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THE CHEMICAL AND STRUCTURAL PECULIARITIES OF THE KAZAN KHANATE CAST-IRON COOKWARE IN THE 14TH-15TH CENTURIES

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ABSTRACT

The article presents the results of the examination of the fragments of cast-iron cauldrons found in the territory of the Kazan Kremlin, which date back to the period of the Kazan Khanate in the 14^{th}-15^{th} centuries. The examination of the samples of cast-iron cookware was carried out using the methods of scanning electron microscopy and optical emission spectroscopy. We analyzed the structure and the micro-trace composition of the samples of Kazan cast-iron and undertook its comparative study with the samples of Bolgar and Juketaw cast-iron cookware. We found out that the fragments of cast-iron articles from the Kazan Kremlin are characterized by a wide variety of technologies and chemical composition, in the sample there are both pro-Bolgar samples and those that are chemically and structurally different from it. The correlation analysis of the trace elements of Bolgar, Kazan and Juketaw cast-iron allowed to establish alleged markers of the iron-bearing ore in the territory of the Volga region, which together with other Golden Horde samples may help to understand the phenomenon of the extension of iron foundry tradition and its artifacts in the region. The study also provided convincing evidence of the existence of a link between iron foundry traditions in the Middle Volga region during the two-century period.

Keywords: cast iron, the Kazan Khanate, the Middle Ages, scanning electron microscopy, optical emission spectroscopy

INTRODUCTION

The medieval city, being in all its manifestations a concentrated expression of the level of development of economic and social relations, is an important integral part of studying the past of the human community. Everyday urban life accumulates and creates artifacts that as a result of archeologization become an important source revealing the lost parts of the history.

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One of the peculiar and significant elements of medieval urban life is handicraft industry. Many types of the craft activity are the subject of long-term focused and systematic studies that enabled us to have accumulated extensive knowledge about the peculiarities of the medieval craft culture and the range of its articles. The metallurgy was a part of the craft culture in the Middle Volga region in the 10th-16th centuries, which was the period of development of Volga Bulgaria and the Kazan Khanate. The examination of materials of archaeological excavations in urban craft areas gave extensive material for understanding the particularities of the development of metallurgy and metalworking in the region.

Kazan is among the well-studied archeological monuments of the Volga region with its handicrafts. Many articles of ferrous and non-ferrous metal were discovered in its territory during the excavations in the strata of the pre-Mongol, the Golden Horde times and the period of the Kazan Khanate. The remains of two copper-smelting furnaces built of fragments of bricks were found at the north-eastern tower of the Kremlin. The presence of handicraft industry associated with the processing of metals is developed in the city throughout its history [2].

MATERIALS AND METHODS

This paper will present the results of the first examination (conducted with the help of natural science methods) of the fragments of cast iron cauldrons found during the archaeological excavations of the Kazan Kremlin in 1990-2000 [3,6-8,11,12] (Fig. 1). For the analyses eight samples of the cauldrons from six excavations, which had been made in the north-eastern part of the Kremlin, were selected (Fig. 1). All these samples come from cultural layers which date back to the 14th-15th centuries [13]. The analyzed samples of cast-iron cookware are represented by fragments of walls and bottom parts, which thickness varies from 4 to 6 mm. Their extension in the Volga region is associated with the penetration of the iron foundry traditions during the Golden Horde period [5] and their consistent development in later times [4].

The earlier examinations of cast-iron cookware from Bolgar and Juketaw settlements of the late 13th-early 15th centuries [9,10] have shown that it is impossible to observe all the structural features at 100-200 times optical magnification. This is due to the highly dispersed and extremely diverse disordered structure of the medieval cast iron. The application of the method of scanning electron microscopy (SEM) with 300 times magnification allows exploring the fine structure and discerning micro-inclusions, which characterize the manufacturing process of cast iron.

