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Plasma-Chemical Method of Silicon Carbide Modification to Obtain Particles with Controlled Surface Morphology

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Abstract—A plasma-chemical method for the modification of silicon carbide particles is presented, which makes it possible to obtain particles with a controlled surface morphology. The variable parameter of particle processing was the ratio of the fraction of plasma-forming (Ar) and additional (H) gases. It was shown that at Ar/H = 100/0, the formation of a carbon shell is observed; at Ar/H ratios of 91/9 and 84/16, the particles are characterized by a carbon shell decorated with silicon nanoparticles or nanowires, respectively. The modified particles were analyzed using scanning electron microscopy and Raman spectroscopy.

Keywords: silicon carbide, plasma chemistry, surface morphology, nanoparticles, nanowires, carbon shell, core-shell

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Silicon carbide (SiC) features a unique combination of physical and chemical properties that include low density, high hardness and strength, chemical resistance to oxidizing environments, and thermal resistance [1]. SiC is more and more often seen as a candidate particulate filler for polymer composite materials (PCMs) [2]. When a polymer matrix is filled with SiC particles, the thermal conductivity [3], the Young's modulus [4], the thermal resistance, and other characteristics improve noticeably. The authors of [5] have also succeeded in preparing a shape-memory composite material based on polyvinyl alcohol and polyacrylic acid with SiC nanoparticles. The method of introduction of SiC particles is unique in that the shape memory effect could be initiated remotely (by microwave irradiation).

When developing particle-filled PCMs with new functional properties, one also needs to ensure that these composites have fine physical and mechanical characteristics, which depend largely on the interphase interaction between the polymer material and the filler surface. Various methods of filler surface functionalization [6] are used to improve the interphase interaction. As is known, SiC is chemically inert, and the options for chemical modification of its surface are limited. The results of computer simulations of the structure of particle-filled PCMs presented in [7] demonstrate that, in addition to a certain type of interaction between polymer chains and the surface of a particulate filler, one needs to take the surface morphology (relief) into account. The authors of [7] found that the polymer density in boundary layers and the free volume in the interfacial region vary greatly depending on whether a particle has a smooth surface or a bristle-like relief. Thus, the resulting properties of a PCM may be adjusted by varying the surface morphology of filler particles.

In the present study, a plasma-chemical method for the modification of silicon carbide particles is presented. This method allows one to obtain particles with an adjustable surface morphology. SiC particles (fraction F800) with sizes ranging from 6 to 8 μm prepared in accordance with GOST 26327-84 (ST SEV 4169-83) were studied.

The modification of particles was performed using an F4 plasmatron of the plasma deposition setup. An electric arc was initiated between a tungsten cathode and a copper water-cooled anode (sprayer) and heated the working gas. The outflowing gas formed a plasma jet. SiC powder was introduced into the plasma jet with a flow of carrier gas (Q_{Ar} = 5 L/min) via a special injector located at the sprayer exit. The arc power was

Table 1. Powder bulk densities and specific surface areas of particles SiC

Parameter	Sample			
	SiC	SiC at Ar/H =100/0	SiC at Ar/H = 91/9	SiC at Ar/H = 84/16
Bulk density ρ_p, g/cm^3	1.261	0.682	0.589	0.479
Specific surface area S_{BET}, m^2/g	3	15	38.8	45

defined by the current strength (500 A) and the voltage that, in turn, depended on the type and the flow rate of plasma-forming gas (Q_{Ar} = 30 L/min).

The ratio of volume fractions of plasma-forming (argon) and additional (hydrogen) gases (Ar/H), which were supplied through an axial aperture in the tungsten electrode, was chosen as an adjustable parameter of plasma-chemical modification. SiC powder was fed using a sampler with carrier gas (Ar) into the section of the plasma jet generated by the plasmatron. This powder was heated in the plasma region, introduced into the reactor with the flow of plasma-forming and additional gases (Ar/H), and then condensed on the water-cooled reactor walls in the form of a disperse powder.

Since the thermal conductivity of hydrogen is considerably (10 times) higher, it intensifies the processes in the plasma-chemical reactor. The primary process, which continues even without hydrogen in the reactor (Ar/H = 100/0), is the sublimation of silicon atoms from the surface of SiC particles. This process may be characterized in the following way.

