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SEM investigation of minor constituents of carbide materials prepared from shungite rocks

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Abstract. **The "SiC–Al_2OC"-based composite prepared from Karelian shungite rocks has been studied by X-ray diffraction analysis and scanning electron microscopy. SEM investigation has been done to determine the mode and distribution of admixture constituents. It is found that the most common minor phase represents Al–Fe–Si–C-based alloys. Special attention has been given to describing the noble metals admixtures. It is revealed that the noble metals phases occur as separate microsized grains, most of which have been indicated as Au–Ag–Hg amalgam and rarely as Pt-rich compounds. The obtained data can be mainly used to advance technologies for manufacturing carbide-based composite materials from natural carbonaceous rocks.**

Keywords. **Shungite rocks; thermal processing; carbide materials; SiC–Al_2OC; admixtures; noble metals.**

1. Introduction

Shungite is a black, precambrian poorly crystalline mineraloid composed mainly of a natural mixture of amorphous carbon and silicate minerals, mainly quartz, alkali aluminosilicates, and ferruginous silicates. These carbonaceous rocks are widespread over the entire eastern Baltic Shield and are best preserved in large quantities in the Lake Onega region, Karelia, NW Russia (Sokolov *et al* 1984; Volkova and Bogdanova 1986; Buseck *et al* 1997; Filippov 2002; Melezhik *et al* 2004).

Thanks to the discovery of natural fullerene-like structures in shungite carbon (Buseck *et al* 1992; Parthasarathy *et al* 1998), these rocks attracted the World attention. Over the last decade, shungite have actively been studied by many researchers (e.g. Kalinin *et al* 1999; Grigor'eva and Rozhkova 2000; Kovalevski *et al* 2001; Rozhkova 2002; Parthasarathy and Vairamani 2003; Cascarini de Torre *et al* 2004; Charykov *et al* 2005; Yefremova 2005; Kwiecinska *et al* 2007; Polonskii *et al* 2007; Strakhov 2008), who examined its physicochemical characteristics as well as ability and reasonable means to use the same for various purposes. So it was revealed that the shungite rocks are natural "agglomerated" charging materials in which carbon forms a strong matrix permeated by a finely dispersed silicate skeleton with a highly developed contact surface. Due to favourable chemical composition which is close to the stoichiometric ratio for reactions (1) or (2), shungite rocks of the medium-carbonaceous variety are very suitable as a raw material for silicon-bearing ferroalloys and silicon carbide production.

$$\{SiO_2 + 2C\}^{shungite} \rightarrow Si + 2CO\uparrow, \quad (1)$$

$$\{SiO_2 + 3C\}^{shungite} \rightarrow SiC + 2CO\uparrow\ . \quad (2)$$

In turn, our tentative estimations and trial experiments show that a shungite of the high-carbonaceous variety has technological advantage over medium-carbonaceous rocks to produce some SiC-containing composites. For example, SiC–Al_2OC composite materials in such case could be prepared according to the following double-step scheme:

$$\{SiO_2 + 9C\}^{shungite} \rightarrow \{SiC + 6C\} + 2CO\uparrow, \quad (3)$$

$$\{SiC + 6C\} + 2Al_2O_3 \rightarrow \{SiC + 2Al_2OC\} + 4CO\uparrow\ . \quad (4)$$

It can become economically prospective and technically effective if some requirements could be fulfilled viz. (i) a weight loss due to volatilization of intermediate products such as SiO and Al_2O must be decreased and (ii) admixtures remaining from raw material must be under control because they affect characteristics of end-products and hence their potential of use. The second requirement needs to gather analytical information on the structural and compositional transformation of shungite during thermal processing. Although the literature related to this subject is extensive (Kalinin *et al* 1999; Kholodkevich *et al* 1999; Nikitin *et al* 2007; Polonskii *et al* 2007), behaviour of the minor and accessory phases has not been sufficiently described. We also found no relevant data on purity of products obtained by the heat

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treatment of shungite. This fact encouraged us to report the results of our research done to determine the mode and distribution of admixtures in the carbide materials prepared from Karelian shungite rocks.