The SEM examinations were carried out on the fracture and longitudinal polished section of 7 samples using optical and electron microscopy in the equipment of Axio Observer Z1, Axio Imager.Z2m and AURIGA CrossBeam with the energy-dispersive spectrometer Inca X-Max in Kazan National Research Technical University named after A. N. Tupolev – KAI (Russia). The methods of preparation of the fracture samples, their dissection and the mode of their examination are given in this work [9].

The SEM allows to determine both the chemical composition on certain areas of the sample surface and the distribution of the chemical elements over the surface, but the sensitivity of the used X-ray fluorescence spectrometer is not more than 0.1-0.5%. Therefore, in order to determine the micro-trace composition, the method of optical emission spectroscopy (OES) was used.

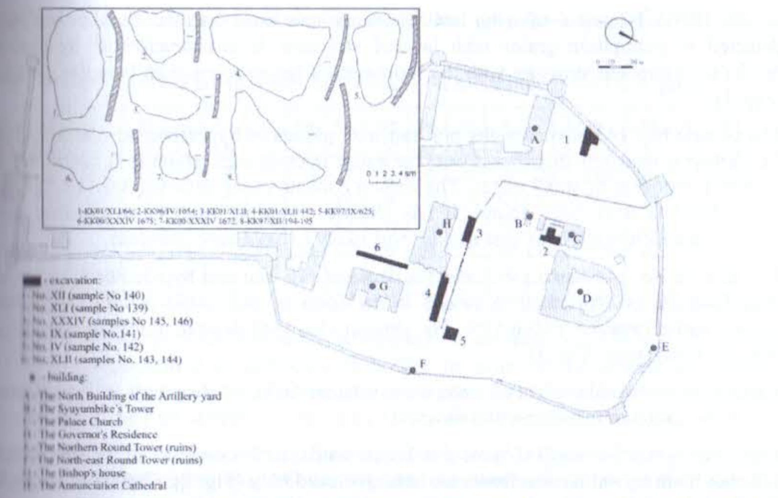

Figure 1. The cast iron fragments and the scheme of the Kazan Kremlin with the excavation marks which they were found

The OES technique is as follows: 10-15 mg of the sample is incinerated until complete evaporation from a carbon electrode crater in an AC arc. The exposure time for highly volatile elements is 30 s at a current of 8 A, after which the spectrum is overlapped and the sample is further incinerated at a current of 18 A. The spectrum obtained using a DFS-458 diffraction spectrograph was registered on PFS-03 photographic plates. The working lattice of the spectrograph is No.3 with 1800 pcs/mm. The obtained spectrograms were formed on a MF-2 spectrophotometer. The researched samples were analysed using a classical method of 3 reference standards represented by stainless steel. The study was conducted at the Institute of Archaeology of Tatarstan Academy of Sciences (Kazan, Russia).

RESULTS AND DISCUSSION

According to the SEM, all the samples of cast-iron cookware from the excavations of the Kazan Kremlin have the structure and chemical composition of pig iron and are characterized by a variety of highly dispersed structure.

The samples No. 139 and No. 141 contain trace copper and silicon. The structure is formed under the influence of numerous endogenous inclusions, which have provoked the formation of numerous crystallization centres (Fig. 3). The carbon content in the sample No. 139 varies between 3.23-16.28%; No. 141 - 4,29-19,49%. There are small quantities of hypereutectic cast iron in the structure. The oxidized ferrite phases can be visualized. Sulphur has been detected in multiphase grains with layered structure. Chlorine constitutes a part of grains with traces of active corrosion processes with loose structure. In the structure of the sample No. 141 in the shrinkage cavities trees with fine lamellar graphite have been detected.

The sample No. 142 contains pig iron with phases of hypereutectic cast iron, the graphite is distributed in phases in the form of small plates (Fig. 3). The carbon content

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is 1.55-18.6%. No micro-alloying trace elements have been detected. Sulphur has been detected in multiphase grains with layered structure. It is characterized by chaotic dendritic multiphase structure with the formation of fan structure with lamellar graphite (Fig. 3).

