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ASPECTS OF METALLURGICAL ACTIVITIES AT SITE ČOKA KAZAK (TIMOK REGION, EASTERN SERBIA)

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ABSTRACT

Results of physico-chemical investigations of slag occurrences from prehistoric site Čoka Kazak (Timok region, Eastern Serbia), obtained by using chemical analysis, XRD analysis, EDXRF spectroscopy, thermal analysis and optical microscopy, are presented in this paper and early activities in copper metallurgy in Bronze Age were proven.

Key words: archaeometallurgy, characterization, Čoka Kazak site

INTRODUCTION

It is well known that mining and metallurgical activities in Timok region (Eastern Serbia) have long history – from prehistory to nowadays. There are a lot of archaeometallurgical sites in this area (Fig.1), starting from Rudna Glava - prehistoric copper mine and iron mine in Roman period, and one of the earliest South-East identified and explored European mines [1-3]. All these sites are situated in the area of the Timok magmatic complex [4], where the great ore deposits of Serbia are located.

Site Čoka Kazak, located about 2.5 km north-east from Bor, presents archaeologically still not completely investigated site. Based on the collected ceramics findings from the surface, it has been preliminary dated to late Bronze Age (1300-1100 B.C.). So, that site could be included in the group of numerous archaeologically investigated (Trnjane, Kučajna, Bor Lake) or just registrated (Hajdučka česma, Čokanjica) sites near Bor from this period. Occurrences of slag are very often at all these sites and point out to early metallurgical activities in this region, which were already confirmed at most of the mentioned sites [5].

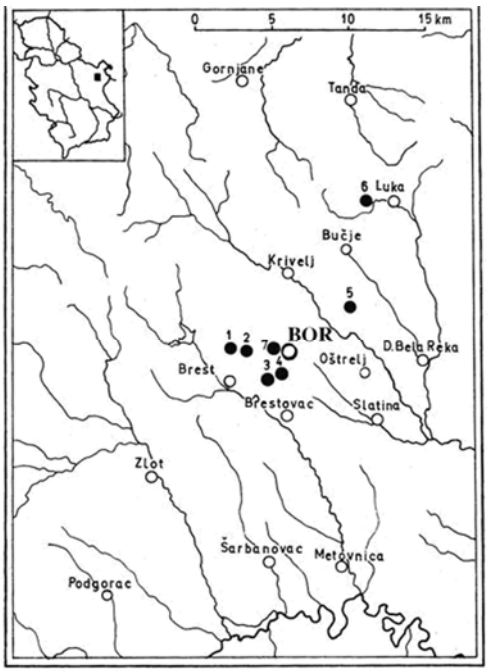


Fig.1 - Archaeometallurgical sites in Timok region, Eastern Serbia [4], (1 – Trnjane; 2 – Trnjane II; 3 – Čokanjica; 4 – Kučajna; 5 – La Štubej; 6 – Kej III; 7 - Čoka Kazak)

Analysis of bronze findings [6], slag and ceramic material [7] from Trnjane (settlement and necropolis, about 4km west from Bor, near Brestovac Spa), one of the most completely investigated sites in this region, showed use of sulphide copper and iron ores and pointed out to mining activity near the site, probably at the area of Bor ore deposit [8, 9].

In recent references on Bronze Age in Timok region, sites located in this region have been presented as new, separate culture from this prehistoric period, called Gamzigrad culture [10, 11].

In order to make further contribution to better knowledge of early metallurgical activities in Timok region in Bronze Age, archaeometallurgical findings from Čoka Kazak, have been considered. Since slag occurrences from this prehistoric site have not been investigated yet [12], different physico-chemical methods were used for their characterization and the results of these investigations are presented in this paper.

EXPERIMENTAL

Samples Five samples (ČK1 - ČK5) of slag origin from Čoka Kazak site were used for the experimental investigation. Photographs of investigated samples are given in Fig.2.