2. Experimental

Shungite rocks of high-carbonaceous variety containing the following principal components of chemical composition (wt.%): C, 62·0; SiO_2, 33·3; Al_2O_3, 1·94; Fe_2O_3/FeO, 1·18, were thermally treated at 1600°C for 1 h to produce SiC–C composite (hereinafter referred to as 'carbidized shungite'). After being ground to powder, synthesized material was mixed with alumina ("Vecton", Russia, TU 6-09-426-75) in a weight ratio of 1:1 which is close enough to the reaction (4) stoichiometry. Prepared powder was compacted into pellets of 20 mm in diameter and 15 mm in thickness which were heated up to 1700°C for 2 h annealing time. Both heat treatment processes were carried out in the electric resistance furnace under inert gas (argon) atmosphere at a stagnant pressure of about 15 psi. Stabilization of the pressure level in reaction zone has been achieved by removing gaseous products from furnace chamber.

The prepared materials were analysed by techniques of powder X-ray diffraction and scanning electron microscopy. X-ray diffraction (XRD) data were collected over a 2θ-range of 10°–80° with a step size of 0·05° at a scan speed of 1 °/min on a Shimadzu XRD-6000 diffractometer using Ni-filtered Cu radiation operating at 30 kV and 30 mA. Imaging and compositional analysis were performed using scanning electron microscope JEOL JSM-6400 equipped with an X-ray energy dispersive system (SEM/EDS) operating at 20 kV and sensitive to elements with atomic numbers from Na to U.

3. Results and discussion

3.1 *Major phase composition*

Through experimental investigation, we have really found that according to reaction (3) the thermal treatment of shungite rocks of high-carbonaceous variety leads to formation of poorly sintered material (carbidized shungite) consisting of intimate mixtures of silicon carbide and slightly graphitized carbon. The XRD pattern of the prepared sample shown in figure 1a points to the presence of a cubic (3C) polytype of SiC as major crystalline phase and also hexagonal (2H) polytype of SiC and iron silicide (FeSi) as minor ones. Thus, obtained results are compared with data presented in the literature (Kalinin *et al* 1999; Kholodkevich *et al* 1999).

As we have already noted, the carbidized shungite may be used to produce various carbide materials viz. our experiments demonstrated that the thermal treatment of mixture of carbidized shungite and alumina leads to the formation of multiphase "SiC–Al_2OC"-based composite cake. XRD pattern shown in figure 1b indicates the composition of major phases in prepared material. Predictably, we have found elemental silicon, both cubic (3C) and hexagonal (6H) polytypes of SiC, and silicon carbide solid-soluted with aluminum oxycarbide – $(Si_{1-x}Al_x)_2C_{2-x}O_x$. Furthermore,

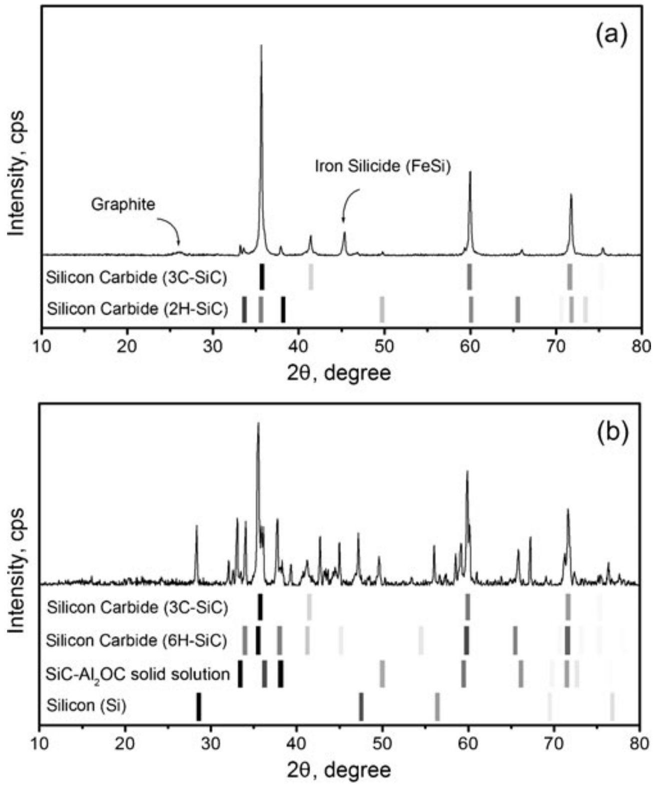

Figure 1. XRD patterns of thermally treated high-carbon shungite rock (**a**) and carbide composite powder prepared from a mixture of carbidized shungite and alumina (**b**). Reference XRD stick patterns for identified major phases are shown at bottom.

