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METALLURGY IN THE MEDIEVAL BRANICEVO****

Abstract

During the archeological researches of the medieval Branicevo at the site Mali Grad-Todica crkva in the Kostolac village, a significant amount of iron slag was discovered. The archeological context is indicative but so far, it does not provide the precise defining the spatial function with archeological and metallurgy findings. For that purpose, the physical and chemical analyses of the archeometal samples were carried out. The results of the investigation show the primary metallurgical activity in Branicevo in the second half of the XI and XII century, while the presence of wüstite (FeO), fayalite and magnetite in most of samples indicates the iron melting. Evidences of the primary iron metallurgy show the economic significance of Braničevo in a new light and the structural analyzes of slag are important for defining the casting process and degree of the iron metallurgy development during the Byzantine government in Braničevo.

Keywords: *Branicevo, iron, smelting, metallurgy, slag*

INTRODUCTION

The medieval town of Braničevo was developed on the territory of the Roman Viminacium, on the banks of the river Mlava. The two fortified structures of the urban core of Braničevo were located on the Mali and Veliki Grad, the natural units at the end of the Sopot Greda above the village Kostolac, while the spacious suburb spread to their base [1]. *(Location Mali Grad in the first half of the XX century was re-named into the 'Todića crkva', and in the literature is reffered to as Mali Grad – Todića crkva)*

As a natural fortification system that protected and controlled the Danube passage, Mali Grad-Todića crkva was of great importance since the Eneolithic, up to the modern age (Fig. 1).

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**** *This paper represents the result of multidisciplinary research on the projects 'Archeological Research of the Medieval Town of Braničevo', supported by the National Museum Pozarevac, and backed up by the City of Pozarevac (lead by the museum advisor, archaeologist Dragana Spasić-Đurić) and the project of the Ministry of Education and Science of the Republic of Serbia. Ethnogenesis of the Serbs during the Middle Ages (until c.1250): a comparative analysis of the historic-cultural heritage, genetic material and artefacts of material culture from the aspect of analytical chemistry (Reg.No. III 47025)*

Fig. 1 *Site Mali Grad-Todića crkva, explored zone with the archeometallurgical findings*

The new archeological researches at this locality, begun in 2007, show the new aspect of political and economic significance of Braničevo during the Byzantine Government in the XI and XII century. On the systematically investigated area of about 480 m^2, primarily on the western periphery of the site, three cultural horizons were discovered: from the Hallstatt, Late La Tène period – early Roman and medieval times. The attention is focused on the earliest, medieval horizon and the period of strong economic and political bloom under the rule of the Komnenos dynasty, at the end of the XI and during the XII century [2].

ARCHEOLOGICAL CONTEXT

The results of researches from 2014 to 2017 are of a big importance. On the area of approximately 20x20 m, in the squares AC23, AC24, AD23- AD25, AE23, AE24 and AF24, a significant amount of scrum and slag (Fig.1) was discovered. Archeometal samples were found in the indicative archeological context consisting of furnaces, fireplaces and waste burial pits. Generally, all collected samples have light or dark brown color; some are metallic and heavy, while the other group has a glassy gloss, porous structure and light weight. Precise functional definition of the explored area is prevented by large devastations, since except for the two preserved furnaces and Burial pits, other objects have not been discovered *in situ*. The discovery of slag from the mold (the so-called 'casting cake') in the Burial pit XXVII is particularly significant, which was preliminarily dated using money from the last decades of the XI and the first decades of the XII century (Fig. 2).

A large concentration of archaeometallurgical findings was recorded in the squares AD24 and AE24 in the zone of two fully preserved furnaces and object-House 8, whose devastated fireplace was discovered in parts outside the original context. It is significant that the fractions of the fireplace, due to high temperatures, were merged with larger pieces of slag.

Fig. 2 *Slag from a mold, the Burial pit XXVII*

According to the dimensions and construction (air vents, so-called "blowers" and larger rectangular chimney at the top), in a functional aspect, the furnace 16 triggers quite a confusion. Its construction elements indicate that it was used to develop high temperature, which further indicates a special purpose [3, 4]. Unfortunately, the furnace was discovered completely cleaned, and after having its bottom part renovated, it was not put into operation again due to the unknown reasons. Therefore, at this stage of research, there is no archaeological evidence to indicate its metallurgical function. The specific archaeological context and certain typological similarities with some casting furnaces from the early Laten and the Late La Tène period from Bavaria do not exclude this assumption completely.