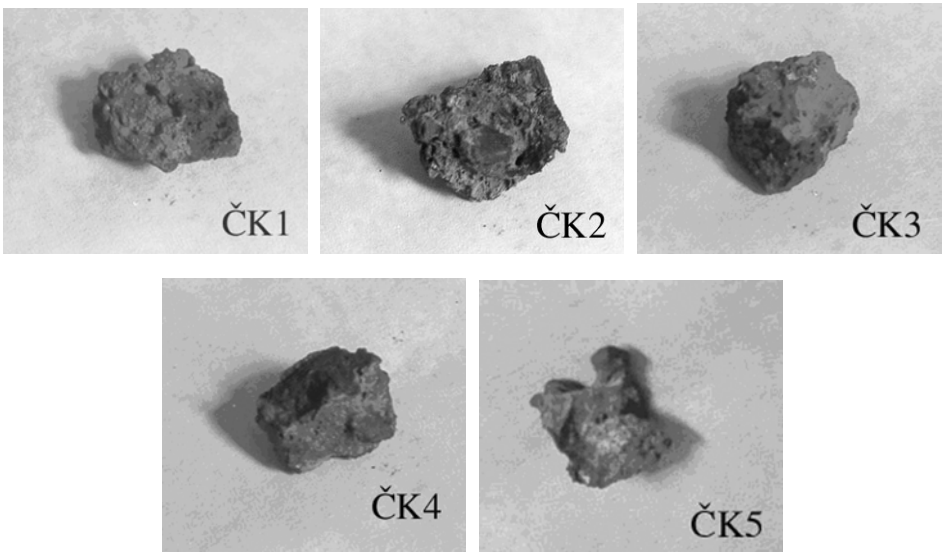


Fig.2 - Photographs of investigated samples (ČK1 - ČK5) from Čoka Kazak site

Those slag samples could be macroscopically described as monolithic, possessing compact structure with not so significant porosity. Dark, black-gray and metallic-gray color is typical at the fractures of most samples, as well as polimetallic brightness. The slag fragments about 5-10cm in size, with no local traces of the ground and no remnants of charcoal and flux.

Techniques For the experimental investigations presented in this paper, following experimental techniques were used: chemical analysis, XRD analysis, EDXRF spectroscopy, thermal analysis and optical microscopy.

Chemical analysis was done using optical emission spectrograph apparatus Jarrell-Ash with microphotometer (model 70.000)) and by standard gravimetric method, also. X-ray diffraction analysis was performed at Siemens apparatus with Cu-anticathode and Ni-filters, with 40kV and 20mA. Energy dispersive X-ray fluorescence spectroscopy was done at Canberra apparatus, using Cd-109 (22.1 keV, activity 740 MBq) radio-isotope for the excitation. DTA-TG-DTG analysis was performed at Derivatograph MOM (Budapest, Hungary) with heating rate of 10^{o}/min up to the maximum temperature of 1000^{o}C. Optical microscopy was performed on apparatus Reichert MeF2.

RESULTS

Results of the chemical analysis, done by optical emission spectrography for the investigated samples (ČK1 - ČK5) from Čoka Kazak site, are given in Table 1. Also, iron content was determined in samples ČK1 and ČK5 by standard gravimetric method and is found to be 32.86% and 24.12%, respectively.

Presence of copper, which is greater than 1% in most of the investigated samples, as well as presence of other non-ferrous metals (lead, tin, silver, nickel, *etc*.), points out to the slag of copper metallurgy. Also, it can be noticed that

mass presence of some components differs from sample to sample, while for some elements, e.g. Mg, Co, Mo, Ag such presence is almost constant for all investigated samples.

Table 1 - Results of chemical analysis (samples ČK1 - ČK5)

Sity:	ČOKA - KAZAK							
Element (%)	Cu	Ag	Ti	Ni	Sn	Pb	Cr	Ba
ČK1	>1	0,001	0,17	0,010	0,0068	0,02	0,0095	0,18
ČK2	0,027	0,002	0,24	0,064	<0,001	0,005	0,056	0,1
ČK3	>1	0,001	0,12	0,01	0,009	0,0064	0,006	0,1
ČK4	>1	<0,001	0,17	<0,01	0,006	0,006	<0,003	0,3
ČK5	0,20	<0,001	0,007	<0,01	<0,001	<0,001	<0,003	0,16
ČK6	>1	<0,001	0,1	<0,01	0,0027	0,0027	0,004	0,3

Sity	ČOKA - KAZAK							
Element (%)	Mn	V	Mo	Co	Ca	Mg	Sb	Ge
ČK1	0,042	0,03	0,001	<0,003	0,45	<0,003	<0,01	0,002
ČK2	0,014	0,024	0,015	<0,003	>1	<0,003	<0,01	<0,003
ČK3	0,014	0,025	0,01	<0,003	0,19	<0,003	<0,01	0,005
ČK4	0,007	0,024	0,01	<0,003	0,2	<0,003	<0,01	0,003
ČK5	0,0072	0,009	0,01	<0,003	0,008	<0,003	-	-
ČK6	0,0062	0,02	0,01	<0,003	0,14	<0,003	-	<0,003

Typical X-ray diffraction diagram for the sample ČK1 is shown in Fig.3, while DTA-TG-DTA curves for the same sample are given in Fig.4.