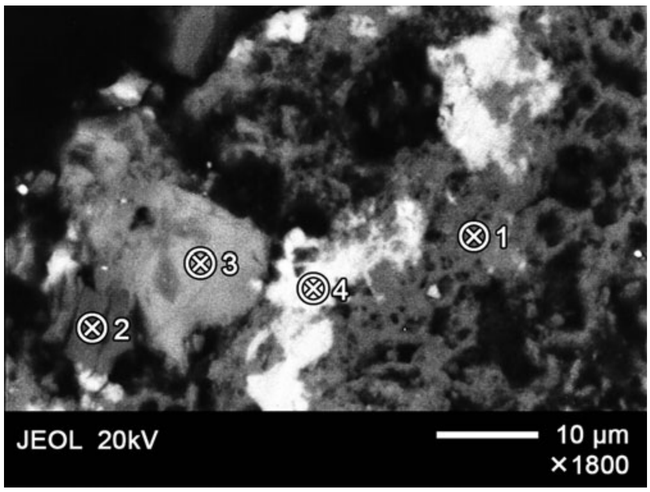

Figure 2. SEM micrograph of carbide composite powder prepared from a mixture of carbidized shungite and alumina. Analysis of EDS spectra from marked points is given in table 1.

Table 1. Microchemical analysis of carbide composite material prepared from a mixture of carbidized shungite and alumina.

Point[a]	Elemental composition (EDS data)[b] (wt.%)	Probable identification
1 [2]	Si – 48·7, Al – 21·5, Fe – 4·4, (C/O) – 25·4	Silicon aluminum oxycarbide
2 [2]	Si – 71·8, (C/O) – 28·2	Silicon carbide
3 [2]	Si – 99·6, Al – 0·4	Silicon
4 [2]	Si – 24·3, Al – 39·5, Fe – 25·9, (C/O) – 10·3	Al–Fe–Si–C alloy
5 [3a]	Si – 3·2, Al – 1·2, Fe – 71·9, (C/O) – 23·7	Iron carbide
6 [3b]	Ti – 60·8, Al – 3·1, Fe – 0·2, Si – 0·5, (C/O) – 35·4	Lower titanium oxide
7 [4a]	Au – 64·5, Ag – 5·7, Cu – 1·7, Hg – 17·8, Si – 2·1, Al – 1·3, Fe – 1·4, (C/O) – 5·5	Au–Hg amalgam and Al–Fe–Si–C alloy traces
8 [4b]	Pt – 44·8, Ir – 3·2, Rh – 0·8, Au – 4·2, Cu – 0·5, S – 0·9, Si – 1·4, Al – 0·4, Fe – 4·1, (C/O) – 39·7	PGE compound and Al–Fe–Si–C alloy traces
9 [5a]	Si – 4·6, Al – 20·3, Fe – 0·6, Cu – 39·4, S – 12·4, (C/O) – 22·7	Al–Si–Cu–S alloy
10 [5b]	Ba – 52·9, S – 12·5, (C/O) – 34·6	Barium sulfide

[a]Bracketed numbers refer to corresponding figures; [b]considerable measurement errors may have occurred because of high roughness of specimen surface.

some other compounds which are probably similar to intermetallic alloys were also detected as minor phases.

Obtained XRD data have been confirmed by SEM/EDS analysis. Indeed, it can be seen from figure 2 and table 1 that the prepared material generally comprises phases that are compositionally close to such substances as Fe-doped Si–Al–oxycarbides (point 1), silicon carbide (point 2), Al-doped silicon (point 3), and Al–Fe–Si–C-based alloys (point 4).

3.2 *Iron and titanium distribution*

Both reactions (3) and (4) are accompanied by the formation and subsequent active removal of CO and some value of other volatile intermediate products such as SiO and Al_2O. Since the iron and titanium are less subject to volatilization, their average content in prepared material is found to be appreciably increased. So it was revealed that Fe and Ti are the most common impurities in the major carbide constituents. But they are dominantly distributed within Al–Fe–Si–C-based alloys (point 4), iron carbides (point 5), and some other compounds such as intermetallics or lower oxides (point 6) forming individual microsized grains and agglomerates which are different in shape and size. The SEM images specially focused upon the representatives of ferruginous and titaniferous phases as shown in figure 3.