The sample No. 143 also contains pig iron with phases of hypereutectic cast iron (Fig. 3). Carbon is unevenly distributed over the entire fracture area, graphite is distributed in phases in the form of small plates. The carbon content varies between 3.09-16.22%, no trace elements have been found. It has chaotic dendritic multiphase structure with endogenous inclusions. This cast iron is most likely to have been remelted.

The sample No. 144 has a mechanical mixture of pig iron and hypereutectic grey cast iron. Graphite is distributed in phases in the form of thin small plates. The carbon content varies between 3.69-6.53%. The structure has well-defined multiphase dendrites mainly of two types (Fig. 3).

There is an increased content of manganese relative to the whole group, it is distributed across the structure together with silicon.

The samples No. 145 and 146 have a structure similar to the structure of the sample No. 144, but their crystallization fronts are arranged randomly (Fig. 2). Carbon is unevenly distributed over the entire fracture area; graphite is distributed in phases in the form of thin small plates. The carbon content in the sample No. 145 varies between 1.40-18.15%, in the sample No. 146 - 2,18-13,12%. Sulphur is detected on certain areas at high magnification. The distribution of oxygen is mainly concentrated in zones of iron impoverishment, which possibly coincides with the presence of oxidized ferrite phases at these points. There is also a correlation of the distribution of Si, Al and Ca. Chlorine has been detected on the area of well-defined graphite, and in three spectra nickel impurities have been found.

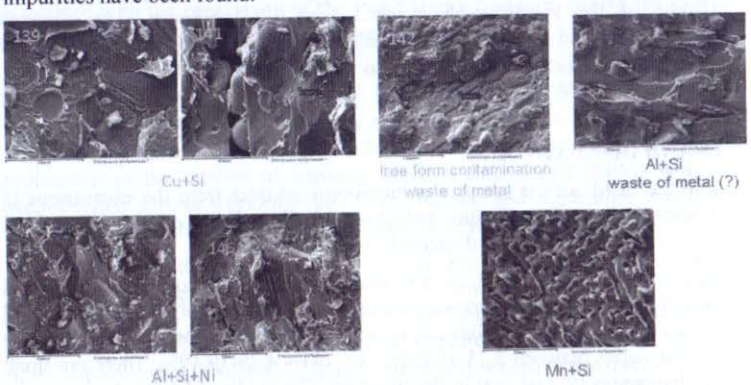

Figure 2. The microstructure of the cast-iron cookware samples from the Kazan Kremlin excavations

In all the samples phosphorus is distributed along the grain boundaries within the layers of the multiphase structure. Shrinkage processes are observed at the interphase boundaries.

The total content of trace elements was determined with the help of the OES method (Table 1).

Table 1. The chemical composition of the cast iron according to the OES (ppm).

[illegible]	Ag	Al	As	Bi	Ca	Cr	Co	Cu	Mn	Na	Ni	P	Pb	Si	Sn	Ti	Zn
[illegible]	0,66	11	3,5	2,5	151	2	17	12	208	45	8,3	345	2,8	7500	5,2	6,4	30
[illegible]	3,6	3,4	3,5	1,8	75	3,5	26	25	53	90	18	235	3,4	5400	41	1,5	25
[illegible]	0,15	0,89	3,5	1,7	190	2	15	8,6	94	30	9,3	435	2,3	2100	2,6	1,1	25
[illegible]	0,1	2,6	5,5	1,9	145	2,5	14	8,3	99	25	14	515	2,4	3400	2,2	1,1	28
[illegible]	0,2	1,1	6	1,5	165	3,5	7,4	2,2	695	45	6,9	230	2,7	1700	2,1	0,7	25
[illegible]	0,1	0,7	5	1,6	145	1	17	7,2	62	30	8,7	350	3	1200	2,3	0,7	33
[illegible]	0,2	20	5	2,3	78	1	21	10	30	90	8,8	855	2,8	12000	6,3	1,4	25

Despite the identity of the structures, comparing the samples No. 139 and No. 141 the OES has demonstrated a significant difference in terms of the content of chemical elements. The chemical composition of the samples No. 145 and No. 146 is almost identical, but the first sample contains much less silicon than the second one.