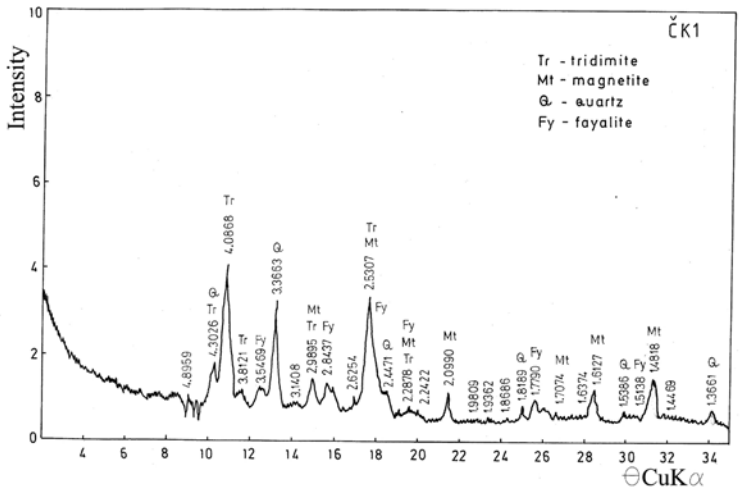


Fig.3 - X-ray diffraction diagram (sample ČK1)

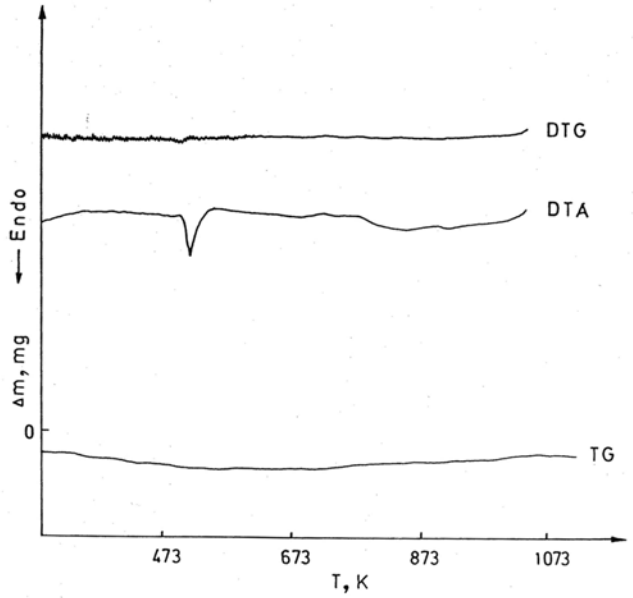
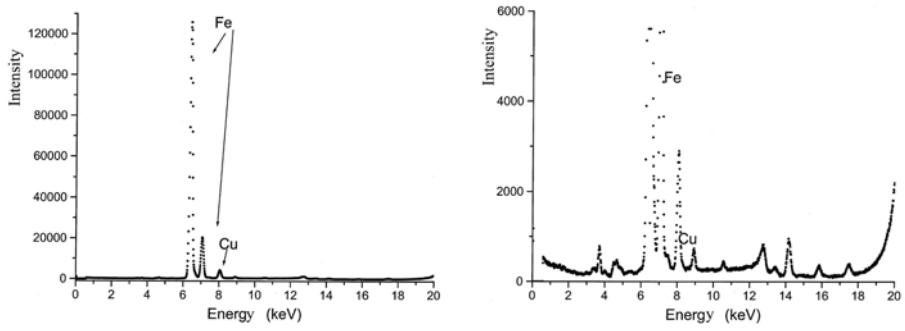


Fig.4 - DTA-TG-DTG curves at 10^o/min (sample ČK1)

Site Čoka Kazak, located about 2.5 km north-east from Bor, presents archaeologically still not completely investigated site. Based on the collected ceramics findings from the surface, it has been preliminary dated to late Bronze Age (1300-1100 B.C.). So, that site could be included in the group of numerous archaeologically investigated (Trnjane, Kučajna, Bor Lake) or just registrated (Hajdučka česma, Čokanjica) sites near Bor from this period. Occurrences of slag are very often at all these sites and point out to early metallurgical activities in this region, which were already confirmed at most of the mentioned sites [5].



a) *b)*

Fig.5 - EDXRF spectra for samples ČK1(a) and ČK5(b)

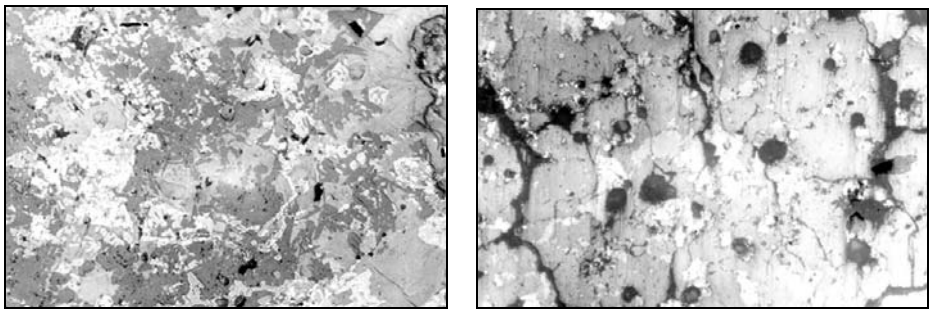
It should be mentioned that presence of huge peaks for iron led to the appearance of SE (Single Escape) peaks, which fall into the area of titanium and

vanadium occurrence and make difficult their identification and quantification, in this case.

