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Structure investigations of siliconized graphite obtained during the elaboration of sintering process technology

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Abstract : The experimental samples of siliconized graphite consisting of raw materials with relevant technological requirements for prototypes production of siliconized graphite were investigated in this work. It is found that the test samples acquire the desired hexagonal lattice after heating at the sintering temperature of 1550 °C. It is determined that the desired structure of the obtained material consists of three main phases corresponding to siliconized graphite: the silicon carbide (SiC), free carbon (C) and silicon (Si). It is found that that microhardness of the obtained samples was: for silicon from 5250 to 8720 MPa and for silicon carbide from 10840 to 15900 MPa which corresponds to known values.
Key words: graphite, sintering, structure, siliconized, microhardness.

Introduction

It is known that the siliconized graphite is one of the widely applied and popular of carbon-bearing material in nuclear energy technology, metallurgy and other fields of industry. All kinds of perspective reactors of IV generation and thermonuclear facilities planned to open in the coming decades provide increasing of doses of irradiation temperature in the core region[1].

Therefore, it becomes impossible use of radiation-resistant steels which are currently the main reactor material. This is precisely why the materials based on SiC are reviewed by experts of developed countries as the most promising for most of the developed world's reactors and thermonuclear facilities of IV generation, because only such materials are able to survive under irradiation up to 150 dpa and temperatures of 700-1000 ° C when operated at reactive environments, among them in the form of molten metals and water vapour etc.[2]

Nowadays, there are a number of different ways of production of siliconized graphite, the choice of someone or other method, at least is determined by the composition and aggregative state of the source of the main component of silicon.

The method of production of the siliconized graphite and its products which consists in impregnating of the carbon base with molten silicon is prevailing in industrial conditions. It compares favourably with other processes by small number of cycles, short production time and relative low cost[3-5].

The end products made of recycled natural raw material[6] used as part of unit of product in the world practice of production process of the siliconized graphite.

The object of this work is development of the manufacturing practice of siliconized graphite, study of the microstructure and physical and mechanical properties of the obtained test samples.

Material and Methods

The components of the charge with following ratio were produced for examination:

Name of the sample	Mass ratio, %	
	SiO_2	Ñ
Sample À	70	30
Sample Â	40	60
Sample Ñ	60	40

The process of charge production was carried out by a combined grinding in the vibrational microgrinder PULVERISETTE (FRITSCH company) to obtain particles less than 50 microns accompanied by control sieving through the sieve of appropriate size. Mixing of components is carried out in the globe mill in the course of 45 min.

The obtained mixture is compressed in the pressing tool made of hardened carbon steel at a pressure of 480 to 500 MPa and at a temperature of 180 C for 30 – 35 minutes. Further, the obtained blanks baked for attainment of the final fabrication characteristics. Sintering is carried out in the graphite crucible at universal high-temperature stand of inductive heating VChG-135.The blanks are placed inside of the graphite crucible, where the graphite spacer plates were mounted between the blanks. The obtained experimental assembly is placed in the working chamber of the induction furnace of the VChG -135 stand, after which the pressure of 10^{-3} Pa is produced in the chamber and filled with inert gas (argon) to normal pressure.

The sintering procedure of blanks includes two periods of heat treatment from room temperature to 800 ºC at exposures of 20–30 min and subsequent heating to 1580 – 1600 ºC with at exposures of 90 – 100 min. Figure 1 shows the heating mode of the sample during sintering at VCHG-135, the control of heating temperature was carried out using thermocouples and spectral distribution pyrometer.

