JOINT INSTITUTE FOR NUCLEAR RESEARCH
Frank Laboratory of Neutron Physics

FINAL REPORT FOR STAGE 1 OF THE INTERNATIONAL STUDENT PRACTICE

"Neutron Tomography and Diffraction for Cultural Heritage Studies"

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Abstract:

The excavations in the necropolis “Volna-1” in Krasnodar Region unearthed nine historical coins that are believed to date from the second quarter of the sixth century to the beginning of the third century BC. The coins are thought to be an indicator of the “Charon’s obol” ceremony in the ancient Greek tradition, which make them both historically and culturally significant. Most of the found coins were covered with a thick layer of a patina. Hence, their primary identification, and the accurate study of their alloy composition are difficult.

As the neutron techniques are increasingly used for quantitative and non-invasive analysis of many aspects of cultural heritage studies, the chemical and elementary composition, and internal arrangement of the components of the copper coins were investigated using neutron diffraction and tomography.

We present our work on two coins labeled as: 467 and 469. The neutron tomography approach supplied 3D data on the spatial distribution of the bronze alloy and patina with corrosion contaminants inside coin volumes. The coins were found to be mostly comprised of a bronze alloy with a 4.4 wt.% tin content , for the 476 coin. The coins were corroded, with corrosion and patina areas occupying 1.65% for the 476 coin and 20.9% for the 479 coin of the original coin volume.

In this report, we present the analysis of the neutron tomography and diffraction data obtained from the experimental work in IBR2 facility, JINR for the purpose of identification of the copper alloy composition and the reconstruction of the initial view of original coins and their remaining parts from under the patina layer.

Keywords: Cultural heritage studies, Neutron tomography, Neutron diffraction and Ancient Greek copper coins

Introduction:

The use of non-destructive techniques to analyze the chemical composition of ancient numismatic materials has steadily carved out a niche in archaeological natural-scientific research. The structural data obtained by these methods broadens the scope of traditional coin studies by revealing information on topics such as coin nominal, the identification of crisis periods, trade and political ties between ancient states and cultural groups, and so on.

Non-destructive physical approaches, such as classic techniques like metallography or X-ray diffraction, are currently being used to analyse coins extensively. In this connection, the neutron tomography and neutron diffraction methods as relatively new structural non-destructive experimental methodologies should also be mentioned.

Since the fundamental difference in the nature of neutron interaction with matter compared to X-rays, the neutron approaches have additional advantages, such as sensitivity to light elements, a significant difference in contrast between isotopes, and a high penetration effect through metals or heavy elements. The components of coin alloys with nearby elements can be separated using neutron imaging and scattering methods: iron and nickel, copper and zinc, copper and silver, copper and lead.

Furthermore, neutron structural methods have been used to determine the bulk composition of coins that has been hidden by corrosion, to identify coins, to reconstruct coinage technologies and sources of mining materials for coins, and to describe coin degradation such as internal corrosion tracks and deterioration areas.

1. The Coin samples and Historical Background

Located 4 kilometers from the village Volna in the south-west of the Taman Peninsula around Mount Zelenskaya, Krasnodar region, Russian Federation, the necropolis “Volna-1” burials date from the second quarter of the VI century BC to the beginning of the III century BC; the main period of its use was the second half of the VI-V centuries BC. The “Volna-1” necropolis was presumably left by the Greek and barbarian population; the earliest burials of the necropolis may have been left by settlers who arrived from the territory of Great Greece. Numerous finds of Bosporan coins and Greek import items like tableware from Attica and Asia Minor, beads from North Africa, amphoras from the islands of the Aegean Sea and southern Pontus with wine and olive oil remains were indications of the well-being and life of the inhabitants of this ancient settlement.

In total, as a result of excavations, nine coins were obtained. Almost everywhere their location was associated with the dead body: in the mouth, in the palm, at the elbow of the buried bodies. This is an indicator of a ceremony in the ancient Greek tradition, the so-called “Charon’s obol”. The deceased person was accompanied by a coin, which he had to give to Charon, the ferryman of souls across the River Styx, which separates the world of the dead from the world of the living. Most of the found copper coins are covered with a thick layer of a patina, and their primary identification, the selection of the restoration procedure and the accurate study of their alloy composition are difficult.

The coins are presented in **Fig1.1 and Fig1.2**. The photos of the coins were obtained using a Leica M165 microscope with a video camera set-up. It can be seen that the surface of all of the coins is covered with a thick rough layer of patina, the minting pattern of the coins is indistinguishable. The green color of the patina indicates a copper alloy

Fig1.1: the two sides of coin 467 as taken by the Leica M165 microscope.

