Heat-treated nano-structured shungite rocks and electrophysical properties associated

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Shungite rocks of two different types were treated at $\sim$ 1400 °C and a set of nanomaterials have been obtained. Among the different materials obtained were: carbon hollow fibers; spherical or ellipsoid particles; silicon carbide amorphous; crystalline nanofibers and nanoparticles having different morphologies; iron and iron silicide nanoparticles encapsulated into carbon shells. Measurements were performed for shielding effectiveness (SE) and the electrical conductivity (σ) of untreated and heat-treated shungite rocks. The shungite rock with dominated hyperfullerene carbon is remarkable for a two-fold increase in the σ and a 10 dB increase in SE with a slight decrease of the carbon content by 1.5 % in relation to the untreated sample. In contrast, the treated shungite rock with high SiC nanofiber content is characterized by a halving of the σ and a 10 dB decrease in SE with a decrease of the carbon content by 6 % relative to the original sample.

Keywords: shungite rocks, carbon, carbon nano-sized shells and fibers, SiC nano-sized fibers, shielding effectiveness, electrical conductivity.

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1. Introduction

The shungite rocks of Karelia (Russia) form a large, diverse group of Precambrian carbon-bearing rocks with poorly-crystallized carbon (shungite) that can be characterized as natural composite materials. Shungite rocks have variable carbon content and mineral composition, which may contain quartz, mica, carbonates and traces of other minerals. Shungite has chemical composition consisting of C with traces of N, O, H and S. All types of these rocks have very variable physico-chemical properties, depending on the shungite structure, C content, the composition and characteristics of minerals and distribution of carbon and minerals in the shungite rocks. For example, type I rocks have a relatively low specific gravity (1.8 – 2.0 g/cm^3), high electric conductivity (about 100 S/cm), and some types have unusually high specific surface areas (up to 500 m^2/g) as measured by the (BET) adsorption of gaseous nitrogen [1]. Shungite is remarkable for the noted occurrence of globules, 3-dimentional closed shells but, more commonly, fractions of such shells that are highly disordered into short bent stacks. Shungite demonstrates fullerene-like signs of the atomic, molecular and band structures [2].

In recent years, it becomes very relevant issue of improving the quality shungite natural raw materials by modification of carbon and mineral component under the influence of a relatively soft – biogenic, or an extreme physical and chemical treatment both in laboratory and natural environment. Practically important indicators of the transformations are the electrical conductivity and shielding effectiveness [3].

2. Experimental

Two shungite rocks with different mineral contents (Table 1) were treated at $\sim$ 1400 °C. The calculation of the content of the amorphous component (carbon) and crystalline phases were determined using the procedure provided with the software Siroquant on the diffractometer ARL X TRA and using zinc oxide (ZnO) as a standard (Fig. 1). The EM-125 electron microscope was used for transmission electron microscopy and selected area electron diffraction study. Trace element compositions of shungites were determined using the UP 266 laser system connected to an X-Series 2 Thermo Fisher Scientific ICP-MS in the Analytical Centre of Institute of Geology of the Karelian Research Centre of RAS (Table 2) [4].

Processes, which consisted of solid phase reactions, including catalytically initiated reactions, between micro- and nanominerals (quartz, mica) and noncrystalline carbon of shungite rocks, occurred at reaction temperature. As a result, a set of nanomaterials have been obtained, primarily, carbon in the form of hyperfullerene structures, hollow fibers (Fig. 2a) and hollow spherical or ellipsoid particles (Fig. 2b) formed by smoothly bent packets of carbon layers. Some were similar to onion-like or fullerene-like carbon spheres with promising electrophysical properties [5,6]. Additionally, similar C-hollow particles have been found in the untreated shungite rocks and the rocks subjected to heating resulted from contact metamorphism [7]. The interaction between carbon and minerals

TABLE 1. Mineral composition and electrophysical properties of untreated and nano-structured shungite rocks

