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PHYSICO-CHEMICAL INVESTIGATION OF SLAG OCCURRENCES
Rgotski Kamen Timok region, Eastern Serbia

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Abstract

Results of physico-chemical investigations of slag occurrences from site Rgotski Kamen (Timok region, Serbia), obtained by using chemical analysis, XRD analysis, EDXRF spectroscopy, thermal analysis, mass spectrometry and optical microscopy, are presented in this paper.

Keywords: archaeometallurgy, characterization, Rgotski Kamen site

Introduction

Among numerous sites in Timok region, there is a site Rgotski Kamen, with defense wall remains of smaller fortification from the Roman period, located about 12.5 km from Bor, Fig. 1. A lot of different researchers have been interested in that site for about 150 years [1], although it has not been completely archaeologically investigated.

Extraordinary geostrategic position of the fortification (built at the plateau of the lime mountain-ridge over deep Crna reka river and accessible only from the southern side) enabled its inhabitants to control important road communications in Roman period. Namely, by road going near the rivers Beli and Veliki Timok one reached village Rgotina (about 3.5 km south-eastern from site), where crossroad led to three different sides: first – to Aqua (Prahovo) and Bononia (Vidin, Bulgaria), second – to Taliata (Donji Milanovac) and third – to Roman mines at Tilva Roš (near Bor) and other mining centers along river Pek at the north-west [2, 3].

Dating of numerous accidental findings of movable material from site Rgotski Kamen corresponds to the findings from Rgotina site, where settlement from II to III cen-

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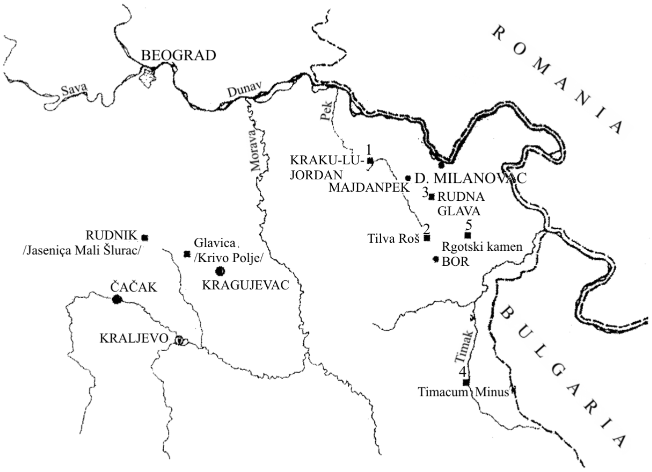

Fig. 1 Archaeometallurgical sites in Timok region (Eastern Serbia) in the Roman period 1 – Kraku lu Jordan; 2 –Tilva Roš; 3 –Rudna Glava; 4 – Timacum Minus; 5 – Rgotski Kamen

tury A. D. and necropolis from IV century A. D. were archaeologically dated [4]. Also, supposition that some late-antique settlements and castels lasted up to VI century A. D. (which influenced presumption about localization of Argentares [5], one of the fortifications among reconstructed castels near village Rgotina in Justinian time, noted in written sources), was confirmed by new findings from Rgotski Kamen.

Beside archaeological findings, mostly ceramics dated to VI century A. D. numerous slag occurrences and different metal objects were found at mentioned locality. Since these metal findings from Rgotski Kamen site have not been investigated yet [6], different physico-chemical methods were used in order to characterize them and the results of these investigations are presented in this paper.

Experimental

Samples

Five samples (RK1–RK5) from Rgotski Kamen site were used for the experimental investigation. Typical photographs of the investigated samples are given in Fig. 2.

The samples RK1, RK2, RK4 and RK5 could be macroscopically described as porous slag of heterogeneous structure, dark-brown colored with some red nuance, which probably responds to oxide iron phases formed by weathering. The slag fragments are very easy, about 5–20 cm in size, irregularly shaped, with numerous traces of the ground remnants. Sample RK3 is found at the locality split in two monolithic parts of regular shape, also dark-brown colored, and with low metallic brightness at the fractures.