PHYSICAL AND CHEMICAL ANALYSES

For the purpose of determining and defining the function of space with higher concentration of slag, as well as the character of the activities that took place at this site during the XI and XII century, the physical and chemical analyses were carried out of individual samples from the Braničevo research in 2015 and 2016, and the results of these analyses represent the focus of this paper

The selected archeometal samples were subjected to the chemical and scanning electron microscopy at the Faculty of Mechanical Engineering in Belgrade (Tables 1, 2, Figures 3 (a-f), 4 (a-g), as well as the X-ray diffraction analysis in the Mining and Metallurgy Institute in Bor (Figures5-10, Tables 3-8).

TEST RESULTS

Chemical analysis

The results of samples subjected to the chemical analysis are shown in Tables 1 and 2.

Table 1 *Results of the chemical analysis of the archeometal samples from the site Mali Grad-Todića crkva*

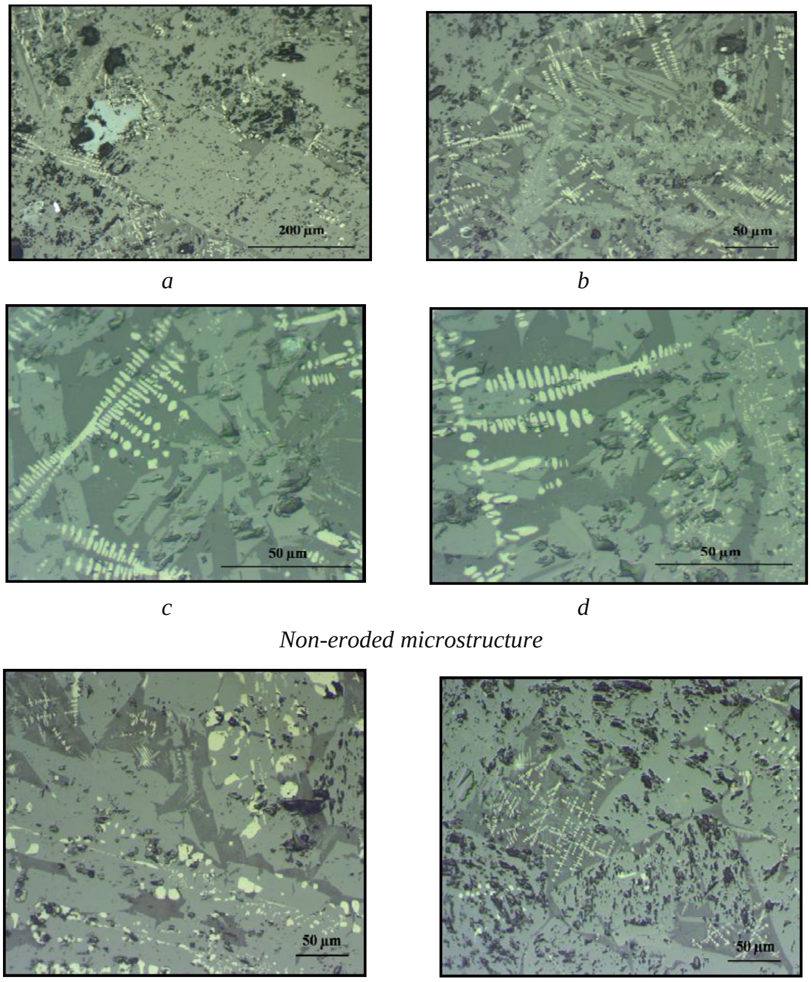
Name **TCI**	***Class*** **Alloy LE FP**		***Date*** **30/11/2016**		***Time*** **11:54:44**		***Duration*** **10.5 s**	
Sample 1	*Fe (%)*	*Si (%)*	*P (%)*	*Al (%)*	*Zr (%)*	*As (%)*	*Ti (%)*	*Pd (%)*
	54.90	31.29	7.62	5.95	0.19	0.05	/	/
Deviation (+/-)	0.723	0.803	0.307	1.238	0.028	0.013	/	/
Rating								
Name **TCI**	***Class*** **Alloy LE FP**		***Date*** **30/11/2016**		***Time*** **11:53:14**		***Duration*** **10.5 s**	
Sample 2	*Fe (%)*	*Si (%)*	*P (%)*	*Al (%)*	*Zr (%)*	*As (%)*	*Ti (%)*	*Pd (%)*
	56.84	28.43	5.96	7.37	0.28	/	0.84	0.28
Deviation (+/-)	0.735	1.005	0.448	1.265	0.028		0.209	0.086
Rating								
Name **TCI**	***Class*** **Alloy LE FP**		***Date*** **30/11/2016**		***Time*** **11:53:51**		***Duration*** **10.5 s**	
Sample 3	*Fe (%)*	*Si (%)*	*P (%)*	*Al (%)*	*Zr (%)*	*As (%)*	*Ti (%)*	*Pd (%)*
	54.60	30.13	7.33	7.71	0.23	/	/	/
Deviation (+/-)	0.739	0.822	0.317	1.303	0.029	/	/	/
Rating								

