OXIDATION-RESISTANT NANO-REINFORCED PC-REFRACTORIES OF MODIFIED PHENOLFORMALDEHYDE RESIN. PART 3. FORMATION MECHANISM OF ORGANIC – INORGANIC COMPLEXES DURING LOW-TEMPERATURE SYNTHESIS OF NANOPARTICLES OF ADDITIONAL ANTIOXIDANTS AND THEIR EFFECTIVENESS[1]

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SiC nanoparticles that could be used as an antioxidant for periclase-carbon (PC) refractories were synthesized from the organic—inorganic complex $(-CH_3)-(SiO_2)_n$ that formed during heating of silicon alkoxide and thermal destruction of its gels. Use of phenolformaldehyde resins modified with silicon alkoxide and its sols was proposed and enabled the formation of an organic—inorganic complex $(-CH_3)-(SiO)_n-C$ with a high C content. This increased the yield of SiC synthesized in the carbon binder. The addition of Ni precursors (additional antioxidant) formed an even more complicated organic—inorganic complex. Use of the complex $(-CH_3)-(SiO_2)_n-Ni(NiO)-C$ together with Al improved the operating characteristics of the PC refractories. It was found that their resistance to oxidation was increased after the complex antioxidant Al + SiC + Ni(NiO) formed.

Keywords: periclase-carbon refractories, antioxidant, phenolformaldehyde resin, organic—inorganic complexes $(-CH_3)-(SiO_2)_n$, $(SiO_2)_n-C$, $(-CH_3)-(SiO_2)_n-C$, $(-CH_3)-(SiO_2)_n-Ni(NiO)-C$.

The sol-gel process is currently becoming more significant in the technology of special ceramics with improved physicomechanical properties. The process is a harbinger of the synthesis of nanoparticles that self-reinforce ceramics or carbon binders, depending on where they are formed, strengthen them internally or fill structural voids and defects, make the manufactured material denser, and increase its wear resistance.

Sol-gel technology of refractories and special ceramics is interesting because it can be used for low-temperature synthesis of not only oxides and their compounds but also oxygen-free compounds including β-SiC or α-Si_3N_4 nanoparticles. It also provides self-reinforcement of ceramics and dispersion strengthening and compaction of a material by building special nanostructures or filling structural defects with nano-sized formations. Methods for enhancing the synthesis of oxygen-free compounds and regulating the carbonization of the clustered gel system in order to increase the yield hold not only scientific but also practical interest. This pertains especially to the fabrication of carbon-containing refractories, including periclase-carbon (PC) ones, for which oxygen-free compounds (metal carbides) can be used equally as well as metallic aluminum (Al) as antioxidants. Therefore, the main goal of using organic—inorganic complexes in PC-refractory charges is to increase the oxygen resistance of these refractories by activating the usually used antioxidant Al. For this, small amounts of nanoparticles of other antioxidants (e.g., SiC, which should be synthesized at low temper-
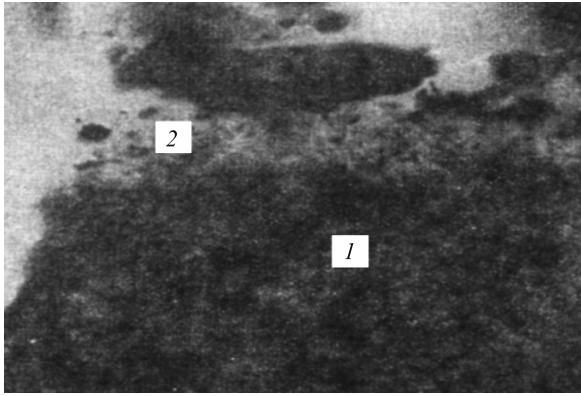

Fig. 1. Contact of sol-gel composite with graphite-diffusion bridge flakes in (SiO$_2$–C) complex in the cross section normal to the {0001} plane in 1.489 immersion: graphite (*1*) and secondary β-SiC (*2*). ×420. Transmitted light.

atures as a result of using sol-gel techniques in the process) are added to the charge.