3.3 *Noble and heavy metals distribution*

From literature it is known that Karelian shungite rocks contain some amount of noble metals. For instance, content of gold in samples from the Maksovo deposit is equal to 9 mg/ton (Filippov 2002). Even though after extensive removal of substance during heat treatment, noble metals generally remain in the end-product. Apparent manifestations of Au, Pt, Ag, Ir, Rh in prepared material are shown in figure 4. So, Au-rich admixtures are found to be separate

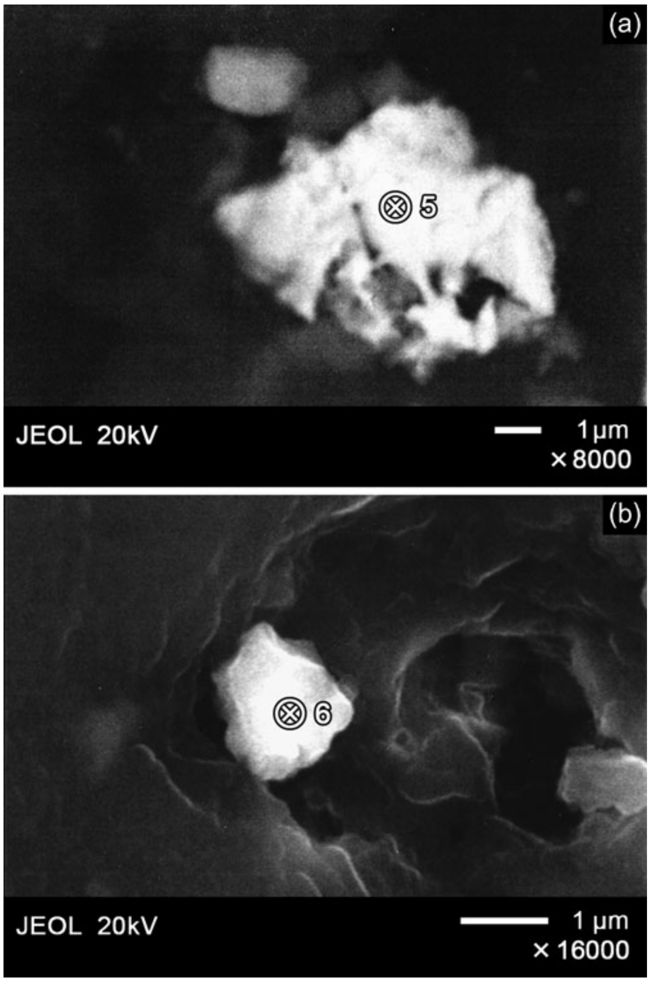

Figure 3. SEM micrographs of ferruginous and titaniferous admixtures occurring in carbide composite powder prepared from a mixture of carbidized shungite and alumina. Analysis of EDS spectra from marked points is given in table 1.

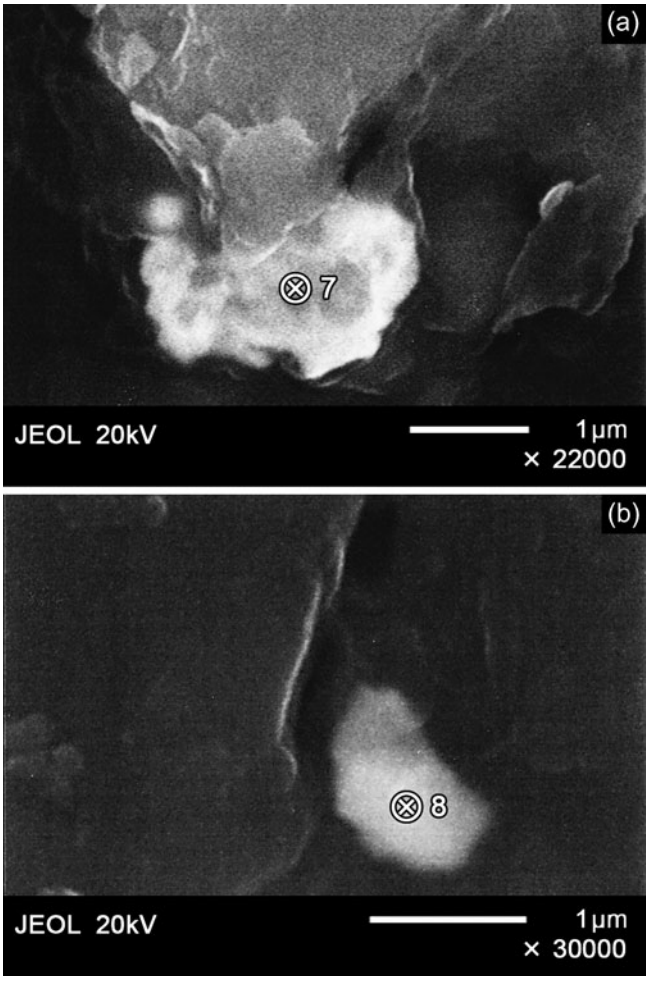

Figure 4. SEM micrographs of noble metals admixtures occurring in carbide composite powder prepared from a mixture of carbidized shungite and alumina. Analysis of EDS spectra from marked points is given in table 1.