Table 2 *Results of the chemical analysis of the archeometal samples from the site Mali Grad-Todića crkva*

Name **TCI**		***Class*** **Alloy LE FP**		***Date*** **30/11/2016**		***Time*** **11:54:09**		***Duration*** **2.5 s**	
Sample-4	*element*	*Fe (%)*	*Mn (%)*	*Sb (%)*	*Sn (%)*	/	/	/	/
	value	96.27	2.43	0.81	0.49	/	/	/	/
	deviation (+/-)	1.301	0.238	0.140	0.147	/	/	/	/
Rating		1.0257 (0.00)	1.2842 (0.53)	/	/	/	/	/	/
Name **TCI**		***Class*** **Alloy LE FP**		***Date*** **30/11/2016**		***Time*** **11:54:45**		***Duration*** **10.5 s**	
Sample-5	*element*	*Fe (%)*	*Si (%)*	*Mn (%)*	*Sb (%)*	*Pb (%)*	/	/	/
	value	92.07	6.34	0.95	0.50	0.14	/	/	/
	deviation (+/-)	0.886	0.527	0.137	0.137	0.036	/	/	/
Rating		1.2542 (3.05)	1.0473 (3.45)	/	/	/	/	/	/
Name **TCI**		***Class*** **Alloy LE FP**		***Date*** **30/11/2016**		***Time*** **11:55:39**		***Duration*** **10.5 s**	
Sample-6	*element*	*Fe (%)*	*Si (%)*	*Mn (%)*	*P (%)*	*S (%)*	*Zn (%)*	*Zr (%)*	
	value	79.60	16.65	2.11	1.18	0.30	0.10	0.07	
	deviation (+/-)	0.777	0.644	0.169	0.201	0.084	0.029	0.022	
Rating		1.2542 (3.90)							

Scanning electron microscopy

Scanning electron microscopy was done on two samples that were, after preparation, photographed by the optical microscope in their non-eroded and eroded state. A part of the sample, broken into fragments, was turned into dust for the purpose of X-ray analysis in order to identify the phases (Figures 3, 4).



a *b*

c *d*

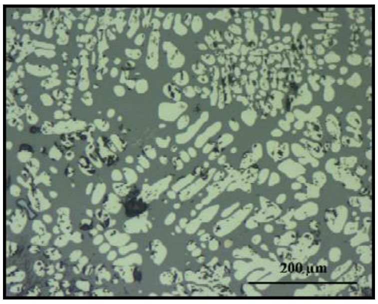
Non-eroded microstructure

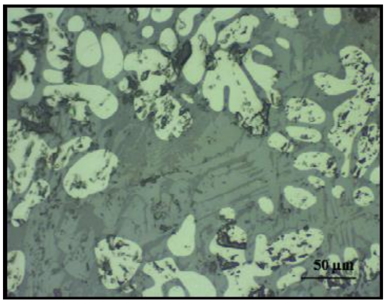
e *f*

Eroded microstructure (nital)

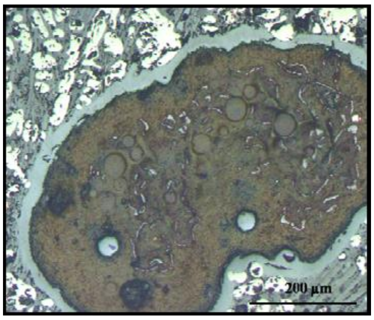
Fig. 3 (a-f) *Structure of the sample No.5 from the site Mali Grad – Todića crkva*

The sample has a very heterogeneous and highly porous microstructure consisting of a large amount of slag in which the metal dendrites (*wüstite*) are separated. The slag is consolidated with an iron metal base that occurs mainly in a dendritic form. The high-content of SiO_2 was identified by the X-ray analysis.