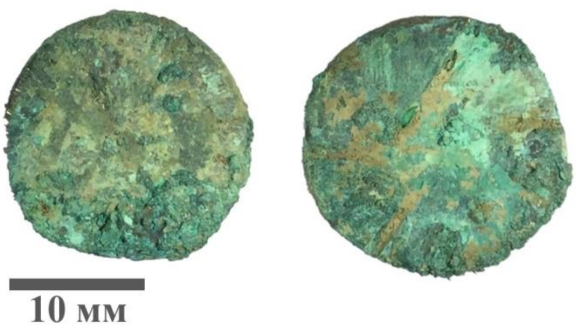

Fig1.2: The two sides of coin 469 as taken by the Leica M165 microscope.

2. The Techniques and the Facility

2.1 The Neutron Diffraction Approach

The phase composition of the volume of the coin was tested using the DN-12 neutron diffractometer at the IBR-2 high-flux pulsed reactor. The neutron powder diffraction patterns were collected at a scattering angle of $2\theta = 90^{\circ}$. The beam size was 5 mm in diameter and the exposition time was 20 min.

2.2 The Neutron Tomography Approach

The experiment were performed at the neutron radiography and tomography facility at the IBR-2 high-flux pulsed reactor (2 x 10^6 n/cm^2/c). The beam size was 20 cm in diameter and the coins were separated by cadmium plates. A set of neutron radiography images was collected by a detector system based on a high sensitivity camera with a Hamamatsu CCD chip. The tomography experiments were performed with a rotation step of 0.5°; the total number of measured radiography projections was 360. The exposure time for one projection was 20s, and measurements were performed for 4 hours in total.

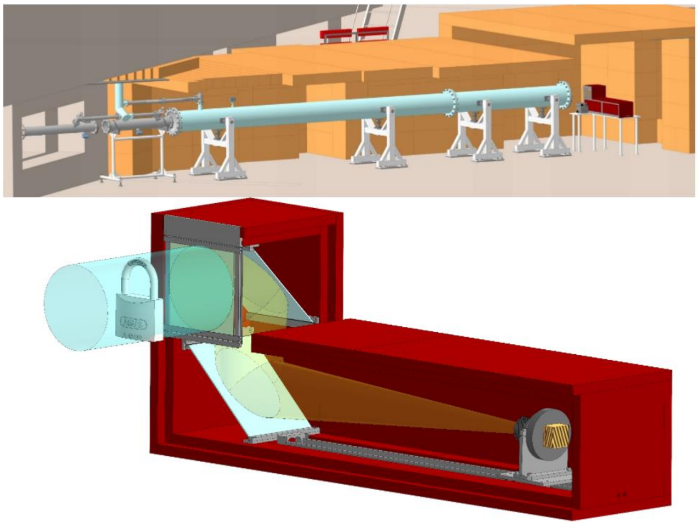

Fig2.2.1 At the top: The layout of the neutron radiography and tomography facility on the 14th beamline of the IBR-2 high-flux pulsed reactor.

3. The Analysis of the Experimental Data

- The imaging data from the CCD camera were corrected by the camera dark current image (or the dark field image) and normalized to the image of the incident neutron beam using the ImageJ software, as shown in **Fig3.1** and **Fig3.2**.
- The tomographic reconstruction was performed by the SYRMEP Tomo Project (STP) software using Direct Fourier Algorithm.
- The obtained data were then exported to Avizo 8.1 software where they were visualized in 3D and analyzed to obtain the volume of the materials with high attenuation coefficient, which we believe to be corrosive parts, as shown in **Fig3.3** and **Fig3.4**.

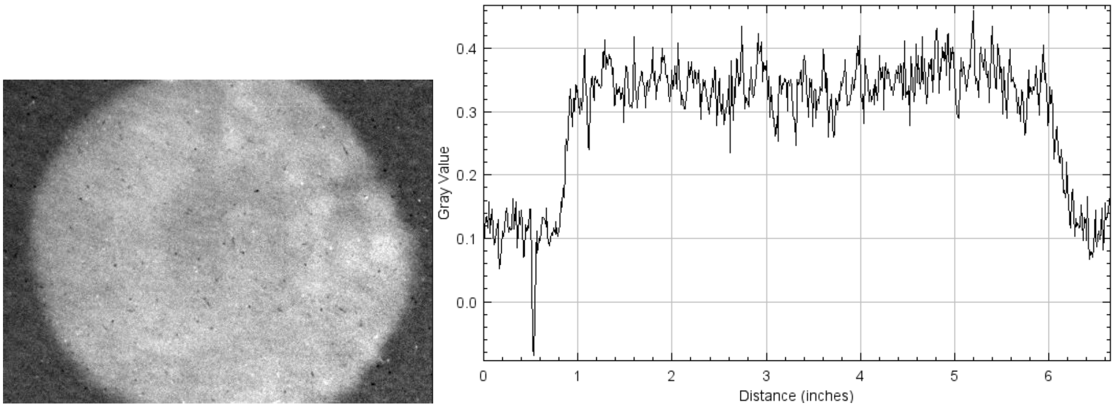

Fig3.1: The neutron radiography image for the coin 467 after the correction using imagej software and the plot profile of the corrected slice