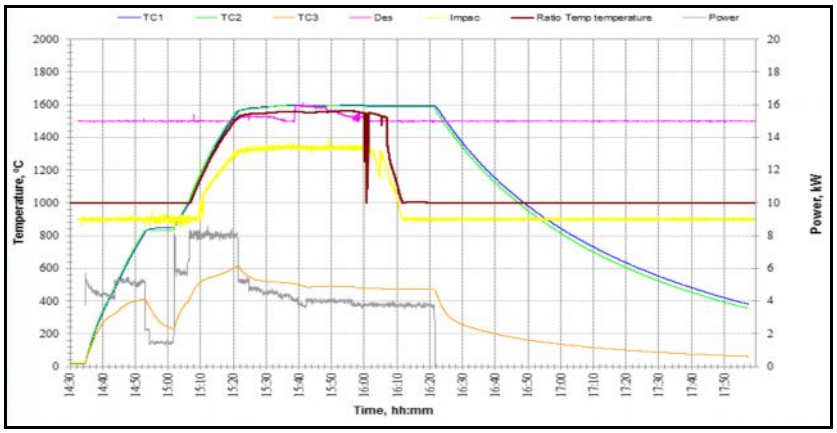


Fig: (1). Temperature heating mode of the samples

The exterior view of the test samples after sintering is shown in figure 2.

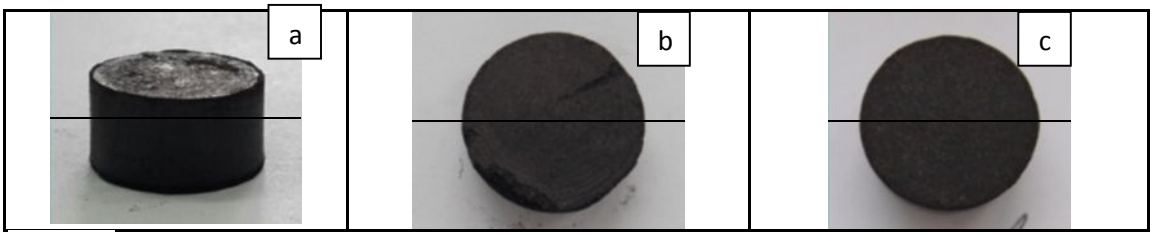


Fig: (2). The test samples after sintering at a temperature of 1550 a) with a mass ratios of 70 % SiO_2 and 30% C; b) with mass ratios of 40 % SiO_2 and 60 % C; c) with mass ratios of 60 % SiO_2 and 40 % C

X-ray phase analysis of the surface layer of the samples was carried out on X-ray diffraction meter DRON-3 using CuK_α- radiation modernized by digital recording system RM-4. Microhardness testing (Hμ) of the samples was conducted by Vickers hardness method at microhardness tester PMT-3M with loads on the indenter-50 g in accordance with standard GOST 9450-76.

The morphology of the surface structure was studied at optical microscope OLYMPUS-BX41M and also SEM-analysis was carried out. in which micrographical investigations and determination of elemental composition at scanning electronic microscope JSM-6390 with energy-dispersive spectrometer JED-2300 were conducted.

Results and Discussions

The microstructure of the obtained sample (at 1550 C; the c charge mixture: 70 % SiO_2, 30 % carbon black) is a two-phase structure presumably made of silicon carbide with a hardness from 15100 MPa to 15900 MPa and $Si(O_2)$ with hardness from 5900 MPa to 8700 MPa. The density of this sample was 2,14 g/cm^3. As you can see in the figure 3, the pores the average size of which is about 20-25 μm were formed in the process of material formation.