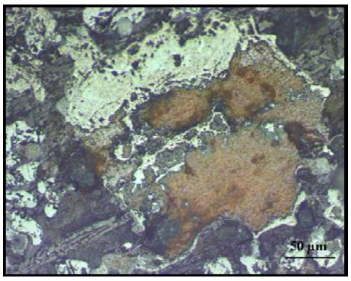


a *b*

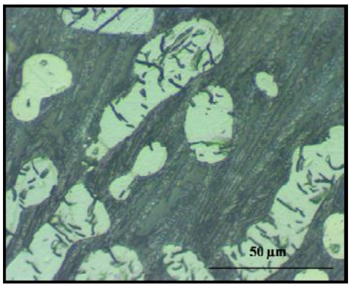


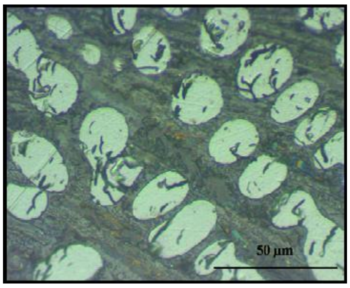
c

Non-eroded microstructure



d *e*





f *g*

Eroded microstructure (nital)

Fig. 4 (a-g) *Structure of the sample No.6 from the site Mali Grad – Todića crkva*

The sample has a very heterogeneous and highly porous microstructure. A high concentration of FeO was identified by the X-ray analysis. The structure of samples indicates that it is a slag created in the process of obtaining iron from the ore iron.

X-ray diffraction tests

The results of X-ray diffraction tests of archaeometallurgical samples from the site Mali Grad – Todića crkva are shown in the X-ray diffractograms in Figures 5-10, and identification of the mineral (phase) composition of the tested samples is shown below the diffractograms in Tables 3 to 8.

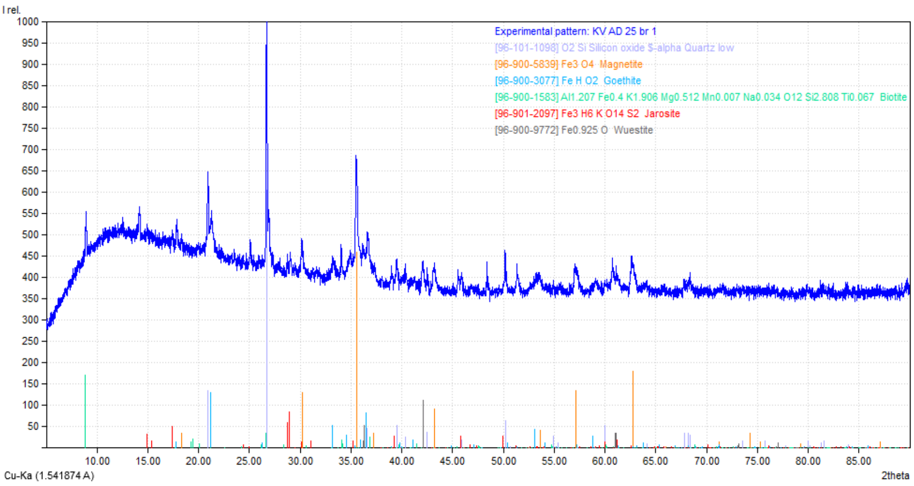


Fig. 5 *Diffractogram of the sample No.1 from the slag AD25*

Table 3 *Results of the X-ray diffraction sof the sample No.1 from the slag AD25*

Identified minerals	Chemical formula
Quartz	SiO_2
Magnetite	Fe_3O_4
Getite	FeO(OH)
Biotite	$K(Mg,Fe)_3AlSiO_{10}(F,OH)_2$
Jarosite	$KFe(OH)_6(SO_4)_2$
Wüstite	FeO