Many researchers have discussed the theoretical aspects of low-temperature SiC synthesis. The temperature ranges for coexistence of SiO$_2$/C and SiO/C were established by construction of phase diagrams of the Si–O$_2$–C system and triangulation of the Si–O$_2$–C triangle for various gas-phase compositions [1 – 3]. It was shown that low-temperature synthesis (~1430°C) of SiC from SiO$_2$ and C was thermodynamically possible although the low-temperature synthesis from SiO could be carried out at significantly lower temperatures (<500°C). The antioxidant SiC should start being synthesized during operation at relatively low temperatures in order to improve the physicomechanical properties of unshaped and unannealed C-containing refractories. Their durability during service increases due to self-reinforcement of the ceramics or carbon binders by ultradisperse particles of the synthesized compounds or their nanoparticles [4 – 9]. The dimensions of the synthesized refractories depend on the size of the precursor cation. The dimensions of the C that will be used in the reaction are important for the SiC particle size. The particle size of the synthesized SiC can be controlled by using organic and inorganic precursors for the synthesis.

The binder for PC-refractories was formerly coal-tar pitch, the use of which was halted due to the ecological hazard. Low-temperature SiC synthesis was observed if ethylsilicate sols were added to the pitch charge [10, 11]. However, the synthesis temperature was 1430°C. The SiC crystals reached several microns in size. A drawback of using the sol-gel binder in PC-refractories with added pitch was the undesirable synthesis of silicates with low melting points if a large amount of SiO$_2$ was added to the PC-refractory charge. Figure 1 shows that ultradisperse β-SiC can be synthesized when the graphite contacts the ultradisperse silica of the

sol-gel composites. It was found that the SiC formation temperature decreased sharply only if it was synthesized from SiO and not SiO$_2$ [12 – 14]. The SiC particle size depended on the size of the carbon precursor. SiC nanoparticles are synthesized more often using reactions on the molecular level and organic components.

The region of coexistence of SiO and C in the Si–O$_2$–C phase diagrams increased significantly and the start of SiC synthesis from these components shifted to lower temperatures if the SiO partial pressure was reduced (Fig. 2). Figure 2 shows that the area of SiO and C coexistence was greater if SiC synthesis started at lower temperatures (point A). The partial pressure of SiO P_{SiO} in the system was controlling (Fig. 3) although the ratio P_{CO}/P_{CO_2} also affected the temperature at which SiC formation started. It was found that SiC was synthesized from SiO and C at 1127°C and lower for $P_{SiO} = 10^{-6}$ atm. The synthesis temperature decreased to 727°C at $P_{SiO} = 10^{-12}$ atm; to 487°C at $P_{SiO} = 10^{-19}$ atm. Thus, the start of SiC synthesis falls by several hundred degrees (200 – 1000°C) if one of the gas-phase components is SiO.

Thermodynamic calculations showed that SiC can be synthesized at very low temperatures (– 457°C) and even at the start of carbon oxidation (P_{CO}/P_{CO_2} = 9:1) if the Si–O$_2$–C system contains the minimum amount of SiO (10^{-19} atm). Therefore, SiC nuclei are expected to be synthesized at rather low temperatures in this gas phase by pyrolysis of tetraethoxysilane, heat treatment of gels, or during mechanochemical synthesis from silicon alkoxide if the refractory fillers are modified with it. A stable carbon system in the sol-gel composite gel cluster should be formed in order to create the organic – inorganic complex (–CH$_3$)–(SiO)$_n$ that provides the SiO needed to react with C in the nanoreactors. The nanoreactors for synthesizing nanoparticles of oxygen-free refractories from the components of the organic – inorganic complexes enable the construction of nano-reinforced matrices and carbon binders for various types of composites and refractories [15 – 21].

