| 62.61| 100 |
| 11                      | 0.39| 0.72| 4.88| 93.81| 100 |
| 12                      | –   | 0.98| 12.55| 86.47| 100 |
| 13                      | 1.51| 1.65| 26.52| 70.32| 100 |
| 14                      | 0.93| 1.55| 18.79| 78.73| 100 |
| 15                      | –   | 1.54| 14.22| 84.24| 100 |
| 16                      | 0.72| 2.13| 20.09| 77.06| 100 |
| 17                      | 0.39| 1.14| 16.95| 81.52| 100 |
| 18                      | 1.44| 1.58| 26.43| 70.55| 100 |
| 19                      | 3.36| 1.32| 21.98| 73.34| 100 |
| 20                      | 0.76| 1.95| 14.38| 82.91| 100 |
| 21                      | –   | 2.07| 6.29| 91.64| 100 |
| 22                      | 1.4 | 1.21| 28.05| 69.34| 100 |
| 23                      | 1.33| 2.44| 18.53| 77.7 | 100 |
| 24                      | 0.32| 0.31| 5.85| 93.52| 100 |
| 25                      | –   | 0.72| 2.05| 97.23| 100 |
| 26                      | 0.36| 4.21| 34.83| 60.6 | 100 |
| 27                      | 0.49| 0.23| 2.13| 97.15| 100 |
| 28                      | 0.43| 0.68| 7.01| 91.88| 100 |
| 29                      | 0.23| 0.91| 17.95| 80.91| 100 |
| 30                      | 1.21| 0.29| 18.87| 79.63| 100 |

Note: color indicates the results of studying the chemical composition of the golden element of the Mongolian warrior’s armor

By measuring the content of gold and other elements in the deepened parts of the surface formed by scratches at different parts of the surface of the object (points 9, 10, 13, 14, 16, 18, 22, 26, as well as point 29 in Fig. 4 and in Table 1), we are convinced that the deeper parts of the alloy contain only 62–80 % gold. Alloys at the surface (points 1–8, 11, 12, 15, 17, 19–21, 23–25, 27, 28, 30 in Table 1) contain gold in the range of 81–98 %.
chemically active and brought out from the surface under the influence of external factors.

In connection with the standardization of the concentrations sum of chemical elements at the level of one hundred percent (Table 1), the content of all chemical elements is partially relative. Therefore, we obtain the criterion value for the concentration ratio, however, we can also judge the absolute indexes of the content of the corresponding chemical elements by studying the spectra (Fig. 7, 8).

Differences in the chemical composition are also clearly visible on emission spectra (Fig. 7, 8). Particularly, point “1” according to the chemical composition corresponds to the substance (gold alloy) at the authentic metal surface (spectrum in Fig. 7), and point “10” (spectrum in Fig. 8) corresponds to the composition at a small depth below the surface. The difference in the concentrations of gold and silver at the surface and “under the surface” sometimes reaches 20%, which indicates the ancient origin of an object.

The emission spectrum (Fig. 9) presents the results of the study of the chemical composition of mineral formations on the metal surface, which coincide with the results of studies of individual particles of the object, using X-ray fluorescence analysis.

![Fig. 7. Emission spectrum obtained from studying the chemical composition of the metal at point “1”](image1)

![Fig. 8. Emission spectrum obtained from studying the chemical composition of the metal at point “10”](image2)

![Fig. 9. Emission spectrum of mineral formations at the surface](image3)
The emission spectrum of these formations indicates that it is a mixture of hydroxides Si, Al, and Fe, that is, opal – SiO$_2$-H$_2$O, boehmite – AlOOH, and goethite – FeOOH.

6. Discussion of results of studying the authenticity of the Mongolian warrior’s arm golden element

Investigation of the microstructure of the golden element of the Mongolian warrior’s armor shows that its surface has acquired a specific roughness, which is a distinct sign of authenticity. The roughness is formed due to the processes of dissolution of the metal and the formation of micro-dislocations at its surface, caused by the dissolution of the alloy in the process of recrystallization. In the study of the fragment of the object’s surface in the zone of mechanical damage, we found significant fragility, which is characteristic only for metals recrystallized by natural way.

The cavernous character of the fracture shows the plasticity of the already recrystallized metal within individual crystals and the high degree of deformability of the metal at the time of manufacturing the product. This conclusion is also confirmed separately by the results of observation of a large number of dislocations of impurities and traces of metal flow on the surface. These structural features of a metal structure are inherent only to objects made by forging.

The complex of the above-mentioned features makes it possible for us to conclude that the object is authentic.

The study into the chemical composition of the gold object in the places of modern scratches showed that the deeper parts of the metal partially retained their chemical composition with a content of gold of only 62–80 %, and the alloy on the surface approximated by the natural way, and thus the content of gold in it was 81–98 %.