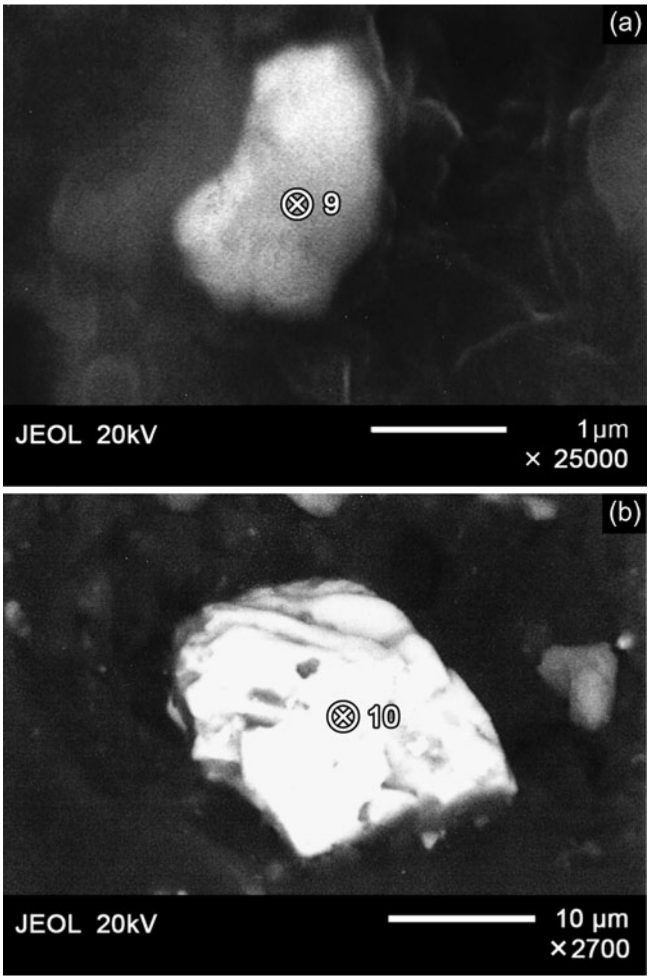

Figure 5. SEM micrographs of sulfurous admixtures occurring in carbide composite powder prepared from a mixture of carbidized shungite and alumina. Analysis of EDS spectra from marked points is given in table 1.

grains of gold–mercury amalgam alloy containing small amounts of silver and copper (point 7). Moreover, our attention has been focused on the assemblage of platinum-group elements (point 8). Observed grains are globular in shape and about 1 μm in size. Data on their chemical compositions are given in table 1.

3.4 *Sulfur distribution*

The presence of sulfur is an important technological characteristic of carbonaceous raw materials, therefore, need to be under special control. We found the total content of sulfur in shungite rocks to vary from 1·8 to 4·5 wt.%. Even though volatile sulfurous compounds are extensively released during the heat treatment of shungite, some amount remains in the end-product. The SEM images specially focused upon the representatives of sulfurous admixtures and are shown in figure 5.

4. Conclusions

Substitution of fine chemicals by the natural raw materials is one of the most profitable courses to develop industrial technologies and processes. But the quality of end-products needs to be controlled in this case because the amount of useless admixtures is large enough. SEM investigation of minor constituents in the '$SiC–Al_2OC$'-based composite material prepared from a mixture of carbidized shungite rocks and alumina revealed the following important features: (i) the most common minor phase represents an Al–Fe–Si–C-based alloy and (ii) the noble metals admixtures occur as separate microsized grains.

The data we report could become a basis for development of technologies for the in-depth processing of natural carbonaceous rocks viz. it is shown that carbidized shungite may be even regarded as a source of noble metals. But mainly the results of present investigation can be used to advance technologies of manufacturing carbide-based composite materials.

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