The sample No. 144 confirmed the data provided by the SEM about the high content of manganese. The samples No. 142 and No. 143 are similar in terms of their chemical composition.

The obtained results of the structural and micro-trace composition of cast-iron cookware samples have been analysed according to the concept of the development of iron founding industry in the territory of the Ulus of Jochi and the Kazan Khanate. This was accomplished with the help of a comparative study with the previously examined samples from the Bolgar settlement (the capital of the Ulus of Jochi) [9] and the Juketaw settlement (a large trade and handicraft settlement in the Ulus of Jochi) [10].

According to the SEM, the samples No. 139, 141-143, 145 and 146 are similar to the Bolgar and Juketaw samples in terms of the structure, but slightly different in terms of the set of impurity elements that they contain. The cast iron No. 139 and 141 mainly contains Cu and Si, while the No. 142 is characterized by burnt structure and the absence of significant impurity content. The sample No. 143 also has structure with signs of hot reheat or remelt, the method allowed to detect only Al and Si. The No. 145 and 146 have been confirmed to have the pro-Bolgar structure due to the presence of the similar set of trace elements, such as Si, Mn and Ni. The sample No.144 has a different nature of crystallization (Fig. 2) and a quite large content of Si and Mn.

The comparative analysis of chemical composition according to the OES was performed on the basis of the previously established correlation relationship between Ni-Cr-Mn and Ni-Co-Cu [10]. The correlation of the contents of these chemical elements is probably due to the origin of iron ore. Figure 3 shows that all the samples were divided into three groups, while the Kazan cast iron was divided into 2 groups. However, the SEM data show that the structure of the samples from the Kazan Kremlin are divided into pro-Bolgar chaotic structure (6 units) and ordered dendritic structure (1 unit). The samples, which contain Co impurity, appear to be in different subgroups. It is most likely due to the fact that the burnout of Mn in the metallurgical process is 2-3 times higher [1] than the burnout of Co and Ni. Cr is also characterized by quite high burnout (2-2.5 times higher than the burnout of Cu) [1]. Besides, its cooperative effect with Al and Si is accompanied by active formation of the dense oxides Cr_2O_3, Al_2O_3, SiO_2,

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which significantly reduce the rate of the oxidation-reduction reaction of iron [1].

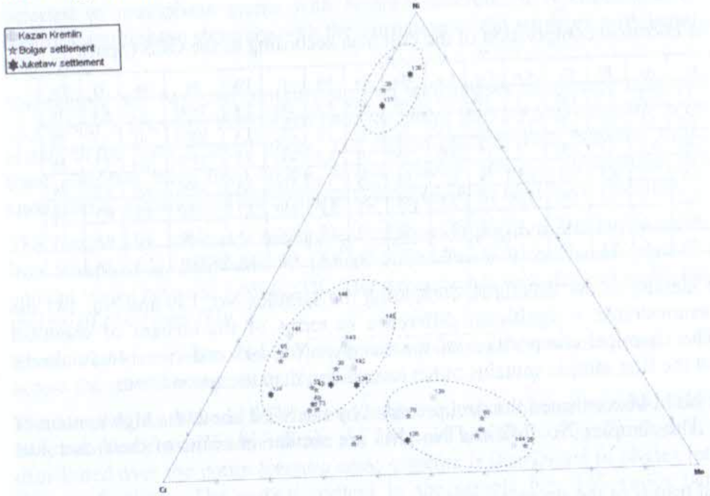

Figure 3. The distribution of the cast-iron cookware found in the territory of the Ulus of Jochi and the Kazan Khanate according to the inherited elements Ni-Cr-Mn