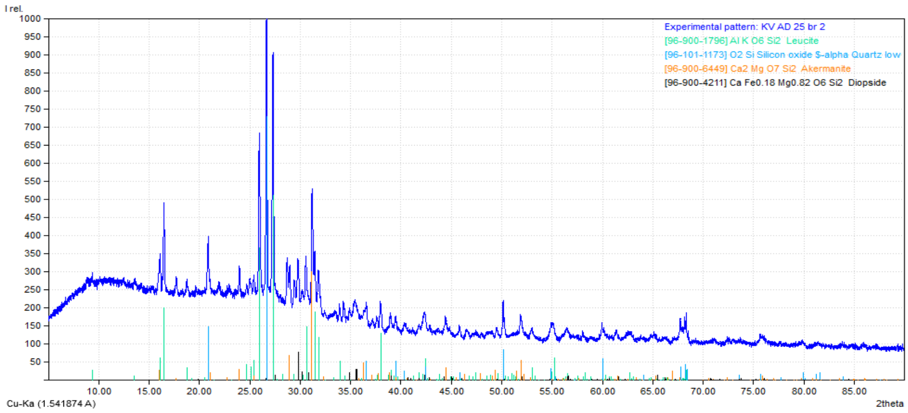


Fig. 6 *Diffractogram of the sample No.2 from the slag AD25*

Table 4 *Results of the X-ray diffraction analysis of the sample No. 2 from the slag AD 25*

Identified minerals	**Chemical formula**
Leucite	$K(AlSi_2O_6)$
Quartz	SiO_2
Accermanite	$Ca_2MgSi_2O_7$
Diopside	$MgCaSi_2O_6$

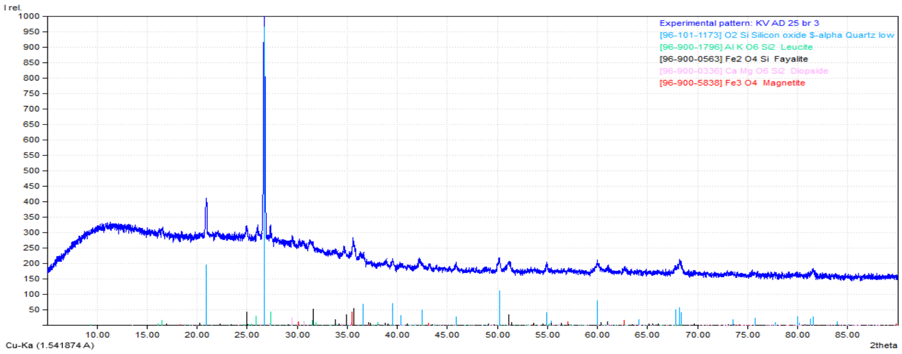


Fig. 7 *Diffractogram of the sample No.3 from the slag AD25*

Table 5 *Results of the X-ray diffraction analysis of the sample No. 3 from the slag AD25*

Identified minerals	**Chemical formula**
Quartz	SiO_2
Leucite	$K(AlSi_2O_6)$
Fayalite	Fe_2SiO_4
Diopside	$MgCaSi_2O_6$
Magnetite	Fe_3O_4

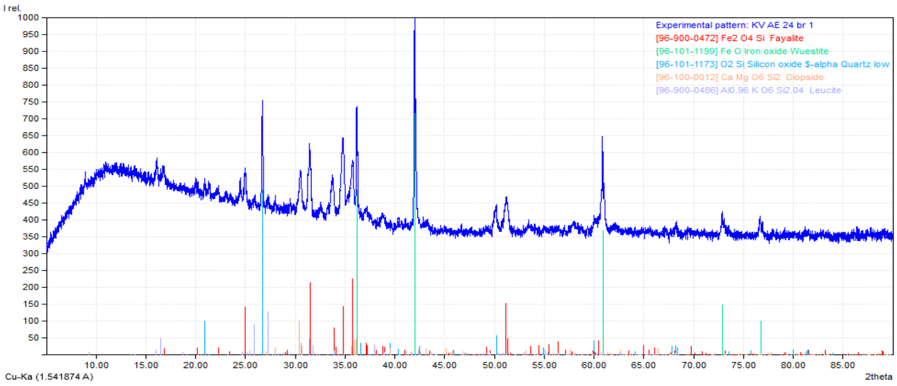


Fig. 8 *Diffractogram of the sample No.1 from the slag AE24*

Table 6 *Results of the X-ray diffraction analyzis of the sample No.1 from the slag AE24*

Identified minerals	Chemical formula
Fayalite	Fe_2SiO_4
Wüstite	FeO
Quartz	SiO_2
Diopside	$MgCaSi_2O_6$
Leucite	$K(AlSi_2O_6)$

