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Hydrophobization of Porous Ceramic Materials Using Supercritical Carbon Dioxide

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Abstract—A process has been proposed for hydrophobizing an inorganic porous material consisting of silica fibers using fluoroalkane dissolution in supercritical carbon dioxide. The process allows one to produce thin, homogeneous polymer coatings both on the surface and in the bulk of the material, ensuring that the material has excellent hydrophobic properties, which significantly improves its performance parameters and extends its potential application field.

Keywords: superhydrophobicity, supercritical carbon dioxide, fluoroalkane, ceramic material

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INTRODUCTION

Porous materials produced from fibers are widely used for heat insulation and other purposes [1–7]. Possible starting materials for the fabrication of fibers are various polymers and ceramics, primarily oxide ceramics. In contrast to polymers, oxides have high melting points, 1728°C for SiO_2 and 2050°C for Al_2O_3 [8], so inorganic porous materials are applicable as well at temperatures above 1000°C. Moreover, they can be used to fabricate fireproof products. Heat-resistant and fireproof materials are necessary for the operation of a multipurpose lifesaver intended for evacuating the stuff in the case of emergencies on offshore oil platforms, which are often accompanied by fire accidents [9]. The device should be capable of operating under Arctic conditions, that is, at high humidity, high atmospheric salinity, and low temperatures, which may lead to icing of structures.

Owing to the high porosity (up to 95%) of the oxides under consideration and the good wettability of their constituent chemical substances by water (the contact angle of a water droplet on a SiO_2 surface is 1° to 5° [10]), the material actively absorbs moisture and sinks in water. The presence of water in spaces between fibers impairs the thermophysical properties and performance of the material, so the possibility of fiber hydrophobization with the aim of preventing water penetration is of great current interest.

A method was proposed previously which utilizes hydrophobizing liquids, but is has a certain drawback. For example, the sixfold use of DC-Z-6079 hexamethyldisilazane (Dow Corning) for rehydrophobization of the thermal protection tile system of the Challenger space shuttle [11, 12] led to a reduction in the strength of the underlayer in its skin, which entailed replacement of several thousand expensive tiles [13]. Researchers at the All-Russia Research Institute of Aviation Materials carried out studies with the use of hexamethyldisilazane as a hydrophobizing agent, in combination with oligomethylsiloxanes in order to reduce turnaround hydrophobization and the amount of released ammonia, which is a corrosion-active species with respect to structural metals and alloys of spacecrafts, but they failed to avoid their release. In addition, they proposed hydrophobizing liquid organosilicon and methyltriethoxysilane compositions and procedures for producing coatings from such liquids on surface fibers of porous ceramic products. The contact angle of water on the surface of the TZMK-10 material treated with a hydrophobic substance is on the order of 90° [14], which cannot be considered satisfactory given the current level of requirements for hydrophobic materials [15].

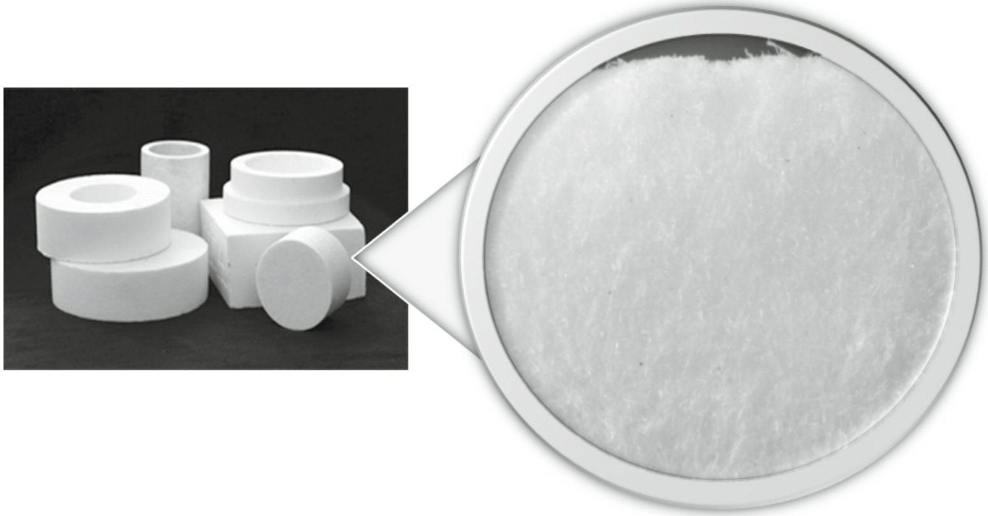

Fig. 1. Appearance of products from the TZMK-10 porous material and enlarged view of their surface.