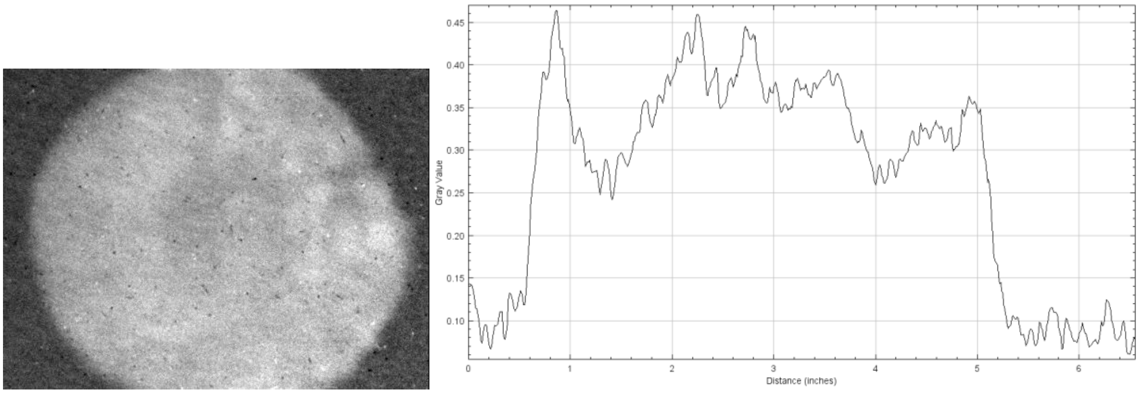

Fig3.2: The neutron radiography image for the coin 469 after the correction using imagej software and the plot profile of the corrected slice.

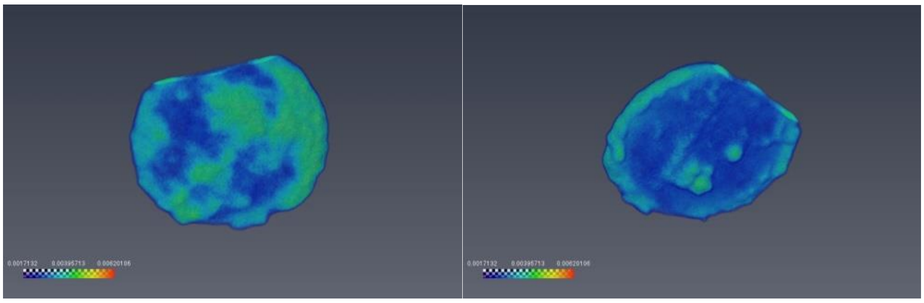

Fig3.3: The coin 467 visulaized in 3D in Avizo 8.1 after tomographic reconstruction.

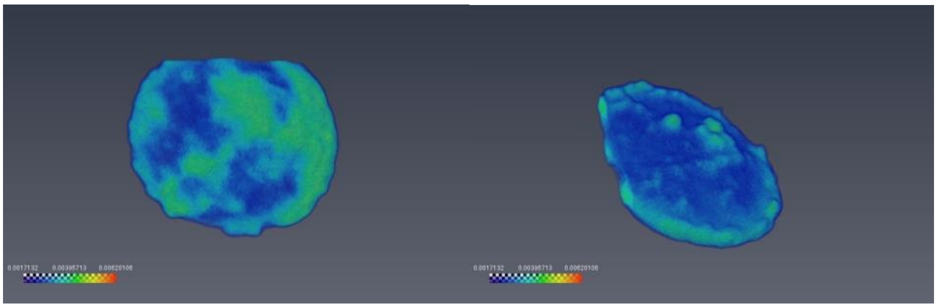

Fig3.4: The coin 469 reconstructed in 3D in Avizo8.1.

- **For the neutron diffraction approach**, the neutron diffraction patterns were analyzed by the Rietveld method using the Fullprof software.
- Knowing from the archeological background and the patina thickness that the coins were made of copper, a model with the copper phase composition was made and introduced to the fullprof software.
- After examining the peak shape, it was believed that some peaks were the result of other present elements in the sample. Experimenting with the minerals that usually accompany copper, enhancements in our model was made and the peak shape was largely enhanced.