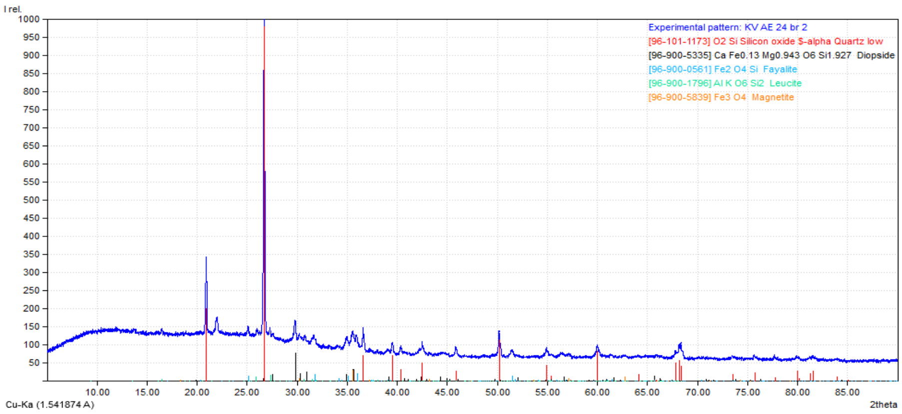


Fig. 9 *Diffractogram of the sample No.2 from the slag AE24*

Table 7 *Results of the X-ray diffraction analysis of the sample No. 2 from the slag AE24*

Identified minerals	Chemical formula
Quartz	SiO_2
Diopside	$MgCaSi_2O_6$
Fayalite	Fe_2SiO_4
Leucite	$K(AlSi_2O_6)$
Magnetite	Fe_3O_4

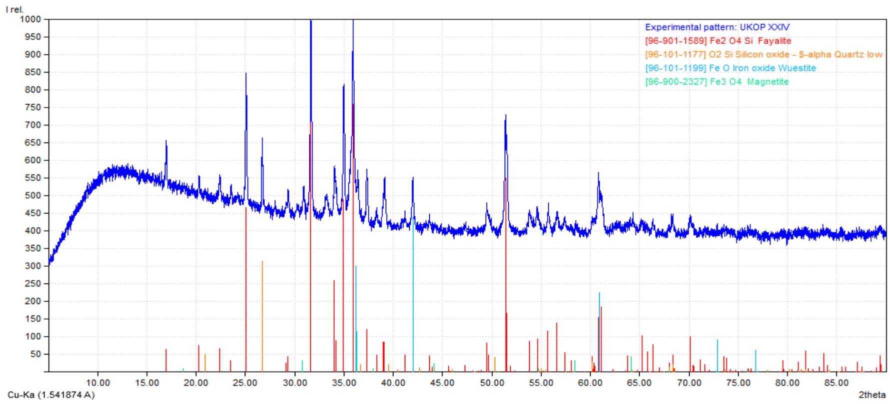


Fig. 10 *Diffractogram of the sample from the Burial pit XXIV*

Table 8 *Results of the X-ray diffraction analysis of the sample from the Burial pit XXIV*

Identified minerals	Chemical formula
Fayalite	Fe_2SiO_4
Quartz	SiO_2
Wüstite	FeO
Magnetite	Fe_3O_4

DISCUSSION OF THE RESULTS

The testing results of archaeometallurgical samples from the site Mali Grad-Todića crkva by the chemical analysis, X-ray diffraction testing and scanning electron microscopy, indicate the presence of wüstite, fayalite, magnetite and biotite in most of the samples. Analyzed samples are characterrized by a greater presence of iron slag, which means the production of iron with limited capacities, probably in so-called ovens (so-called "Grne"). Based on the X-ray diffraction analysis of the sample from Table 3 (Fig. 5), it can be concluded that the sediment of magnetite ore was used as the starting material for iron production, which in itself, due to the influence of time and conditions in the environment, contained the iron transformations such as: goethite, biotite, jarosite and wüstite.

The other samples relate to the slag, and the presence of fayalite Fe_2SiO_4, wüstite, FeO and magnetite, Fe_3O_4 and they indicate that the melting process, which incorporated these components into slag, did not allow complete reduction of ore (Fe_3O_4) into metal (Fe). In other words, the iron obtained from the ore (i.e. the degree of metal utilization), in qualitative terms, was not at a high level. The reason for this was probably the lower reduction temperature, whereby all iron oxides (Fe_3O_4, FeO) could not be reduced to the metal (Fe).