Carbonization of modified phenolformaldehyde resin (PFR) causes pyrolysis of tetraethoxysilane or ethylsilicate and forms ultradisperse SiO$_2$ and carbon binder from coke. These components of the modified binder create the SiO$_2$–C complex and are the starting materials from which micron-sized SiC is synthesized. It also results from the reaction of pitch with ultradisperse SiO$_2$ of the sol-gel composite, which is formed via pyrolysis of tetraethoxysilane or thermal destruction of the gel:

$$Si(OC_2H_5)_4 \rightarrow SiO_2 + 4C_2H_2 + 2H_2O, \qquad (1)$$

$$Si(OH)_4 \rightarrow SiO_2 + H_2O. \qquad (2)$$
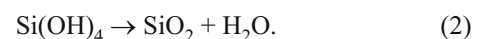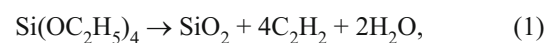
It was found that a carbon system in an SiO$_2$ cluster with the β-cristobalite structure had to be created in order to syn-

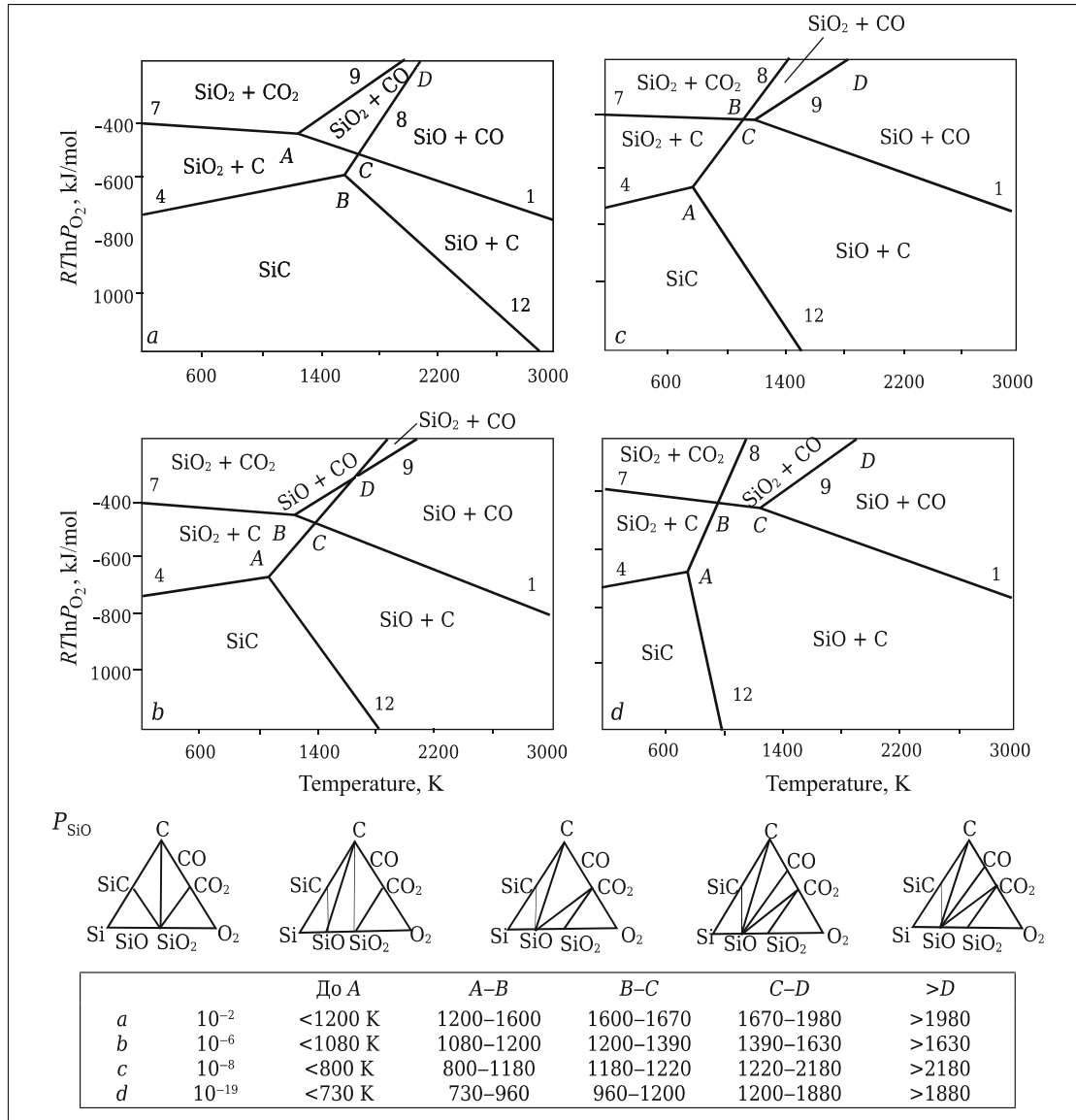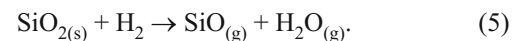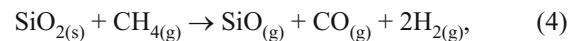|		До A	A–B	B–C	C–D	>D
a	10^{-2}	<1200 K	1200–1600	1600–1670	1670–1980	>1980
b	10^{-6}	<1080 K	1080–1200	1200–1390	1390–1630	>1630
c	10^{-8}	<800 K	800–1180	1180–1220	1220–2180	>2180
d	10^{-19}	<730 K	730–960	960–1200	1200–1880	>1880