When a SiC particle enters a hot region of plasma flow, its surface temperature exceeds 1500°C, and the bond of a silicon atom in plane (0001) with unsaturated valence breaks. It evaporates and forms a discontinuity in the upper layer (dimple) [8]. At the same time, a carbon atom seeks to form a bond with one of the neighboring carbon atoms. A single compact cluster (islet) of several graphene cells forms gradually in

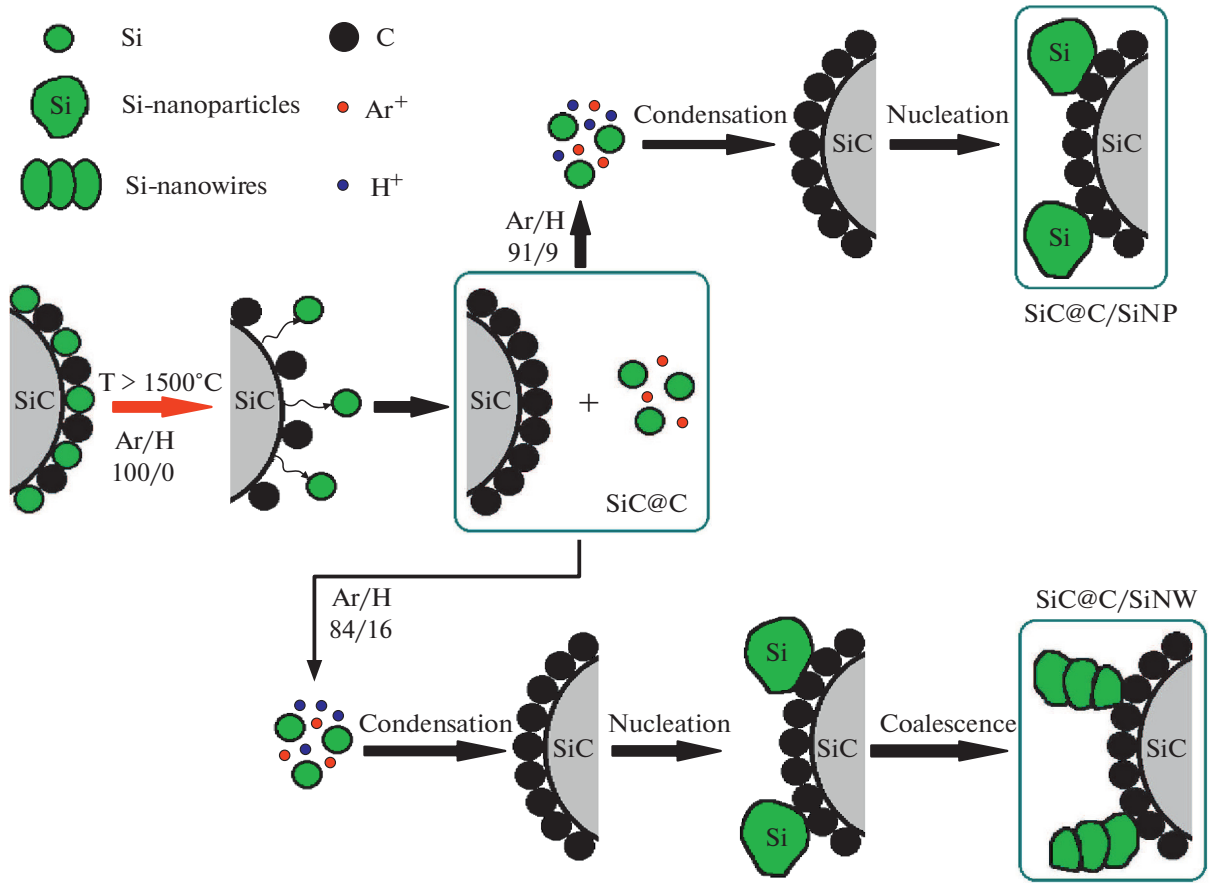

Fig. 1. Schematic diagram of processes of modification of SiC particles in the plasma-chemical reactor (a color version of the figure is provided in the online version of the paper).