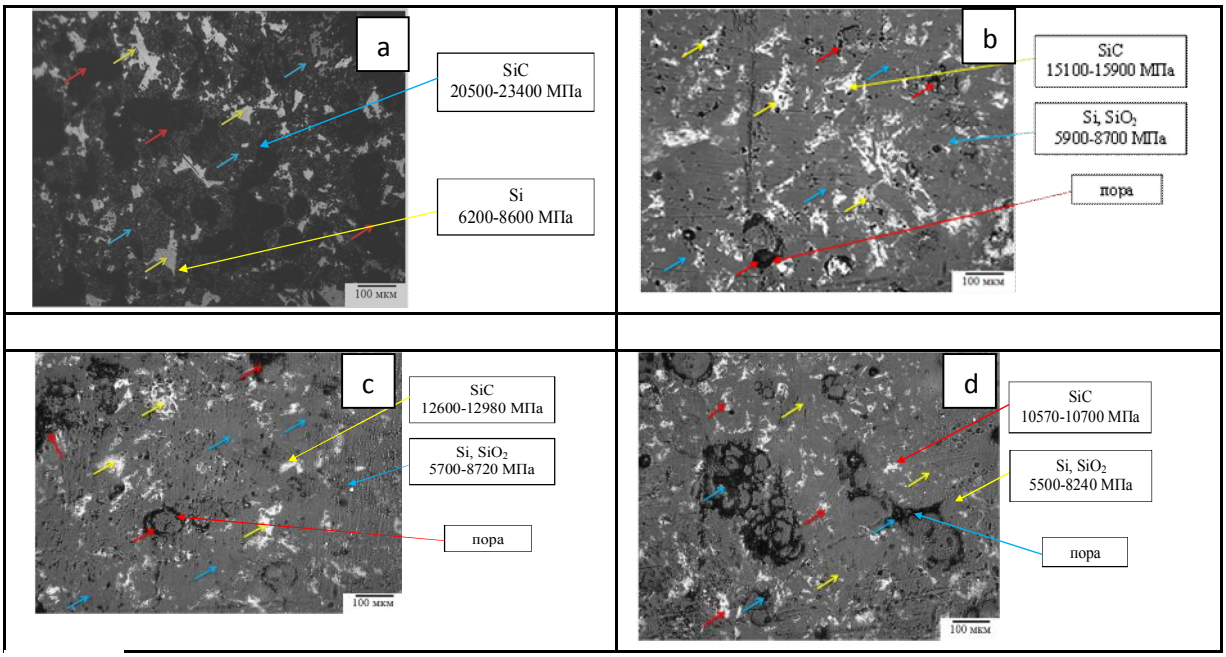


Fig: (3). Microstructure of surface of the obtained samples at micro-hardness at different areas a) prototype of the siliconized graphite b) with mass ratios of 70 % SiO_2 and 30% C; c) with mass ratios of 40 % SiO_2 and 60 % C; d) with mass ratios of 60 % SiO_2 and 40% C

The microstructural examination in the different areas of the surface has shown that in any part of the sample always recorded the presence of two heterochromatic phases (dark and white). It was also found that the

pores and a large precipitates (presumably not reacted particles of the silicon and carbon) were formed on the grinding surface. At some optimum size of pores is provided their functioning to transportation of the silicon melt inside of the blank, at a speed sufficient for response reaction of formation of silicon carbide in the whole volume of the blank[7-10].The presence of three phases which are different in color and in contrast was detected at the analysis of the microstructure of samples surfaces. It was also found that the shape and intermediate sizes of the particles of each phases and manner of collocations of neighboring particles of different phases remained the same throughout the sample section. Silicification leads to fast blocking of the transport pores and amplitude of silicification is not achieved at small pore sizes.

At large pore sizes, the silicon melt flows through the blank with high speed which is not contribute to the formation of silicon carbide, partially flowed from it. Only at some optimal pores size is provided their functioning to transportation of the silicon melt inside of the blank at a speed sufficient for formation of silicon carbide in the whole volume of the blank.