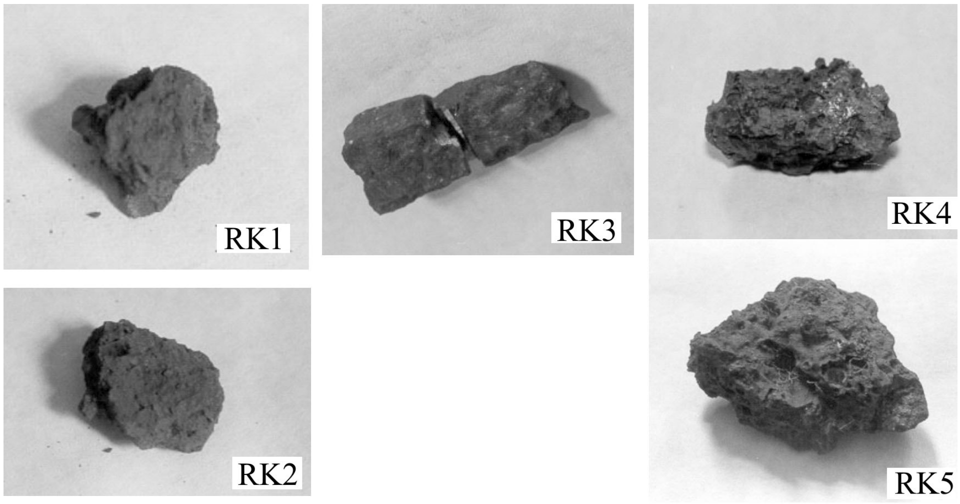

Fig. 2 Photographs of RK1–RK5 samples from Rgotski Kamen site

Techniques

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

Chemical analysis was done using optical emission spectrography at apparatus Jarrell Ash with microphotometer model 70.000) and by standard gravimetric method. X-ray diffraction analysis was performed at Siemens apparatus with Cu-anticathode and Ni-filters, with 40 kV and 20 mA. 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 (Hungary) with heating rate of 10°C min^{-1} up to maximum temperature of 1000°C. Mass spectrometry was carried out by spectrometer JMS-O1BM-2 Spark Source Mass Spectrometer (Jeol, Japan). Optical microscopy was performed on apparatus Reichert MeF2.

Results

Results of the chemical analysis of the investigated samples (RK1, RK2, RK4, RK5) from site Rgotski kamen are given in Table 1, while results of mass spectrometry for sample RK3 are presented in Table 2. Also, iron content in samples RK1 and RK5 was determined by standard gravimetric method and is found to be 50.63 and 64.68%, respectively.

Obtained results of the chemical analysis point out to the main presence of iron in the investigated samples RK1, RK2, RK4 and RK5, relatively high percent of cal-

Table 1 Results of chemical analysis (samples RK1, RK2, RK4, RK5)

	Element content/%											
Sample	Cu	Ag	Ti	Ni	Pb	Cr	Ba	Mn	V	Mo	Co	Ca	Mg
RK1	0.015	<0.001	1	0.010	0.001	0.0076	0.04	0.30	0.11	0.001	0.003	>1	<0.003
RK2	0.01	<0.001	0.47	<0.001	0.001	0.014	0.04	0.2	0.11	0.001	0.008	>1	<0.003
RK4	0.02	<0.001	0.14	<0.001	<0.001	0.014	0.04	0.2	0.11	0.001	0.008	>1	<0.003
RK5	0.037	<0.001	0.53	0.001	<0.001	0.012	0.04	0.23	0.072	0.004	<0.003	>1	<0.003

Table 2 Results of mass spectrometry (sample RK3)

Element	%	Element	%	Element	%
*Fe	99.9	Ge	ND	Nd	ND
Li	Qual.	As	0.001	Sm	ND
Be	ND	Se	ND	Eu	ND
B	0.00002	Br	ND	Gd	ND
F	0.02	Rb	ND	Tb	ND
Na	0.009	Sr	0.0001	Dy	ND
Mg	0.02	Y	ND	Ho	ND
Al	Qual.	Zr	ND	Er	ND
Si	0.04	Nb	ND	Tm	ND
P	0.01	Mo	ND	Yb	ND
S	0.007	Ru	ND	Lu	ND
Cl	0.002	Rh	ND	Hf	ND
K	0.09	Pd	ND	**Ta	ND
Ca	0.07	Ag	ND	W	ND
Sc	ND	Cd	ND	Re	ND
Ti	0.007	In	ND	Os	ND
V	0.004	Sn	Qual.	Ir	ND
Cr	0.001	Sb	Qual.	Pt	ND
Mn	0.01	Te	ND	Au	ND
Fe	–	I	ND	Hg	ND
Co	0.004	Cs	ND	Tl	ND
Ni	ND	Ba	Qual.	Pb	Qual.
Cu	0.02	La	ND	Bi	ND
Zn	ND	Ce	ND	Th	ND
Ga	0.001	Pr	ND	U	ND

Obtained by standard chemical analysis
Qual. – Only qualitative presence determined
ND – not detected element

cium, titanium, manganese and vanadium and low percent of chromium, cobalt and nickel. Considering the sample RK3, chemical qualitative analysis shows main presence of iron and manganese, and chromium and nickel in traces, which is in accordance to the results of mass spectrometry.