Fig. 2. Phase diagrams of Si–O_2–C system with P_{CO}/P_{CO_2} = 9:1 and P_{SiO} = 10^{-2} (*a*), 10^{-6} (*b*), 10^{-8} (*c*), and 10^{-19} atm (*d*) and triangulation of Si–O_2–C concentration triangles.
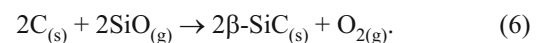
thesize SiC nanoparticles. The cluster resulted from the polycondensation of silicon alkoxide hydrolysis products and its derivatives. Also, organic—inorganic complexes $(–CH_3)–(SiO_2)_n$, the components of which would act as precursors of C and SiO required for low-temperature SiC synthesis, had to form. The starting compound formed by thermal destruction of the radical $(–CH_3)$ and SiO_2 was a silicon alkoxide such as tetraethoxysilane and its derivatives (ethylsilicates and sols based on them). Thermal destruction of all aforementioned compounds gave the organic—inorganic complex $(–CH_3)–(SiO_2)_n$, i.e., the source of atomic C and SiO for the low-temperature SiC synthesis. Carbon formed via radical recombination:

$$2(–CH_3) = 2C + 3H_2. \qquad (3)$$
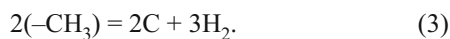
Ultradisperse SiO_2 was reduced to SiO through the reactions:

$$SiO_{2(s)} + CH_{4(g)} \rightarrow SiO_{(g)} + CO_{(g)} + 2H_{2(g)}, \qquad (4)$$

$$SiO_{2(s)} + H_2 \rightarrow SiO_{(g)} + H_2O_{(g)}. \qquad (5)$$

Then, SiC was synthesized via the reaction:

$$2C_{(s)} + 2SiO_{(g)} \rightarrow 2\beta\text{-}SiC_{(s)} + O_{2(g)}. \qquad (6)$$