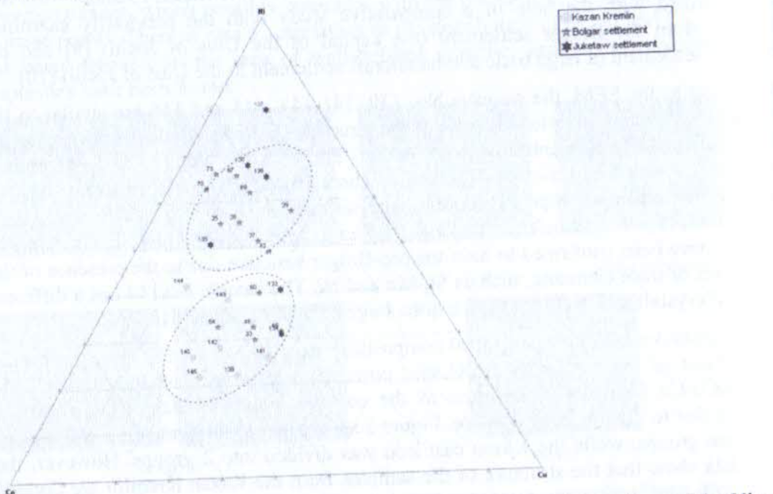

Figure 4. The distribution of the cast-iron cookware found in the territory of the Ulus of Jochi and the Kazan Khanate according to the inherited elements Ni-Co-Cu

Therefore, another set of inherited chemical elements – Ni-Co-Cu provides a more vivid demonstration of the division into groups (Fig. 4). This division allowed to make more correct groups of medieval cast iron samples. This is indirectly confirmed by the fact

that the new time cast iron from Juketaw and the sample No. 144 with atypical structure from the Kazan Kremlin were not included in any of these groups. Thus, it is Co, Cu and Ni that are more likely to be taken as hereditary markers of raw iron sources.

CONCLUSION

The found fragments of cast-iron articles from the Kazan Kremlin are characterized by a wide variety of technologies and chemical composition. This may be due to the cast-iron cookware brought to the city from other regions, which was made with the help of different craft traditions, as well as with a wide chronology of the cultural layers of the Kazan Kremlin, where the examined artefacts were found.

Some of the cast iron samples have clear signs of remelting and solidification different from the Bolgar and Juketaw modes. In the sample No. 142 no trace elements have been found, which demonstrates that the steel or iron scrap was remelted, since the trace elements contained in the original crude ore evaporated during the remelting process. The two samples differ in terms of the content of trace elements according to the SEM (No. 139 and 141). The sample No. 144 has high manganese content, which together with a solidification mode different from other samples probably caused a fine dendritic well-defined structure with extensive shrinkage processes. The samples of Kazan cast iron No. 142, 143, 145, 146 according to some signs have structure similar to the structure of the samples from the excavations of the Bolgar and Juketaw settlements, and the No. 139, 141 are close to this group, but their main structure-forming element is copper, not manganese. In general, the structure of all the examined samples from the Kazan Kremlin is characterized by greater clarity of dendritic phases, but inside dendrites still have complex multiphase structure. There are also endogenous inclusions in the form of separate grains inside dendrites or at the phase boundaries. The strong liquation of the chemical composition in all the samples is due to the immaturity of the technology, no traces of structure regulation have been found.

According to the SEM, relatively low sulphur content and high phosphorus content probably indicate that charcoal was used as fuel for the metallurgical process.

The presence of Al and Si confirms the hypothesis of the use of local iron-bearing ore – clay-bond ironstones [5]. Besides, the presence of these elements can be explained by the use of silicates as fluxes.

The micro-trace analysis according to the OES allowed to clarify the assumption about the relationship of the Bolgar and Kazan iron founding and to distinguish the main hereditary characteristics. Two groups of the Middle Volga region cast iron and two exceptional samples are distinguished. The first group consists of nine samples of Bolgar cast iron and three samples of Juketaw cast iron, the second one - all the samples from the Kazan excavations, five Bolgar and two Juketaw samples. A sample of Kazan cast iron, which is very different in terms of structural and chemical characteristics, and a sample of new times cast iron were not included into the groups.

