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Archaeometric analysis of cast iron dishware from the towns of Volga Bolgaria: Bolgar and Juketaw

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Abstract – **The paper is dedicated to the study of the transverse fractures of cast iron dishware samples discovered in the territory of Juketaw settlement (Tatarstan Republic, Russian Federation). It allowed to perform a comparative study of industrial metallurgical schools located in Bolgar - the capital of Volga Bolgaria, and Juketaw - one of the largest and most important trade towns of the Trans-Kama region.**
Keywords – **iron, metallurgy, Golden Horde, Volga Bolgaria, Bolgar, Juketaw.**

I. INTRODUCTION

In the 14th-15th centuries Volga Bolgaria represented one of the largest regions of the Golden Horde. According to written sources [1], less than 10 towns were located in its territory. A vast number of large settlements with a great potential for archaeological findings are still waiting for their turn to be studied. One of the large Oriental towns of Volga Bolgaria which remains understudied is Juketaw. It is located approximately 100 km upstream of the Kama, which is the second largest river in the region. In accordance with the results of archaeological excavations the town's history began in the second half of the 10th century. In the second half of the 14th century the town was plotted on a map by the name of Sacetim compiled by Pizzigano brothers. The town was repeatedly mentioned in ancient Russian chronicles in the second half of 14th – early 15th cc. as Zhukotin [1]. Numerous artefacts have been found in the territory of Juketaw. They signify not only active land development and trade, but also the emergence of a domestic craft industry of ceramics, ferrous and non-ferrous metals. Interestingly, the majority of metal items discovered in the cultural layer of the 14th century are made of iron [1]. The remains of a blacksmith shop and numerous fragments of cast iron dishware signify the existence of metallurgical cast iron production in the 14th-15th century.

II. MATERIALS AND METHODS

A total of six fragments of cast iron cauldrons were have been obtained as a result of archaeological excavations in the territory of Juketaw settlement (Chistopol, Tatarstan Republic, Russia) Five of them are dated 14th century, or the late Golden Horde period. One of them represents a fragment of a factory cauldron dating back to a later period - the 17th-18th centuries. It was studied in order to compare the handicraft and factory manufacturing techniques.

Studies were conducted on fractures of six samples with the use of optical and electron microscopy using the following equipment: Axio Observer Z1, Axio Imager.Z2m и AURIGA CrossBeam with an energy-dispersive spectrometer Inca X-Max at Kazan National Research Technical University named after A.N.Tupolev – KAI.

The technique of sample preparation is presented in work [2].

The preparation technique is specified below: the sample was secured on an aluminium holder using electrically conductive carbon adhesive tape. The secured sample was placed in the chamber of an electron microscope. Probing was performed from a selected area on the surface of the sample.

Electron-microscopic analysis included the use of the VPSE method (detection of secondary electrons in low vacuum mode) for the visualization of general surface morphology during panoramic photography, and for the performance of quantitative and qualitative microprobe analysis (20 kV, 800 pA).

Microprobe X-ray spectral analysis of samples with the use of INCA X-Max energy-dispersive spectrometer (with 127 eV sensitivity) includes the determination of sample composition and the plotting of spectra and element distribution maps.

Photographs for the visualization of composition determination areas were taken with AxioObserver Z1 optical microscope.

A comparative analysis was performed on 15 previously unstudied samples of cast iron dishware discovered in the territory of Bolgar settlement (Bolgar, Tatarstan Republic, Russia) [2,3].

III. RESULTS AND DISCUSSION

A comparative analysis of the surface morphology and shape of Bolgar and Juketaw cast iron dishware has not revealed significant differences, except for the cast iron sample dated the 17th-18th centuries.

According to the results of SEM study of Bolgar samples, all of them were found to have a distinct chemical composition and structure of steel-making iron. Typical microstructure of the items is preseted in Figures 1 and 2. Strong segregation of cast iron's chemical composition is observed.

Sample No.6 dating back to a later historical period has an well-ordered structure with round grains (Figure 3).

The aggregate chemical composition across the area of the researched sample is given in Table 1.

Table 1. Chemical composition of cast iron.