The components required to synthesize SiC accumulated in the gel cluster voids because of steric factors during heating of the gel or modification of refractory powders by silicon alkoxide. The reducing medium in the microscopic vol-
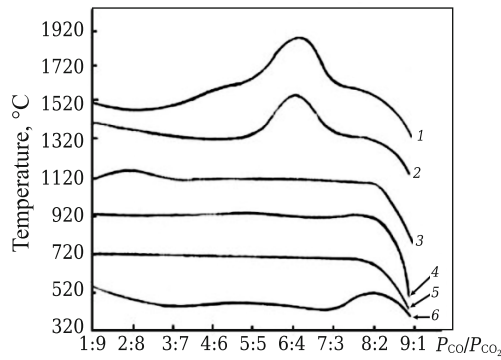
Fig. 3. Temperature of initial SiC formation as a function of P_{CO}/P_{CO_2} for $P_{SiO} = 10^{-2}$ (*1*), 10^{-4} (*2*), 10^{-6} (*3*), 10^{-8} (*4*), 10^{-12} (*5*), and 10^{-19} atm (6).
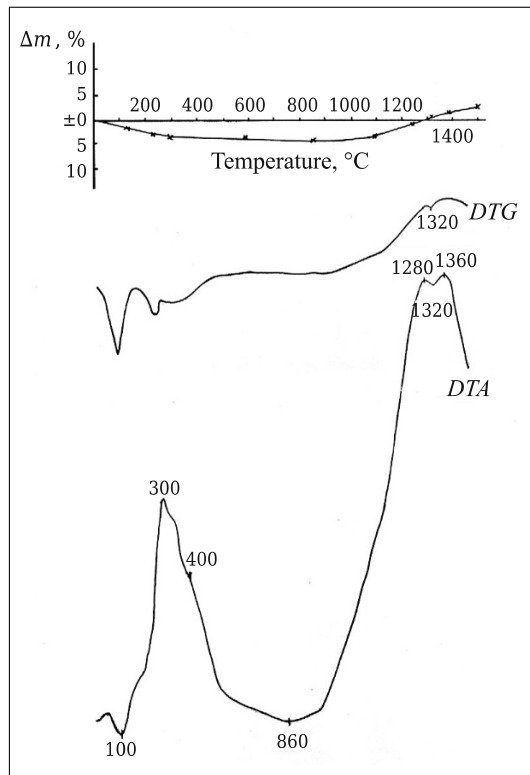

Fig. 4. DTA and DTG curves of ETS 32/60 gel modified with glycerin and mass change Δm during heat treatment of organic—inorganic $(-CH_3)-(SiO_2)_n-C$ complex at 10°C/min.

Fig. 5. Diffraction pattern of PC refractory with Al and organic—inorganic $(-CH_3)-(SiO_2)_n-C$ complex modifier after heat treatment at 1000°C before (a) and after (b) slag resistance tests at 1400°C: MgO (●), C (■), and $MgAl_2O_4$ (▲).

plenish the amount of carbon in the reaction mixture by creating the organic—inorganic complex $(-CH_3)-(SiO_2)_n-C$, which was accomplished during carbonization of PFR modified with TEOS or its sol, in order to increase the β-SiC content.

Simultaneous use of PFR and silicon alkoxide, the carbon-containing component of the PC-refractory charges and sols, formed the organic–inorganic complex $(-CH_3)-(SiO_2)_n-C$, which was similar to filling the sol-gel composites with glycerin. The amount of synthesized SiC nanoparticles increased if the organic—inorganic complex $(-CH_3)-(SiO_2)_n$ was filled by carbon from organic molecules. The amounts of oxynitride and silicon nitride increased in an N_2 atmosphere. Crystalline whiskers grew from the melt and reinforced the matrices and improved their physicomechanical properties [20, 21].