Mineral composition and properties	Shungite No. 1		Shungite No. 2	
	untreated	heat-treated	untreated	heat-treated
C %	55	56	46	40
Quartz	6	3	37	15
Muscovite	3	–	16	–
Pyrite	–	–	2	–
Chlorite	32	–	–	–
Albite	4	<2	–	–
Cristobalite	–	3	–	2
SiC	–	21	–	33
$FeSi_x$	–	15	–	10
σ (1 kHz), S/m	715	1530	340	140
SE (10/100/750 MHz), dB	53/54.5/71.5	61/67.5/–	46.5/47/55.5	38.5/38.6/41.5

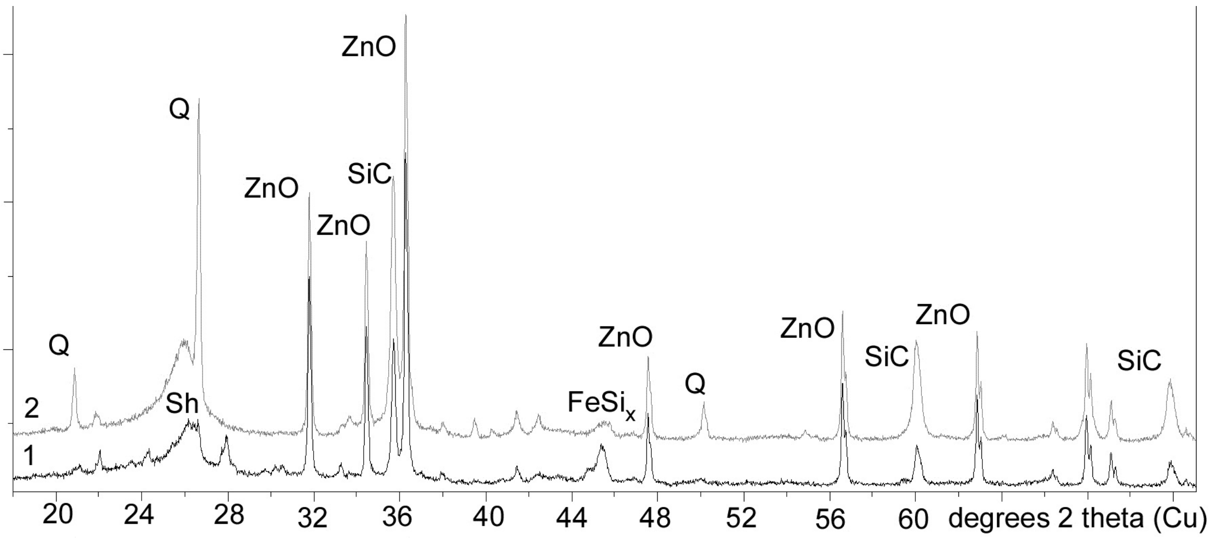

FIG. 1. X-ray diffractograms of nano-structured shungite rocks (No. 1 and 2) with zinc oxide (ZnO) as a standard, where, Q is quartz and Sh is shungite carbon

TABLE 2. Trace element compositions of the untreated shungite rocks

Shungite rocks	Some catalytically active and heavy trace elements (ppm)								
	Ti	V	Cr	Mn	Ni	Cu	Mo	Ba	Pb
Sh 1	2717	223	108	439	101	59	11	195	4
Sh 2	1839	222	74	41	72	21	9	373	14

leads to the formation of silicon carbide nanofibers and nanoparticles with different morphologies and structures (amorphous and crystalline) (Fig. 3a,b), and iron and iron silicide nanoparticles encapsulated into carbon shells grow. The processes of nanostructure formation are very sensitive to the type of shungite rocks and experimental conditions. The obtained nanomaterials possess unique properties, for example, encapsulated FeC_x particles are in the superparamagnetic state [8], similar to the nanoparticles encapsulated separately by the polymer [9]. A compound of this type can be used as fillers of new composite materials [10].