The presence of diphaside $MgCaSi_2O_6$ indicates that, as a solvent for lowering the SiO_2 melting point, a smaller amount of solvent in the form of dolomite $CaCO_3$ x $MgCO_3$ was most probably used.

2CaO x SiO_2, whose production requires a relatively higher temperature of iron reduction, is missed in a slag that according to the obtained results, was the demerit of a smelting process in Branicevo.

In the primary phase, iron was poured into the molds. After cooling, the content (metal and slag) was removed from the mold. The metal was further used, and a hardened slag, which was above metal, would retain the shape of the mold and was left aside. This is indicated by discovery of the slag in the shape of a mold from the Burial pit XXVII (Fig. 2).

Structures of archaeometallurgical samples from the site Mali Grad-Todića crkva, unambiguously indicate the primary iron metallurgy.

According to the qualitative characteristics of the analyzed samples, the casting process of obtaining iron from the ore in Branicevo was not at a high technological level, which is a general feature of the casting technologies at the other medieval sites. The main problem for the smelters in those times during the reduction process was the inability to achieve high temperatures [3,6,7].

From the perspective of today's technological processing, in the primary metallurgical processing, the iron needs to be heated to over 1535°C, in order to convert into a liquid state of honey density, which as such lies at the bottom of the casting furnace, which would then collapse, in order to reach the arched iron at the bottom. Archaeological discoveries of casting furnaces and other metallurgical installations from the ancient and medieval period indicate that in the process of iron dissociation, it was not possible to achieve such a high temperature [5,6].

The obtained iron, depending on the reduction process, was, to a greater or lesser extent, contaminated with slag (fuel residues, solvent), which was impossible to completely separate during the primary melting. The iron thus obtained (the so-called porous iron) was then subjected to the secondary metallurgical processing. The secondary reduction involves re-heating and forging, whereby the process of removing impurities, i.e. separating the iron from the slag, proceeded mechanically [3,7,8].

CONCLUSION

The results of physical and chemical analyses of archeometallurgical findings of research at the site Mali Grad-Todića crkva, obtained by the chemical analysis methods, scanning electron microscopy and X-ray diffraction tests, indicate that during the XI and XII century there was a smelting activity related to the iron metallurgy in Branicevo. This is evident from the structures of the samples with the presence of wüstite, fayalite and magnetite. The sediment of magnetite ore was identified as the starting material for obtaining iron.

The analytical methods confirmed the archeological assumptions based on a specific archaeological context with some archaeometallurgical elements and installa-tions due to devastation, were not enough to make precise conclusions about the function of the explored space.

Findings of slag are frequent occurrences in archaeological sites. They are usually the result of a secondary reduction, i.e. refining process, or successive heating and coating of crude iron. As mentioned, this is preceded by the phase of casting by the primary metallurgy process, where the casting pro-cess of the ore took place outside the residential territory [5,9].

Whether the smelting process of limited capacities in the medieval Branicevo was carried out within the fortification, i.e. area marked in Fig. 1 or in its immediate vicinity, perhaps below the during the XI and XII century, on the bank of the Dunavac, remains a dilemma that can be resolved only by the archaeological research and discovery of a melting furnace *in situ*.

On the other hand, the results show the significance of analysis of slag for defining the medieval smelting technologies and the level of knowledge of the smelters in those times, since the structural analysis of slag elements provide the important data on the final stage of smelting process [6,7,8].

The results received from a limited number of samples indicate the 'underdeveloped' technology and inability to achieve the required temperature in the process of thermal dissociation and iron extraction. However, the final conclusions about the character of the primary metallurgical process in Branicevo during the XI and XII century will be formed after analyzing a larger number of samples.

At the present level of research the site Mali Grad-Todića crkva, the presented results present the unambiguous proof of the primary iron metallurgy in Braničevo during the Byzantine Government and they represent a significant contribution to the knowledge of medieval mining in Serbia during the XI and XII century.

Also, the analysis of archaeometallurical samples from the site Mali grad-Todića crkva affirms the necessity of interdisciplinary research in order to solve numerous issues of ore origin, methods of supply, melting site location, metallurgical processes and defining the degree of iron metallurgy development in the medieval period.

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