Transformations occurring upon heating in gel modified by glycerin confirmed that the yield of synthesized oxygen-free compounds increased for $(-CH_3)-(SiO_2)_n$ complexes filled with carbon of organic compounds [22, 23]. The DTA curve (Fig. 4) of gel ETS-32/60 modified by glycerin for heat treatment to 1500°C at 10°C/min showed one small endotherm at 130°C that corresponded to removal of traces of H_2O and EtOH and two large exotherms with maxima at 360°C and 1250 – 1400°C. The latter exotherm corresponded to the synthesis of the compounds because the mass

umes and point (local) temperature and pressure excursions enhanced low-temperature SiC synthesis because the microscopic volumes already contained the carbon substrate and gaseous SiO. The amount of synthesized SiC depended on the content of organosilicon compound. If a small amount (from 1 to 3%) of organosilicon compound was used to modify the PFR or refractory powder during milling, the content of synthesized β-SiC was insignificant. It was desirable to re-
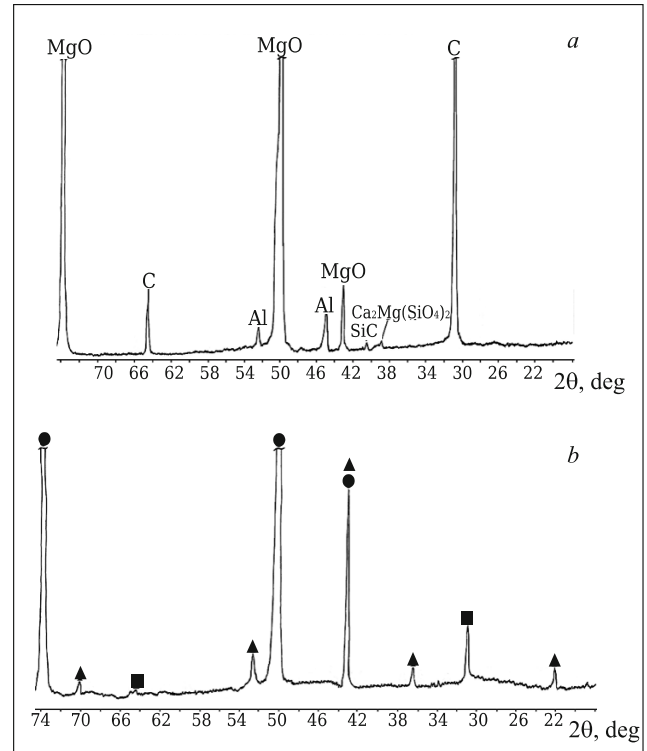
of the heat-treated gel began to increase above 1150°C. The mass increased by 8% in the range 1400 – 1450°C despite the fact that the new compounds reacted with β-cristobalite of the silica cluster to form a melt at 1320°C. The resulting melt shielded the carbon components of the organic—inorganic complex $(-CH_3)-(SiO_2)_n$ from oxidation and thereby promoted the synthesis of nanoparticles and nanowires of silicon carbide and nitride, especially if an oxygen-free binder was used and the charges were annealed in an N_2 atmosphere. DTA was performed in air. Therefore, N-containing compounds could be synthesized via reaction with atmospheric N_2. However, an x-ray phase analysis (XPA) of gels after heat treatment did not detect any new compounds except for β-cristobalite, probably because of,

Fig. 6. Diffraction pattern of PC refractory with Al and organic—inorganic $(-CH_3)-(SiO_2)_n-Ni(NiO)-C$ complex modifier after slag resistance tests at 1400°C: MgO (■), C (●), $MgAl_2O_4$ (△), $CaMgSiO_4$ (monticellite) (▲), and $MgCO_3$ (possibly) (○).

on one hand, the low amounts and, on the other, the small sizes of the new compounds. Electron-microscope studies confirmed that nanoparticles and crystalline whiskers had formed [20].

It was found that the silica framework became amorphous if gel ETS 32/60 was modified with glycerin. The O–Si–C bonds formed in the gel cluster structure were precursors of Si–C bonds. Thus, nano-sized silicon carbide and nitride could be synthesized from the $(-CH_3)-(SiO_2)_n$-C complex filled with glycerin carbon. However, they were synthesized at higher temperatures than those from the $(-CH_3)-(SiO_2)_n$ complex that was formed by heat treatment of pure gel or thermal destruction of tetraethoxysilane. Modification of PFR with silicon alkoxide or sols based on it formed the organic—inorganic complex $(-CH_3)-(SiO_2)_n-C$ in PC-refractories based on PFR. SiC was synthesized from this complex at ~1000°C [18, 19].