Table 2 - Results of EDXRF spectroscopy

Element, X-line integration limits	ČK1 sample	ČK5 sample	Element, X-line integration limits	ČK1 sample	ČK5 sample
Fe ($K_{\alpha 12}$) – 6.398keV 6.1011 - 6.8167 keV	1994337 ± 1431	1477897 ± 1232	Mo($K_{\alpha 12}$)–17.441keV 17.1327–17.848 keV	6298 ± 128	6437 ± 130
Fe ($K_{\beta 13}$) – 7.057keV 6.8498 – 7.2681 keV	294225 ± 589	219102 ± 510	Sr ($K_{\alpha 12}$)–14.140keV 13.8849-14.4244 keV	4823 ± 120	15584 ± 157
Cu ($K_{\alpha 12}$) – 8.040keV 7.7966 – 8.3030 keV	61770 ± 298	40819 ± 242	Rb($K_{\alpha 12}$)–13.373keV 13.1362-13.6537 keV	4875 ± 134	2500 ± 110
Cu ($K_{\beta 13}$) – 8.904keV 8.7654 –9.0627 keV	6324 ± 152	4369 ± 121	Zr ($K_{\alpha 12}$)–15.744keV 15.4813-16.1088 ke	2542 ± 97	4571 ± 112
Mn($K_{\alpha 12}$) – 8.894keV 5.7158 – 6.0571 keV	0	0	Pb($L_{\alpha 12}$)–10.541keV 10.2077-10.8573 keV	5131 ± 176	3138 ± 138
Ca ($K_{\alpha 12}$) – 3.690keV 3.5689 – 3.8441 keV	2527 ± 108	5509 ± 111	Pb ($L_{\beta 12}$)–12.628keV 12.3986-12.9384 keV	18077 ± 226	9597 ± 173

Typical microphotographs for the samples ČK1 and ČK5 are shown in Fig.6.



a) *b)*

Fig. 6 - Results of the optic microscopy
(Enlargement: x144- ČK1 (a) and x72 - ČK5 (b))

Presence of the great quantity of very large crystals of light-gray phase could be noticed in the non-homogenous structure. According to the results obtained by different methods, it could be supposed that it correspond to the metastabile α-tridimite. Also, crystals of irregular shapes could be seen, as well as the occurrence of black phase, presented in spheric shape, and mostly polygonal white phase. Having in mind the complexity of the investigated samples, it is difficult to give more detailed explanation of such results without the application of some other analytical methods.

DISCUSSION OF RESULTS AND CONCLUSION

According to the results of the experimental investigations obtained by presented techniques, following conclusions could be made:

- No samples of ore, remains of furnaces and metallurgical fuel were found at investigated site Čoka Kazak, only numerous slag fragments. Since deposits and occurrences of sulphide ore exist in this part of terrain, it can be assumed that ore from local sources was used. The other conditions for metallurgical activities were very good, due to the existence of water and woods at this locality.

- The content of copper and other non-ferrous metals in the investigated samples, as well as the iron content distributed into fayalite and magnetite, indicate to the activities in copper metallurgy.

- It could be proposed that reduction smelting was used for melting of probably local ore sources, concerning that copper metallurgy in this part of Europe is proven already in that period in the example of numerous archaeological localities near Bor [6-9].

- The mineral contents of investigated slag samples correspond to the area of fayalite slag (which melts in the temperature interval 1100-1200^{o}C), in which phases of tridimite and fayalite occur. Occurrence of quartz and magnetite as separate phases, points out to the application of primitive furnaces in which there was no homogenization of the melt.

- Used furnaces probably were not closed completely, influencing oxidation of the part of FeO by oxygen from air at one hand, and remaining quartz as separate phase at the other hand.

- Copper content in some investigated samples is greater than 1%, which points out that there was no possibility for the complete separation of slag from matte in such furnaces.

- It can be supposed that quartz sand was used as the flux during the melting process, while charcoal was probably used as a fuel.

- Compaction of the investigated slag samples may point out that melted mass was thrown out from the furnace gradually in small quantities. During the exhaust it was much warmer and more liquid, with less viscosity, which enable gas flow from the upper part.

- Also, since there are no remnants of the ground in it, one can conclude that slag was probably poundered to the prepared place or ladle.

All these results and conclusions, obtained for the site Čoka Kazak near Bor, presents a contribution to a better knowledge of early metallurgical activities in Timok region in Bronze Age and may enable further confirmation of prehistoric Gamzigrad culture in this region.

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