Typical X-ray diffraction diagram for the sample RK1 is shown in Fig. 3, while DTA-DTG curves for the same sample are given in Fig. 4.

According to obtained XRD recordings, identification of the mineralogical composition was done and main presence of magnetite, wüstite, hematite and quartz was determined for investigated samples. Results of thermal analysis, given for sam-

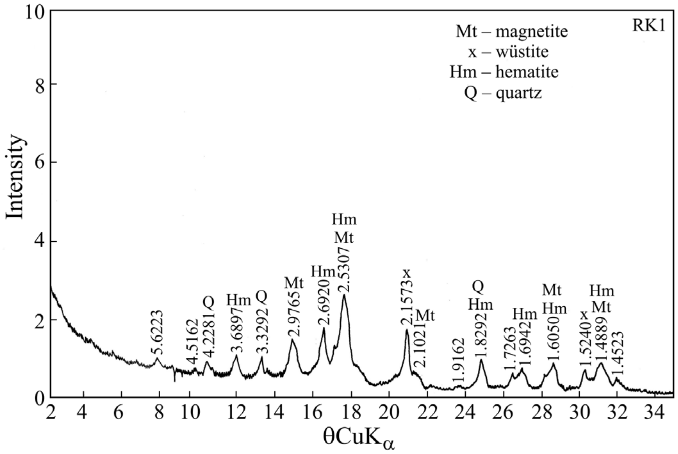

Fig. 3 X-ray diffraction diagram (sample RK1)

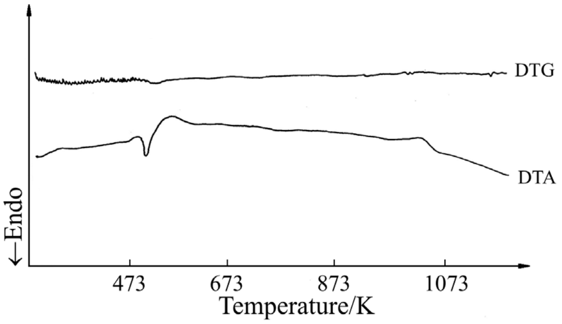

Fig. 4 DTA-DTG curves at 10°C min^{-1} (sample RK1)

ple RK1, show one endothermic peak at 510 K and slight exothermic peak at 1035 K, which probably correspond to the SiO_2 phase transition [7] and transformation of $(\beta\rightarrow\gamma)Fe_2O_3$, respectively [8].

EDXRF spectra obtained for the samples RK1 and RK5 are presented in Fig. 5, while peak areas, corresponding errors and X-lines values are given in Table 3.

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.

Typical microphotographs for the samples RK1 and RK5 are shown in Fig. 6.

Presence of light-gray phase, in the form of cell or dendritic crystals, is mostly noticeable in the structure of the investigated samples and it probably corresponds to the wüstite phase. Great quantity of such wüstite occurs in the base of gray-phase, with random, but rare appearance of white phase, for which could be supposed that correspond to the metallic iron. Dark fields presented in the microphotographs are probably due to the pores in the samples.