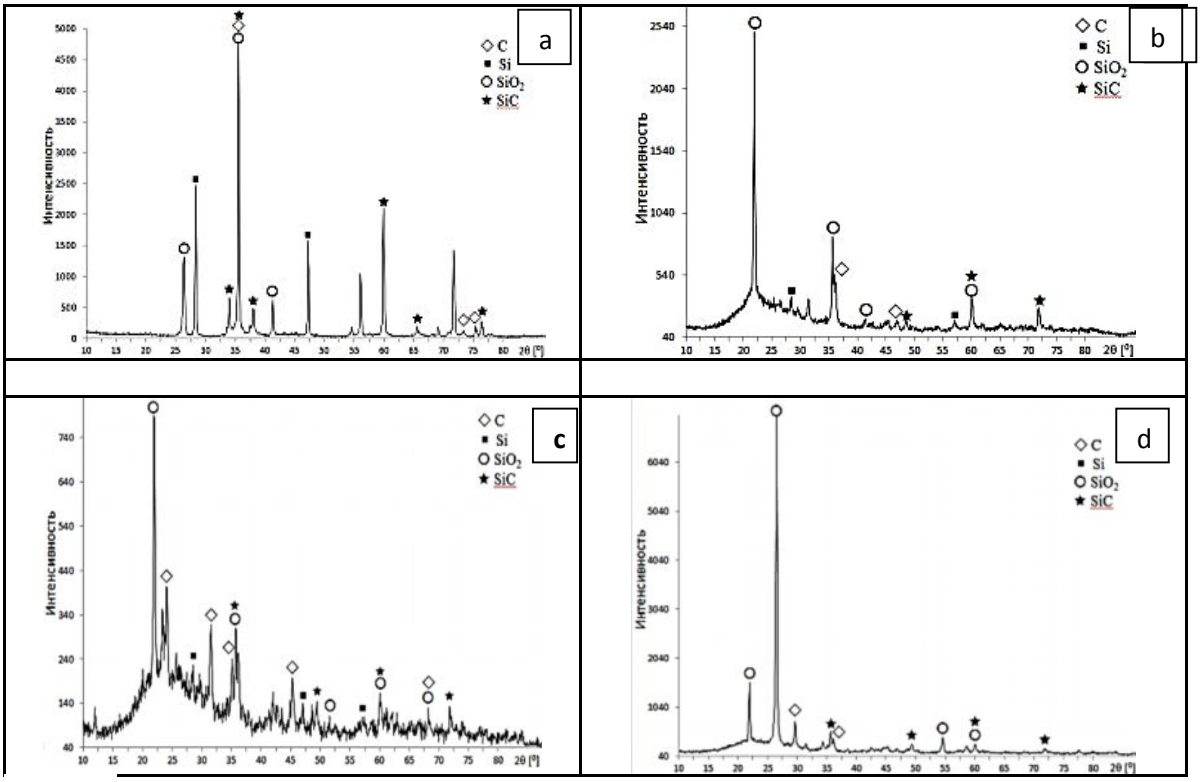
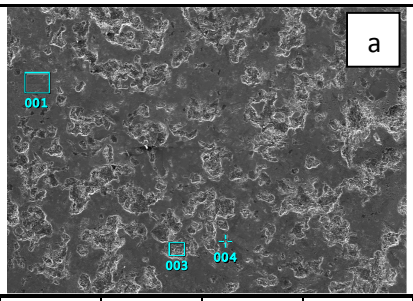


Fig: (4). X-ray phase diffractogram of the test the samples a) a prototype of the siliconized graphite b) with a mass ratios of 70 % SiO_2 and 30 % C; c) with a mass ratios of 40 % SiO_2 and 60 % C; d) with a ratios of 60 wt% SiO_2 and 40 % C

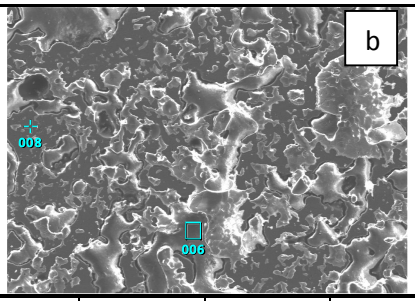
The prototype of the material is the siliconized graphite of the SG-M grade.

According to X-ray phase analysis (figure 5) it can be seen that the material obtained at interaction of carbon black with siliceous sand has an amorphous state. It was observed that also was found: carbon, silicon, which leads to preheating of the system followed by formation of carbide (SiO_2+3C → SiC+2CO), which corresponds to the structure of the siliconized graphite. However, at the production processes of the siliconized graphite, the phase of silicon dioxide (SiO_2) which has high hardness and strength was preserved.