Potentially attractive hydrophobizing materials are fluoropolymers [16]. At certain surface roughnesses, they allow one to reach a superhydrophobic state [15], which minimizes the influence of moisture. In this context, it is reasonable to produce fluoropolymer coatings on the surface of ceramic fibers, but this is difficult to implement because the fluoropolymers are poorly soluble and their melts have high viscosity, which makes it difficult to introduce fluoropolymers into the bulk of porous materials. Coating can, in principle, be produced using telomeric tetrafluoroethylene solutions in organic liquids [17] or commercially available F-4 D suspensions [18]. Such approaches are, however, difficult to apply for processing inner regions of porous materials; additional heat treatment is required to ensure continuity of the coating; and the process uses foreign substances, which influence the performance of the coating. Processing conditions should be adjusted to each porous material, telomeric solution, and suspension, which requires special research in each particular instance. In the case of suspensions, it is difficult for fluoroplastic particles to penetrate small pores, which leads to clogging of the bulk of the material.

As shown earlier [19–21], low-molecular-weight fractions of the FORUM fluoropolymer and fluoroalkanes [22] dissolve in supercritical (SC) carbon dioxide (SC CO_2), which made it possible to produce fluoropolymer coatings down to several nanometers in thickness. The method is attractive in that, in an SC state, molecules of CO_2 and soluble substances have mobility characteristic of gases and density of liquids, which facilitates processing of fibers in the bulk of the material. The process has only one step and is easy to implement. The solvent (carbon dioxide molecules) can be easily and completely removed from the product, which rules out incorporation of foreign substances. The technology was used to produce coatings on flat surfaces [23–26], but no attempts have been made to apply it to porous ceramic materials.

In this paper, we report the use of SC CO_2 for hydrophobizing TZMK-10 porous silica. As a hydrophobizing agent, we use the PPU-90 fluoroalkane, manufactured by OOO GaloPolimer–Kirovo-Chepetsk according to an appropriate technical specification.

EXPERIMENTAL

The TZMK-10 fibrous thermal-protection material is made of silica fibers produced by blowing molten 99.9%-pure natural silica (All-Russia Research Institute of Fiberglass Plastics and Glass Fiber).

The process for the fabrication of this material comprises many steps: dispersion of silica fiber in an aqueous suspension in a blender equipped with an offset-axis propeller stirrer; fabrication of a blank by evacuating the water–fiber suspension through a perforated plate; homogenization of the aqueous suspension, containing, in addition to the dispersed silica fiber, boron-containing additives as sintering aids, an organosilicon binder, and surfactants; fabrication of a fibrous block of preset geometric dimensions by evacuating the water–fiber suspension through a perforated plate into a holder; drying of the fibrous block under pressure at a temperature of 300°C; and high-temperature heat treatment of the fibrous block at temperatures of up to 1250°C.

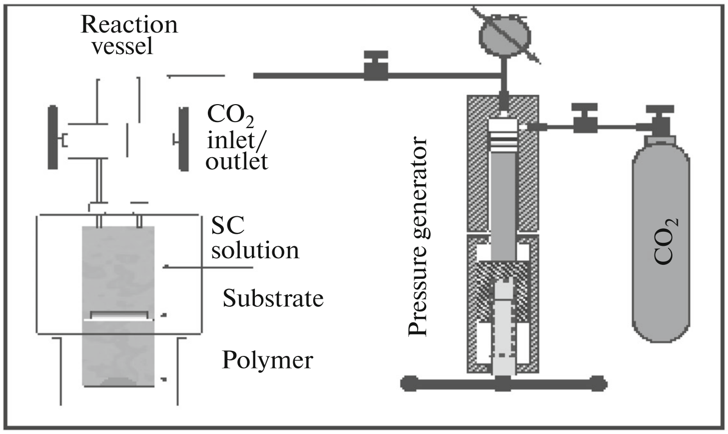

Fig. 2. Schematic of the high-pressure chemical reactor.