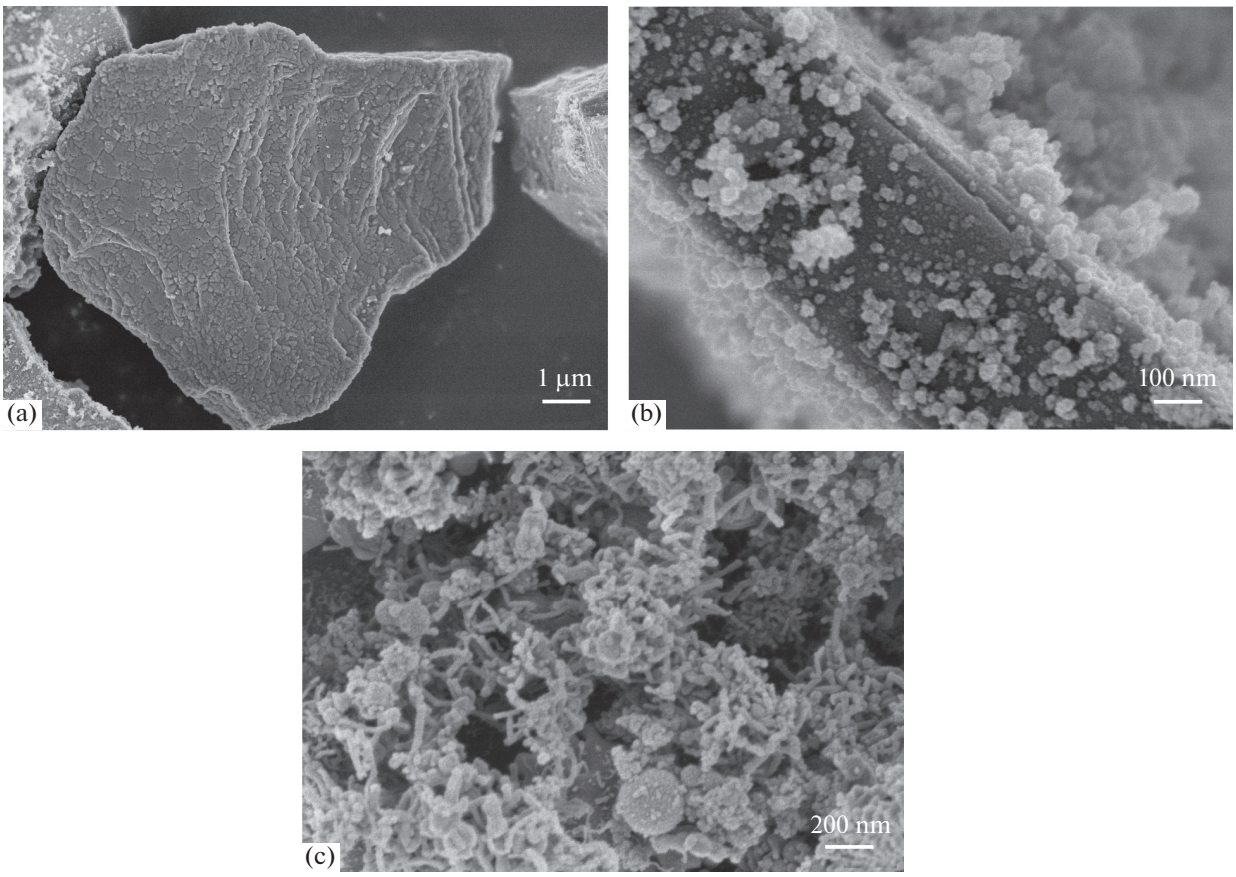

Fig. 2. SEM images of modified SiC particles at different ratios of plasma-forming and additional gases Ar/H: (a) 100/0, (b) 91/9, (c) 84/16.

the region of disruption of the upper SiC layer (dimple). This process continues until the particle reaches a cold region of plasma flow and its surface cools.

If up to 9 vol % of hydrogen are introduced into the reactor (Ar/H = 91/9), these processes intensify, and sublimating silicon atoms still remaining in the hot plasma region condense on the "cooler" carbon shell of the neighboring particle. This is followed by the process of nucleation and growth of silicon nanostructures. Their size depends on the time spent by particles in the hot plasma region. This time interval may be extended by introducing additional hydrogen into the reactor and raising its content to 16 vol % (Ar/H = 84/16). A continuous supply of Si atoms to nucleation centers induces their further growth into 1D structures (Fig. 1). If more than 16 vol % of hydrogen are introduced, the process is reversed: silicon atoms sublimate from the surface of already formed silicon nanowires (NWs). This is the reason why SiC particles modified at Ar/H = 77/23 and 72/28 are not considered further in this report.