	Fe	C	P	S	O	Al	Si	Cr	Ca	Mn	Ni
1	83.56	10	1.13	0.26	4.41	0.12	0.25	0.04	0.06	0.16	0
2	84.63	9.71	2.96	0.14	2.33	0	0.12	0	0	0.1	0
3	75.8	12.1	0.41	0.14	10.85	0.06	0.07	0	0.27	0.24	0
4	85.15	10.52	0.24	0.07	3.04	0.1	0.33	0	0.37	0	0.18
5	85.86	8.45	1.97	0	3.36	0.08	0.11	0	0	0	0.16
6	50.47	43.85	0.6	0.07	3.93	0	0.61	0.1	0	0.36	0

Sample No.1 is characterized by homogeneous carbon distribution (Figure 4), whereas phosphorus (Figure 5) and sulphur are concentrated along the borders of small and large grains. Carbon and phosphorus content vary within the range of 2.49…10.00% and 0.00…7.6%. The oxidation is non-homogeneous, corresponding to the arrangement of ferrite in the microstructure. Endogenous inclusions and grains with small-sized flake graphite are deposited across the entire area of the fracture. The samples have a dense, grain-oriented and laminated structure. No shrinkage hollows or porosity is observed. Rare cracks probably formed during sampling.

The distribution of carbon (Figure 4), phosphorus (Figure 5) and sulphur is similar to that of sample No.1. Carbon content varies in the range of 1.44…16.09%, and phosphorus content does not exceed 8.43%. Oxidation of the sample is non-homogeneous. Endogenous inclusions are chaotically arranged. Unlike sample No.1 the microstructure of this item is characterized by larger shapes, which allows more accurate visualization of small graphite plates.

Fig. 1. Structure of sample No.3

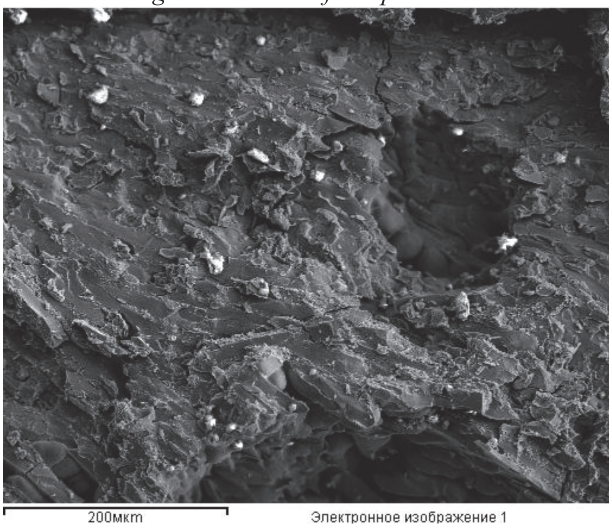

Fig. 2. Structure of sample No.5

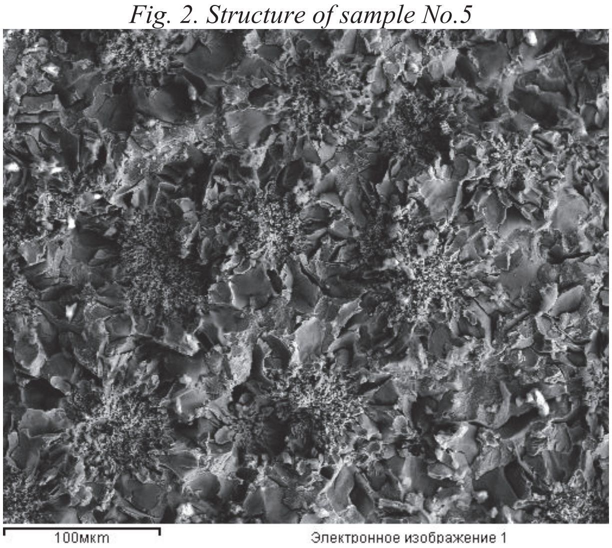

Fig. 3. Structure of sample No.6

Sample No.3 (Figure 1) is characterized by both distributed (Figure 4) and concentrated arrangemet of carbon across the area of the fraciton. Carbon content is 4.79…19.93%, and phosphorus content does not exceed 1.95%. The structure of the sample is dense фтв coarse-grained with endogenous inclusions. Flake graphite is well-visualized, and hollow graphite channels are observed.