In modern scratches, the gold alloy contains a higher concentration of Ag and Cu than that at the surface. This can be explained by the fact that in the process of natural recrystallization of the metal that has been going on for many centuries, a metallic alloy pushed a significant amount of chemical impurities on the surface. Hence there were mineral formations that were remained (after mechanical cleaning of the surface). The remaining impurities, forming soluble salts, were removed into the environment. Thus, the authenticity of an object is also confirmed by the ratio of the concentrations of silver on its surface and in the deepened areas.

Copper and iron concentrations can also serve as indicators of natural aging of the alloy, however, due to their low concentrations, which are often commensurate with the error in determining their content, conclusions are not sufficiently substantiated.

We should also note that the most active of the alloy is the removal of silver, less active copper. Iron accumulates in cracks in the form of hydroxides (goethite). It also indicates the natural differentiation of substances in ancient alloys, as well as suggests that the primary composition of the gold alloy corresponds to the ratio of chemical elements observed at points 9, 10 and 26 (Table 1).

The observed phenomenon of differentiation of chemical composition of metals proves the authenticity of archaeological sites.

7. Conclusions

1. Taking into consideration the results obtained during the investigation of the chemical composition and microstructure of the golden element of the Mongol warrior’s XIV–XV centuries armor, we conclude that the subject is authentic and there are no traces of its restoration. This item should be considered fully authentic and considered to be rare and valuable for museum collections and private collectors as an example of historical objects – artifacts of ancient history.

2. In addition, we proved the high efficiency of using electronic microscopy in the tasks on confirming the authenticity of ancient historical artifacts. All the described features of recrystallization and differentiation of matter in the alloy are not inherent to modern products or products manufactured in the near past.

References

1. Indutniy V. V. Otsinka kulturnyk tsinnosti. Kyiv: KNTEU, 2016. 880 p.
2. Livshic B. G. Metallografiya. Moscow: Metallurgiya, 1990. 236 p.
3. Bolhovitinov N. F., Bolhovitinov E. N. Atlas makro- i mikrostruktur metallov i splavov. Moscow: Mashgiz, 1959. 88 p.
4. Shalev S., Shechtmann D., Shihstein S. S. A study of the composition and microstructure of silver hoards from Tel Beth-Shean, Tel Dor, and Tel Misne, Israel // Archaeological and Anthropological Sciences. 2013. Vol. 6, Issue 3. P. 221–225. doi: https://doi.org/10.1007/s12520-013-0149-0
5. Metallurgical investigation on fourth century BCE silver jewellery of two hoards from Samaria / Ashkenazi D., Gitter H., Stern A., Tal O. // Scientific Reports. 2017. Vol. 7, Issue 1. doi: https://doi.org/10.1038/srep40639
6. In-situ non-destructive analysis of Etruscan gold jewels with the micro-XRF transportable spectrometer from CAN / Scrivano S., Roburo C., Gómez-Tuibo B., Mazzini G., Ortega-Feliu I., Ager F. J. et. al. // Journal of Archaeological Science: Reports. 2017. Vol. 16. P. 185–193. doi: https://doi.org/10.1016/j.jasrep.2017.09.032
7. Non-destructive micro-analytical system for the study of the manufacturing processes of a group of gold jewels from “El Carambolo” treasure / Scrivano S., Ortega-Feliu I., Gómez-Tuibo B., Ager F. J., de la Bandera M. L., Respaldiza M. A., Ontalba-Salamanca M. A. // Radiation Physics and Chemistry. 2017. Vol. 130. P. 133–141. doi: https://doi.org/10.1016/j.radphyschem.2016.08.008
8. Guerra M. F., Rehren T. In-situ examination and analysis of the gold jewellery from the Phoenician tomb of Kirion (Cyprus) // ArchaeoSciences. 2009. Issue 33. P. 151–158. doi: https://doi.org/10.4000/archeosciences.2148
9. Technological study of gold jewellery pieces dating from the Middle Kingdom to the New Kingdom in Egypt / Troalen L. G., Guerra M. F., Tate J., Manley B. // ArchaeoSciences. 2009. Issue 33. P. 111–119. doi: https://doi.org/10.4000/archeosciences.2095
10. Conventi A., Neri E., Verità M. SEM-EDS analysis of ancient gold leaf glass mosaic tesserae. A contribution to the dating of the materials // IOP Conference Series: Materials Science and Engineering. 2012. Vol. 32. P. 012007. doi: https://doi.org/10.1088/1757-899x/32/1/012007
1. Introduction

A large number of injuries are reported globally every year. Among the injuries of musculoskeletal system, up to 25% account for open fractures. Treatment of fractures that do not heal without surgical fastening the pieces is performed by using implants made of different materials in the form of various sophisticated structures (pins, needles,