The morphological features of the powder were visualized using a high-resolution FE-SEM S-5500 (Hitachi Ltd., Tokyo, Japan) scanning electron microscope (SEM) at an accelerating voltage of 3 kV and a beam current of 20 nA. The microphotographs of samples obtained at Ar/H = 91/9 and 84/16 reveal the formation of nanoparticles and nanowires, respectively, on the surface of modified SiC particles (Fig. 2). The diameter of nanoparticles falls within the range from 30 to 60 nm, while NWs have a diameter of approximately 50 nm and a length of 300–400 nm.

Figure 3 shows the room-temperature Raman spectra measured with a Bruker RFS 100/S spectrometer. A continuous Nd:YAG laser with an excitation line of 1.064 μm was used as a light source for Raman excitation. The spectra were measured within the 2–1800 cm^{-1} range (the working spectral resolution was 2 cm^{-1}). The principal modes of transverse acoustic and optical branches characterizing the structure of polytype 6*H*-SiC are present in the spectra of initial SiC microparticles. The principal peaks remain after microparticle treatment, and new peaks *D* and *G* at 1320 and 1600 cm^{-1} emerge due to the presence of ordered carbon. The emergence of an additional peak of "defects" *D*3 (~1510 cm^{-1}) may be indicative of the presence of intralayer and interlayer defects in the molecular structure. In addition, the spectra of samples obtained at Ar/H = 91/9 and 84/16 feature an

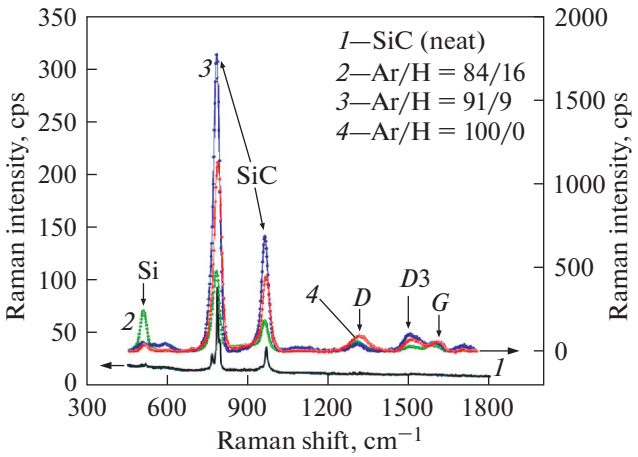

Fig. 3. Raman spectra of modified SiC particles.

intense peak at 508 cm^{-1} that is related to the oscillation of Si phonons at the interface between the Si nanocrystal surface and the SiO_2 oxide layer [9].

The bulk density (ρ_p) of powders of modified SiC particles was determined in accordance with GOST 19440-94. It can be seen from the table 1 that the bulk density of samples decreases significantly as the concentration of hydrogen in the plasma-chemical reactor increases. For example, ρ_p at Ar/H = 84/16 is more than 2.5 times lower than the density of unmodified SiC particles.

The texture parameters of samples of the studies materials were measured with an ASAP-2420 system (Micromeritics, USA). Prior to measurements, the surfaces of materials were degassed at a temperature of 250°C and a pressure no higher than 20 μm of mercury for 8 h. A known mass of material was then subjected to gas adsorption measurements at a temperature of 77 K, and the adsorption isotherm was recorded within the range of relative pressures P/P_0 = 0.005–0.995. The analytical gas (nitrogen) was dosed in small amounts. The measurement results were processed using Brunauer–Emmett–Teller (BET), Barrett–Joyner–Halenda (BJH), *t*-plot (de Boer method), and α-S models. The obtained data revealed that the specific surface area (S_{BET}) increased with hydrogen concentration in the reactor. SiC particles at Ar/H = 84/16 had the maximum value of *S*BET, which was 15 times higher than S_{BET} of the initial SiC particles. This confirms the fact that plasma-chemical treatment of SiC particles allows one to obtain particles with a highly developed surface with a complex relief.

Thus, a plasma-chemical method for the modification of SiC particles and production of particles with an adjustable surface morphology has been proposed for the first time. It was demonstrated that a carbon shell forms even with no hydrogen present in the reactor. SEM data and Raman spectroscopy data revealed that carbon shells are decorated with silicon nanoparticles or nanowires when 9 or 16 vol % of hydrogen, respectively, are introduced into the reactor. Modified SiC particles have a highly developed surface: their specific surface area is 15 times higher than S_{BET} for the initial SiC particles. Modified SiC particles may be used as a filler for PCMs.

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CONFLICT OF INTEREST

The authors of this work declare that they have no conflicts of interest.

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