Antioxidants, most often metallic Al powder [24, 25] and usually 2 – 3%, are added to PC-refractories in order to increase the oxidation resistance of the graphite. The Al activity can be enhanced by using other antioxidants in smaller amounts. However, trace additives are difficult to apply or to distribute in the charge evenly. Therefore, the precursor of an additional antioxidant should be added during modification of the PC-refractory charge components, e.g., sol-gel composites with added inorganic or organic precursors of the required antioxidant are deposited on the graphite surface.

The use of organic – inorganic complexes $(-CH_3)-(SiO_2)_n-C$ and $(-CH_3)-(SiO_2)_n-Ni(NiO)-C$ for modification of PC-refractory charge components (e.g., graphite) was proposed. A sol based on ethylsilicate hydrolysates that were produced using inorganic nickel salts for the hydrolysis and a sol-gel composite with added nickel organic precursor or a mixture of a nickel organic precursor with an organometallic compound that was used to create the $(-CH_3)-(SiO_2)_n-C$ complex by PFR modification were proposed for this [26, 27].

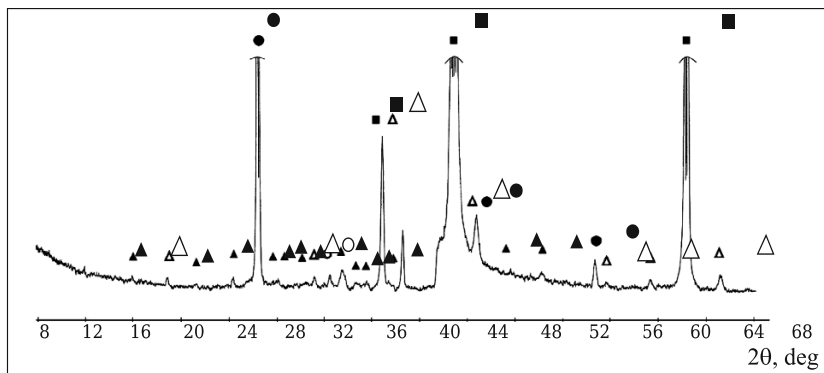Graphite was protected reliably from oxidation for a long time by the synthesized additional antioxidants SiC and

Ni(NiO) together with the main antioxidant Al. Thus, although the peak size of carbon was 25 – 30 rel. units after slag-resistance tests with the organic—inorganic complex $(-CH_3)-(SiO_2)_n-C$ and antioxidant Al in the PC-refractory (Fig. 5), the peak size was nearly 100 rel. units, i.e., the graphite was not oxidized, with the organic—inorganic complex $(-CH_3)-(SiO_2)_n-Ni(NiO)-C$ in the PC-refractory (Fig. 6). This occurred because Ni and SiC nanoparticles formed a dense layer around the graphite flakes according to XPA results and were oxidized, fulfilling their roles as antioxidants. The oxidation of SiC formed SiO_2 that reacted with the periclase filler and CaO of the slag to form monticellite, the peaks of which appeared in the diffraction pattern of the PC-refractory layer on contact with slag after slag-resistance tests (Fig. 6b). Basic slag of composition (mass%) SiO_2 38.63; Al_2O_3 7.54; CaO 46.84; MgO 4.46; MnO 0.31; FeO 0.37; S 1.85; CaO/SiO_2 1.21 was used for the studies.

The PC-refractories with added organic—inorganic complexes and Al antioxidant contained the complex antioxidant Al + SiC or Al + SiC + Ni(NiO) after the lining was heated to 1000°C. The XPA data confirmed that SiC was synthesized (Fig. 5a). Heating to 1400°C caused not only a reaction with slag components but also oxidation of the antioxidants and graphite. Oxidation of Al synthesized the refractory compound $MgAl_2O_4$ with increased volume. Oxidation of SiC formed ultradisperse SiO_2. Ni was converted to the oxide but was not detected by XPA because of the low content.