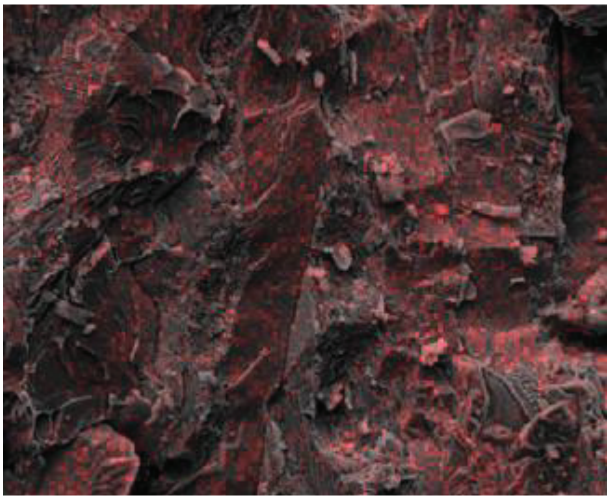

Fig. 4. An example of homogeneous carbon distribution across the area of the fracture (sample No.2)

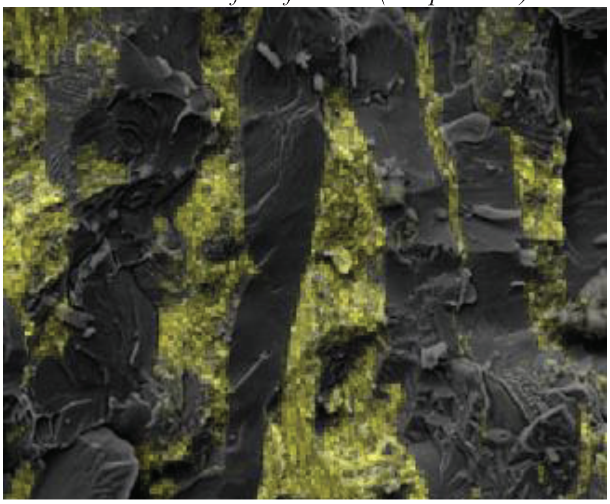

Fig. 5. An example of phosphorus distribution across the area of the fracture (sample No.2)

Sample No.4 is characterized by homogeneous distribution of phosphorus (constituting not less than 0.58% of the composition) across the entire area of the fracture. Carbon content varies within the range of 1.65…17.54%. Carbon features a layered distribution. Its structure is finely-layered, featuring minor phase inclusions. The layered distribution of iron oxide (oxidized ferrite) also signifies a highly dispersed structure. Endogenous inclusions are present, and small hollow graphite channels are visible. Gas porosity is observed.

The nature of carbon and phosphorus distribution in sample No.5 corresponds to that of samples No.1 and No.2 (Figures 4 and 5). Carbon content varies within the range of 3.79…18.70%, and phosphorus content amounts to 8.07%. minimum Structure of the sample is chaotic, coarse-grained with sorbitic graphite (Figure 2). Oxidation of the sample is homogeneous. Gas porosity is observed.

Sample No.6 is characterized by a uniform structure with distinct centres of crystallization (Figure 3). The grains have a circular shape. Large plates of graphite radiate from the centre to the edge, forming well-defined dendrites. Ferrite grains are uniformly distributed across the area of the fracture corresponding to the arrangement of iron oxides. Carbon content varies within the range of 9.27…79.99%, and phosphorus content does not exceed 1.67%. Carbon distribution (Figure 6) corresponds to that of silicon. Phosphorus (Figure 7) and sulphur concentrations are observed around the borders of the grains. Sulphur arrangement corresponds to the distribution pattern of manganese.