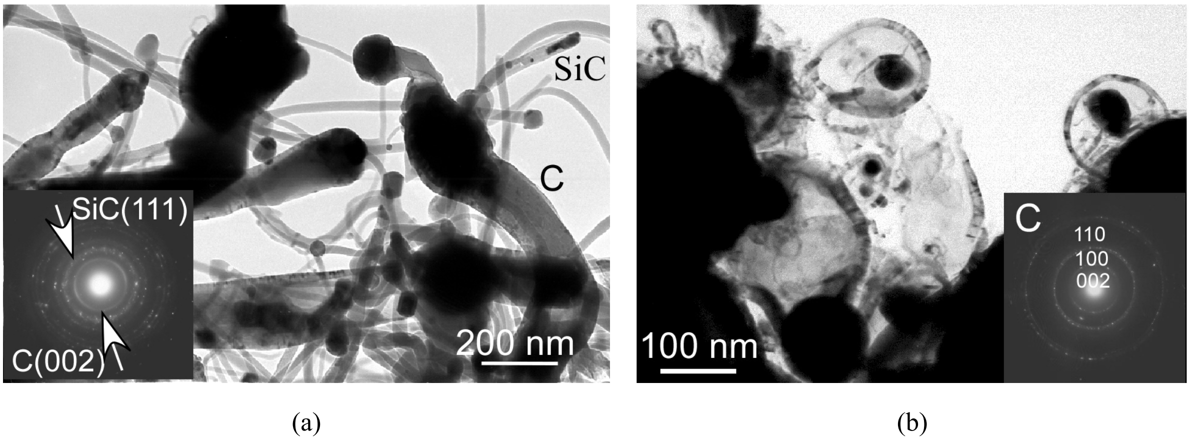

FIG. 2. Transmission electron microscopy images and selected area electron diffraction (inserts) of hollow carbon fibers (a) and hollow carbon particles (b) of nano-structured shungite rocks

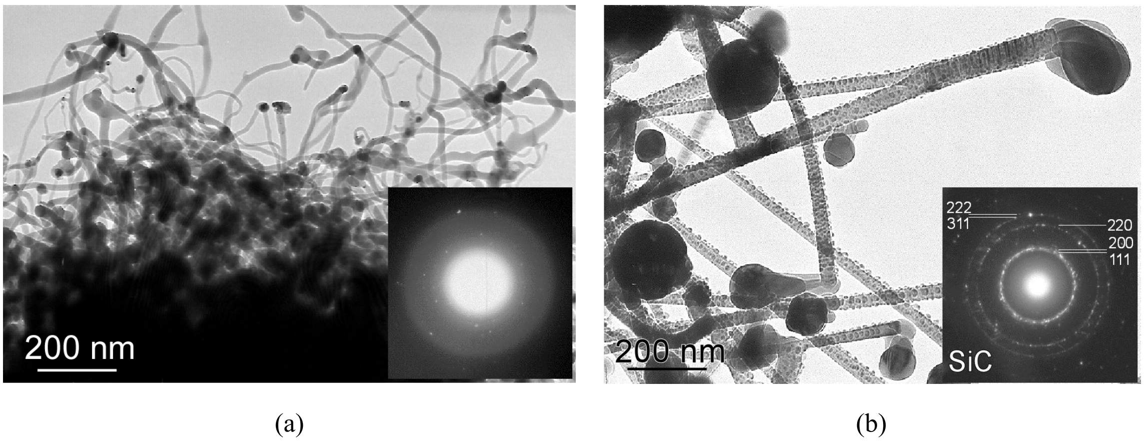

FIG. 3. Transmission electron microscopy images and selected area electron diffraction of amorphous (a) and crystalline (b) SiC fibers of nano-structured shungite rocks

To enrich the nanostructured shungite rocks with specified components for use as a filler and modifier of composites, we investigated the processes of dispersion in liquids of different density, such as alcohol, water and tribromethane [11]. However, despite the dispersion, it was impossible to obtain narrow fractions of components present in the nanostructured shungite rock. This circumstance is caused by both complex composition of samples and critical processes of dispersion, that requires further research on the selection of modes and processing schemes. Therefore, at this stage, the initial nanostructured rocks were used for manufacturing the composites.