Therefore, it was found that graphite was oxidized more extensively if the organic – inorganic complex $(-CH_3)-(SiO_2)_n$ together with Al antioxidant was used than if the organic—inorganic complex $(-CH_3)-(SiO_2)_n-Ni(NiO)-C$ together with Al antioxidant was used. The graphite peaks were stronger in Fig. 6 than in Fig. 5b. This confirmed that the complex antioxidant Al + SiC + Ni(NiO) was more effective for protecting graphite from oxidation upon reaction with slag despite the fact that the reaction with slag formed monticellite (a small amount).
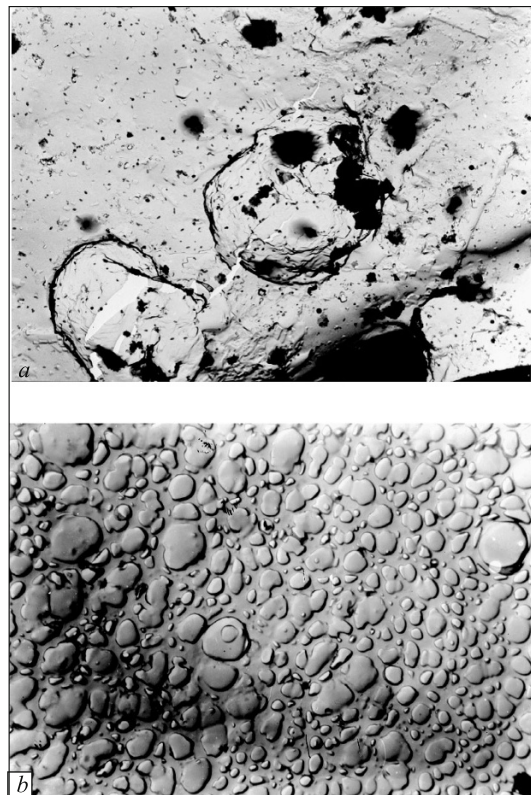
Fig. 7. Surface of PC refractory on modified PFR before (*a*) and after contact with slag (*b*) that was accompanied by formation of a non-wetting film on it.

A dense layer of carbon binder that was nano-reinforced by SiC nanoparticles with Ni(NiO) particles and possibly fused monticellite appeared around the graphite flakes. This shielded the graphite from further oxidation for a certain time and increased the resistance of the PC-refractory to reactions with metal and slag because a non-wetting slag film also formed on the lined surface of the heating system (Fig. 7). Because the formed frameworks would probably have different porosities after heat treatment of the aforementioned organic – inorganic complexes, they could have different effects on compaction of the carbon binder of the PC-refractories and their physicomechanical properties.

CONCLUSION

Formation of organic – inorganic complexes based on $(-CH_3)-(SiO_2)_n$ enhanced the synthesis of SiC nanoparticles at low heat-treatment temperatures. Filling of this complex by carbon increased the amount of synthesized nanoparticles. Use of silicon alkoxide to modify PFR and graphite of PC-refractories also formed the complex $(-CH_3)-(SiO_2)_n-C$ with an increased carbon content after carbonization of PFR-modified material at $180 - 220°C$. SiC that was synthesized from various carbon precursors was present after heat treatment during operation to $1000°C$ owing to the presence of atomic carbon in addition to coke in the carbon binder. Nanoparticles of atomic carbon were generated from the radical $(-CH_3)$. Organic – inorganic complexes $(-CH_3)-(SiO_2)_n-Ni(NiO)-C$ were proposed for activating the Al antioxidant in the PC-refractories. This would also facilitate the simultaneous synthesis of additional antioxidants as nanoparticles that self-reinforced the carbon binder and improved not only the physicomechanical properties of the PC-refractory but also its oxidation resistance. This was confirmed by petrographic analysis and XPA results.

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