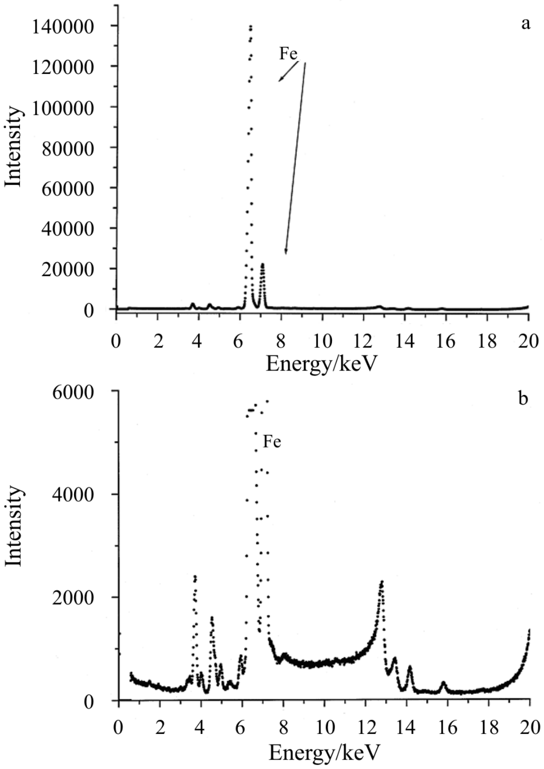

Fig. 5 EDXRF spectra for samples a – RK1 and b – RK5

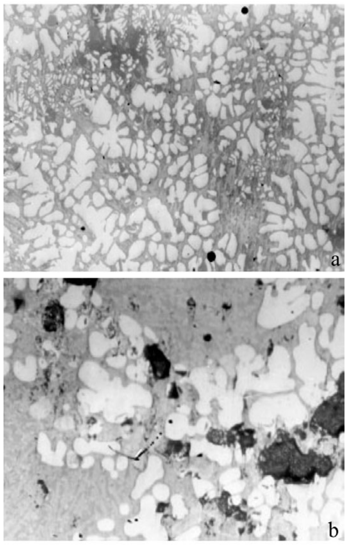

Fig. 6 Results of the optic microscopy (Enlargement: a – x144 – RK1 and b – x72 – RK5)

Table 3 Results of EDXRF spectroscopy for samples a – RK1 and b – RK5

Element, X-line integration limits	RK1	RK5 sample
Fe($K_{\alpha12}$)–6.398 keV 6.1011–6.8167 keV	2217477±1508	2699235±1664
Fe($K_{\beta13}$)–7.057 keV 6.8498–7.2681 keV	319265±615	388466±678
Cu($K_{\alpha12}$)–8.040 keV 7.7966–8.3030 keV	2050±169	1708±196
Cu($K_{\beta13}$)–8.904 keV 8.7654–9.0627 keV	–	195±139
Mn($K_{\alpha12}$)–8.894 keV 5.7158–6.0571 keV	7038±137	5490±136
Ca($K_{\alpha12}$)–3.690 keV 3.5689–3.8441 keV	23845±196	20300±185
Mo($K_{\alpha12}$)–17.441 keV 17.1327–17.848 keV	2073±110	248±102
Sr($K_{\alpha12}$)–14.140 keV 13.8849–14.4244 keV	10499±137	8828±135
Rb($K_{\alpha12}$)–13.373 keV 13.1362–13.6537 keV	6008±140	8759±166
Zr($K_{\alpha12}$)–15.744 keV 15.4813–16.1088 keV	8305±128	3789±111
Pb($K_{\alpha12}$)–10.541 keV 10.2077–10.8573 keV	–	771±209
Pb($K_{\beta12}$)–12.628 keV 12.3986–12.9384 keV	17637±238	26280±289

Discussion of results and conclusions

According to obtained experimental results of the physico-chemical investigations, following conclusions about the antique activities in iron metallurgy at Rgotski kamen site could be made:

- No samples of ore, remains of furnaces and metallurgical fuel were found at investigated site Rgotski kamen, only numerous slag fragments and rarely metal objects. The conditions for metallurgical activities at this locality were very good, due to the existence of water and woods.
- Iron metallurgy is proven based on the high content of iron in the form of hematite, magnetite and wüstite and low content of non-ferrous metals (Cu, Zn, Pb) in the investigated samples.
- It could be supposed that smelting process was done with presence of CaO flux, using wood and charcoal as the fuel.

- Since presence of fayalite has not been determined in the samples, obviously the reduction process was done at lower temperatures.
- According to the low content of phosphorus and sulfur, it can be supposed that very rich iron oxide ore and very clean, related to impurities, was used as the raw material.
- Having in mind that there are occurrences of such oxide iron ores, especially limonite, in the vicinity of this locality, one may conclude that local ores were used for the production. There are references in [9] about processing of limonite ores in Majdanpek, near Bor, in antique period, which confirm that conclusions.
- Great porosity of the investigated slag samples may be due to the separation of gas, formed by combustion of wood and charcoal from the melt.
- Also, since there are remnants of the ground in slag samples, the slag was robably poundered from furnace to the ground directly.

It has to be mentioned that physico-chemical characterization as an approach to the investigation of ancient findings and objects is of a great importance in the field of archaeometry, as was already proved in recent references [10, 11].

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