The shielding effectiveness (SE) measurements were carried out using the coaxial transmission line method in the frequency range of 0.01 – 1000 MHz. The electrical conductivity (σ) was measured at a frequency of 1 kHz. The two different shungite samples were powdered and electrophysical parameters, such as the conductivity and the shielding effectiveness were measured. Measurements of shielding effectiveness (SE) and the electrical conductivity (σ) of untreated and heat-treated different shungite rocks were carried out as reported elsewhere [12]. For the heat-treated nano-structured shungite rock with dominated hyperfullerene carbon, the σ doubled in magnitude and SE increased by 10 dB with an increase of carbon content by 1.5 % over the untreated sample. In contrast, for the heat-treated nano-structured shungite rock with a high SiC nanofiber content, there was a decrease of carbon content by 6 % after treatment, the σ value was halved and the SE was decreased by 10 dB (Table 1, Fig. 4).

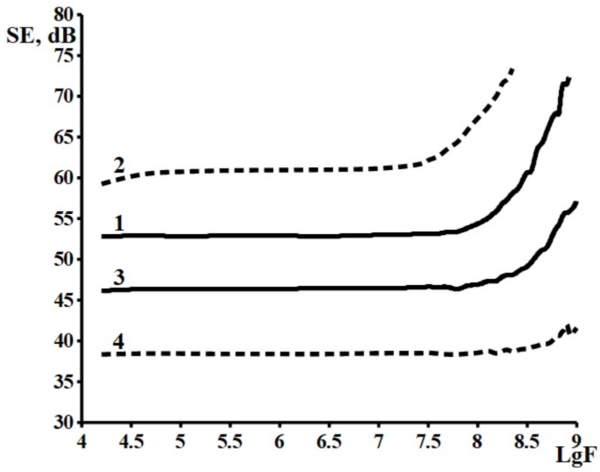

FIG. 4. Dependence of shielding effectiveness of shungite rocks on electromagnetic field frequency. Shungite 1: 1 – untreated, 2 – heat-treated; Shungite 2: 3 – untreated, 4 – heat-treated

3. Discussion of the results

Shungite is non-graphitized carbon and very resistant to heat treatment. Significant changes of those are observed only at temperatures above 2100 °C, and are associated with increasing of coherent scattering regions and reducing the carbon layer distortion. The band structure and electrophysical properties of those change consequently. On the contrary, shungite rocks are characterized by the fine nature of the mineral distribution and the large contact area of the carbon and mineral components that provide a high content of carbon and silicon, determine the possibility of their mutual crystallogenesis, including formation carbides and silicides, not at such high temperatures, since 1400 – 1600 °C. The difference of shungite rocks by the rock-forming minerals and trace element composition leads to the synthesis of different morphologies and the structural state of carbon and composite components (see Tables 1 and 2). In particular, carbides of silicon, having a microcrystalline structure and a well-defined crystallographic form can be obtained. However, the most interesting and promising in the technological aspect are the micro- and nano- fibrous carbides of silicon. In shungite rocks with the different rock-forming minerals and trace element compositions, the synthesis of mono- or polycrystalline, and amorphous nano-sized fibrous silicon carbides, having different morphological structure, length, and diameter occur. The diversity of morphological and structural forms of silicon carbide indicates different mechanisms of their growth, which can be determined by the change in the kinetic crystallogenesis processes influenced by the distribution and morphologies of carbon and minerals as well as trace elements.

Due to the formation hyperfullerene structures during the heat treatment for the shungite No.1, higher shielding effectiveness values than the untreated shungite have been obtained. In addition, according to electron microscopy, some hyperfullerene structures, presumably filled with iron and/or iron carbide, which can also contribute to the shielding of electromagnetic energy. Therefore, we can assume that the presence of hyperfullerene structures make a special contribution to the shielding ability of the modified shungite rocks. But as their number and sizes depend on the structural characteristics of the shungite rocks, then it becomes important to pre-selection of the type of shungites for modifications and future use in the creation of radio-shielding materials. The presence of various nanostructured rocks with fundamentally different physical properties makes it possible to predict the creation of new composite materials on their basis.

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