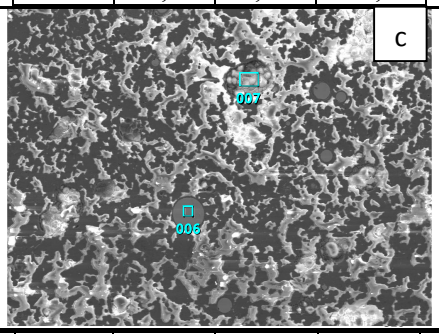
The photographs of the morphology of the sample with the distribution of phases and their ultimate composition across the sample (figure 5) were obtained as a result of examination of prototype sample and samples A, B, C. Ultimate analysis of the sample of the prototype showed that the chemical composition includes: carbon (C) and silicon (Si) in different proportions (figure 5 a), and the chemical composition of the samples also includes oxygen (figure 5 b, c, d).



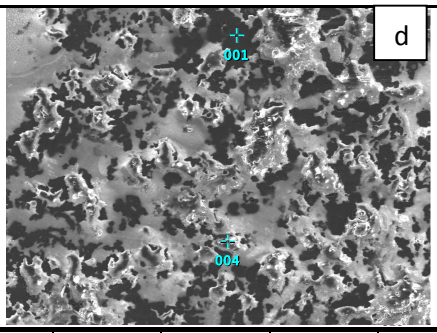
ID	C	Si	Total
001	34,45	65,55	100,00
003	85,48	14,52	100,00
004	96,06	3,94	100,00



ID	C	Si	Total
006	99,90	0,10	100,00
008	57,11	42,89	100,00



ID	C	O	Si	Fe	Total
006	7,50	-	22,38	70,11	100,00
007	26,98	38,85	34,17	-	100,00



ID	C	O	Si	Total
001	33,05	-35,17	31,79	100,00
004	74,97	-	25,03	100,00

Fig: (5). Results of EDS-analysis. The distribution of elements in wt.% a) the prototype of the siliconized graphite b) with mass ratios of 70 % SiO^2 and 30 % C; c) with mass ratios of 40 % SiO_2 and 60 % C; d) with mass ratios of 60 % SiO_2 and 40 % C

The results of ultimate analysis confirm that the properties of the samples (prototype and samples A, B, C) correspond to the properties of siliconized graphite. Based on the results of the analysis it can be expected that the material consisting of free carbon (C), silicon (Si) and silicon carbide (S) has a high-wearing feature in hard conditions of abrasive wear and high temperatures, which in turn is provided combination of high hardness and high thermal conductivity[11-12].

Conclusion

Performing the analysis of the obtained experimental data on examination of test samples of siliconized graphite, we can draw the following conclusions:

– the basic requirements to components for production of the siliconized graphite (ratio by weight: sample A - 70% SiO_2 and 30% C; B- 40% SiO_2 and 60% C; C - 60% SiO_2 and 40%C) were determined experimentally;

– technical regimes of sintering were developed, at this date the optimum temperature (1550°C) and process life (50 min after cooled to room temperature in the inert media of the working chamber of the VChG-135);

– by metallographic examinations methods determined that the structure of the obtained material consists of three main phases corresponding to siliconized graphite: silicon carbide (SiC) with micro-hardness from 10840 MPa to 15900 MPa, free carbon (C) and silicon (Si) with micro-hardness from 5250 MPa to 8720 MPa. The presence of the primary component of silicon dioxide (SiO_2) detected as the impurity phase;

– by X-ray diffraction method determined that the obtained basic phase has the desired hexagonal structure of silicon carbide (SiC) with crystalline parameter of 0,3073 nm.

Based on the results, it can be seen that the sample with the ratio of components of the charge 60% SiO_2 and 40% C has a more similar structure with the sample prototype of the siliconized graphite. Based on the obtained data, it should be noted that the further work on production and material analysis of siliconized graphite will be continued.

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