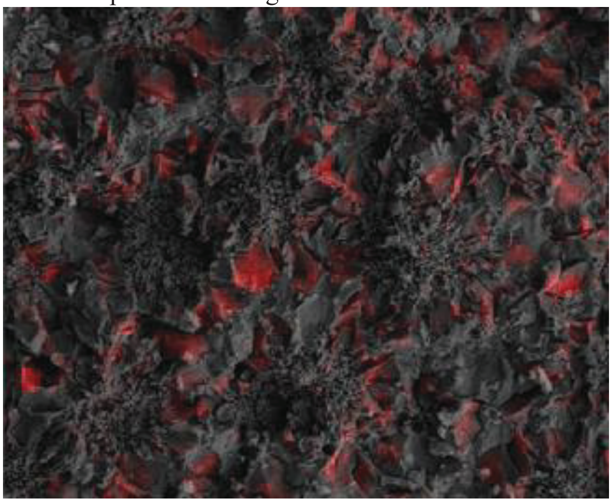

Fig. 6. Distribution of carbon across the fractured area of sample No.6

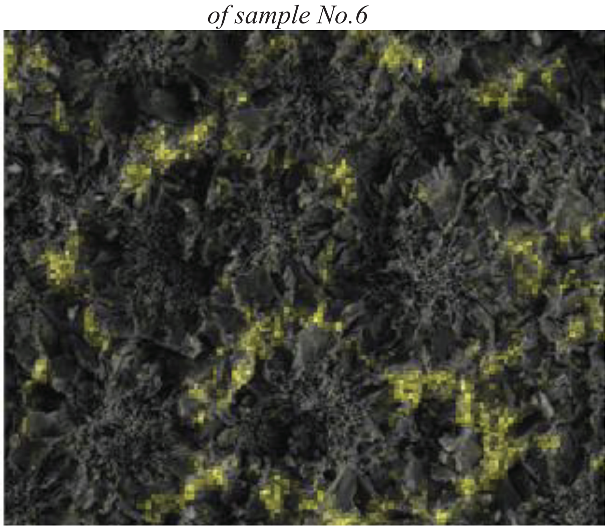

Fig. 7. Distribution of phosphorus across the fractured area of sample No.6

IV. CONCLUSION

The structure of 14th century samples has a chaotic nature and contains endogenous inclusions. Graphite is uniformly distributed in the form of small plates. The chemical composition and structure of all researched samples corresponded to that of pig iron. Two samples feature casting defects in the form of gas porosity. This indicates that the manufacturing technology of cast iron and its castings was imperfect. Cauldrons manufactured with this material were presumably very fragile. It is indirectly confirmed by a large amount of fragments in the overall volume of discovered cast iron artefacts [1-3].

High phosphorus content in the group of samples from an earlier time period signifies that firewood was used as fuel for the metallurgical process. It is confirmed by the fact that their structure has pig iron nature, as wood fuel cannot provide uniform heating and high temperature of metallurgical processes.

A large number of endogenous inclusions and a rather small size of grains signify that melt temperature could be lower than the liquidus point. It is confirmed by high segregation of the samples in terms of their chemical structure.

The absence of characteristic radial cracks presumably indicates that all studied samples constitute fragments of a cauldron located above the fire heating level, and thus were not subjected to temperature extremes.

Unlike Bolgar cauldrons [2] the amount of discovered shrinkage and gas porosity was comparatively small.

Sample No.6 dating back to a later period is an example of grain-oriented structure of cast iron. Compared with this sample, Bolgar and Juketaw cast iron was evidently not subjected to deoxidation or modifications. All admixtures contained in cast iron of the earluer period have a random nature and presumably vary as a result of non-standard handicraft manufacturing technique of cast iron and its forgings.

It signifies that the handicraft metallurgical schools of Juketau and Bolgar were similar, but does not provide sufficient ground to conclude that the handicraft schools were identical.

Presently, lateral polished sections of Juketau cast iron samples are subjected to metallographic examination.

Apart from that, the project comprises the use of the abovementioned technique in the research of samples from not less than two towns of Volga Bolgaria and Kazan Khanate which feature traces of metallurgical cast iron manufacture, and a comparison of research results with the results of samples from Bolgar and Juketau in order to determine the similarity of handicraft schools.

V. ACKNOWLEDGEMENTS

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