4. Results and Discussion

From the neutron diffraction approach, we identified the diffraction peaks as additional phases of cuprite Cu_2O and copper chlorite CuCl phase, as presented in **Fig4.1.**

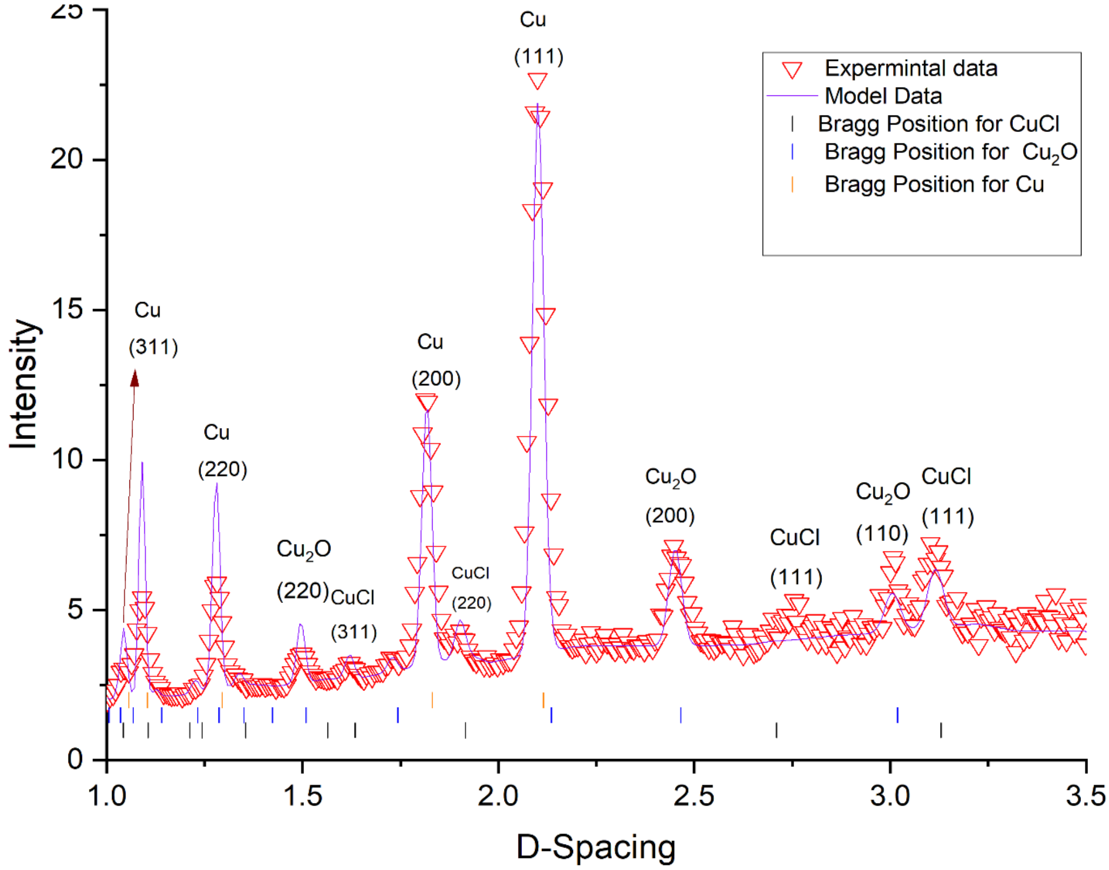

Fig4.1: The neutron diffraction pattern for the 476 coin, from which we obtained the elemental and phase composition of the material.

Knowing the lattice parameters, we calculated the tin content in the coin 467, using Vegard's law, which yielded 4.4 wt. %. It could be noted that knowing the tin content in the sample may hold a great value from archeological point of view, as this is a rare element present only in certain geographical locations in the world which can be a sign of trades in the past.

From the neutron tomography, the internal arrangement of the components of the coins was studied and it was found that the coins 467 and 469 had corrosive parts with percentage 1.65% and 20.9%

It should be noted that this corrosion percentage is calculated only by taking into account the materials with the high attenuation coefficient, but from the neutron diffraction we know that there are other present corrosion parts like Cu_2O that has low attenuation coefficient and not taken into account in our model.

Conclusion:

Using the data from the neutron diffraction, the phase and elemental composition of the 476 coin was studied and it was found that sample contains two additional phases of cuprite Cu_2O and copper chlorite CuCl, as presented in Fig4.1, the tin content, which holds an archeological value was found to be 4.4 wt. % of the whole volume.

The neutron tomography data enabled us to study the internal arrangement of the components of the coins, the corrosion and patina areas occupy 1.65% of the original coin volume of the original coin volume or the 476 coin and 20.9% for the 479 coin.

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