The comparative analysis of structural and chemical composition of the cast-iron cookware fragments from Bolgar and Juketaw with the Kazan Kremlin samples indicates the existence of a stable technological tradition in Volga Bulgaria in the 14th-15th centuries. Perhaps this is due to the emergence of iron founding techniques, inherent in the Middle Volga region. This assumption requires analyses of a wider range of samples from other monuments of the Golden Horde.

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REFERENCES

[1] Belov V.D., Vdovin K.N., Kolokoltsev V.M., Kovalevich E.V., Ten E.B., Ri Khosen, Ri E.Kh., Proizvodstvo chugunnih otlivok, Magnitogorsk, Izd-vo Magnitogorsk.gos.tech.un-ta im. G.I. Nosova, 2011.

[2] Huzin F.Sh., Sitdikov A.G., Srednevekovaya Kazan' v svete novyh arheologicheskih issledovanij, Tatarika, №1 (2), pp. 114–124, 2014.

[3] Huzin F.Sh., Nauchnyj otchet ob arheologicheskih issledovaniyah v Kazanskom Kremle letom 1997 godu, Kazan, Arhiv IA AN RT, Str.3. N.f.2, Opis 1, Ed. hr. 37.

[4] Ryazanov S.V., Chugunolitejnoe remeslo v Zolotoj Orde, Izvestiya Altajskogo gosudarstvennogo universiteta, №4/2, Barnaul, pp.159-168, 2008.

[5] Semykin Yu.A., Chernaya metallurgiya i metalloobrabotka na Bolgarskom gorodishche// Gorod Bolgar, Remeslo metallurgov, kuznecov, litejshchikov, Kazan, pp. 89-153, 1996.

[6] Sharifullin R.F., Otchet ob arheologicheskih issledovaniyah v Kazanskom Kremle na raskope XXXIV v 2000 godu, Kazan, Arhiv IA AN RT, Str.3, N.f.2. Opis 1, Ed. hr. 112.

[7] Sharifullin R.F. Otchet ob arheologicheskih issledovaniyah na raskope XLI v Kazanskom Kremle vesnoj i letom 2001 goda, Kazan, Arhiv IA AN RT, Str.3, F. 2739, Opis 1A 1321.

[8] Sharifullin R.F., Otchet ob arheologicheskih issledovaniyah na raskope XII v Kazanskom Kremle v 1997 godu, Kazan, Arhiv IA AN RT, Str.1. F.2. Opis 1 Ed. hr. 40.

[9] Shaykhutdinova E., Belyaev A., Sitdikov A., Yanbaev R., Archaeometric analysis of cast iron dishware from the towns of Volga Bolgaria: Bolgar and Juketaw, Proceedings of IMEKO International Conference on Metrology for Archaeology and Cultural Heritage (MetroArchaeo 2016), October 19 - 21, 2016, Torino, Italy, pp. 270-273, 2006.

[10] Shaykhutdinova E., Khramchenkova R., Nabiullin N, Belyaev A., Yanbaev R., Sitdikov A., Interdisciplinary Research of Iron Casting Technologies in the Town of Juketaw during the Golden Horde Period, Acta Imeko, Vol 6, No 3, pp. 87-9, 2017. DOI: http://dx.doi.org/10.21014/acta_imeko.v6i3.461.

[11] Sitdikov A.G., Kazanskij Kreml, Kazan: Foliant, 288 p., 2003.

[12] Sitdikov A.G., Huzin F.Sh., Otchet ob arheologicheskih issledovaniyah na territ Kazanskogo Kremlya v 1997 godu, Kazan, Arhiv IA AN RT, Str.2, F.2, Opis 1, Ed. hr. 38.

[13] Sitdikov A.G., Otchet ob arheologicheskih issledovaniyah na raskope XLII 200 goda, Kazan, Arhiv IA AN RT, Str.3.