Varying the fiber concentration in the aqueous suspension, one can tune the density of the material in the range from 120 to 200 kg/m^3. Materials differing in density differ in mechanical characteristics. In particular, the tensile strength in the weak direction is 0.32–0.36 MPa for the samples with $\rho = 120$ kg/m^3, 0.43–0.48 MPa for the samples with $\rho = 144$ kg/m^3, and 0.65–0.7 MPa at $\rho = 200$ kg/m^3. After 36 h of testing, the linear shrinkage of the samples at 1250°C ranges from 4 to 8% [27].

Homogenization of the water–fiber suspension and boron-containing additives in the presence of an organosilicon binder and surfactants is accompanied by uniform deposition of the additives onto the surface of the silica fibers. During high-temperature heat treatment of the fibrous block, the boron-containing additives form a low-melting-point eutectic at intersections of the fibers, which ensures bonding between the fibers and stiffness of the material.

The process allows one to obtain products of various geometric shapes (Fig. 1). The TZMK-10 material, with a density of 144 kg/m^3 and porosity of 95%, possesses high hydrophilicity, as evidenced by sorption of 600–700 wt % water when it is immersed in water. A water droplet placed on the surface of the material becomes sorbed in less than 1 s, which makes it impossible to measure the contact angle of the as-prepared sample. We studied TZMK-10 plates 15 × 10 × 3 mm in dimensions, with millimeter-scale roughness and distinguishable fibers (Fig. 1). Fluoroalkanes were deposited from solutions in supercritical carbon dioxide using a setup schematized in Fig. 2.

The TZMK-10 plates and fluoroalkane powder (weighing $m = 0.23 \pm 0.1$ g) were loaded into a 10-cm^3 autoclave, which was then hermetically sealed. Next, the autoclave was placed in a thermostat and the temperature was brought to $t = 70$°C. After thermodynamic equilibrium was reached (15 min), CO_2 was pumped into the autoclave at a pressure of 20 MPa, which ensured a supercritical state of the carbon dioxide. Under these conditions, the density of CO_2, evaluated using NIST's program, was about 660 kg/m^3. During autoclaving for 3 h, fluoroalkane molecules dissolved in the SC CO_2 and penetrated the sample. Next, the pressure in the autoclave was released over a period of 30 min, and the autoclave and processed TZMK-10 sample were withdrawn from the thermostat.

The technology has a number of distinctive features regarding the processing of porous materials. The dependence of the dissolving power of SC CO_2 on temperature and pressure allows one to ensure optimal conditions for the growth of polymer films of controlled thickness. The SC phase ensures the penetration of the deposited material into open pores in the sample. Since SC CO_2 has no surface tension, the size of the pores accessible to the polymer is only determined by the dimensions of the polymer macromolecules. The fact that CO_2 does not exist as liquid phase at atmospheric pressure rules out restructuring of the polymer coating under the effect of surface tension forces after solvent removal. The high rate of diffusion processes in SC solutions reduces the time needed for producing polymer coating. An additional advantage is that CO_2 as a solvent is environmentally safe, in contrast to many noxious chemical substances, which suggests that the use of SC CO_2 is a "green" technology.

To obtain microimages of the samples and determine their chemical composition, we used X-ray microanalysis and X-ray mapping on a Carl Zeiss NVision 40 scanning electron microscope (SEM) equipped with an Oxford Instruments X-Max X-ray detector (80 mm^2) and operated at an accelerating voltage of 20 kV. Before analysis, a conductive layer (Au/Pd) ≃7 nm in thickness was sputter-deposited

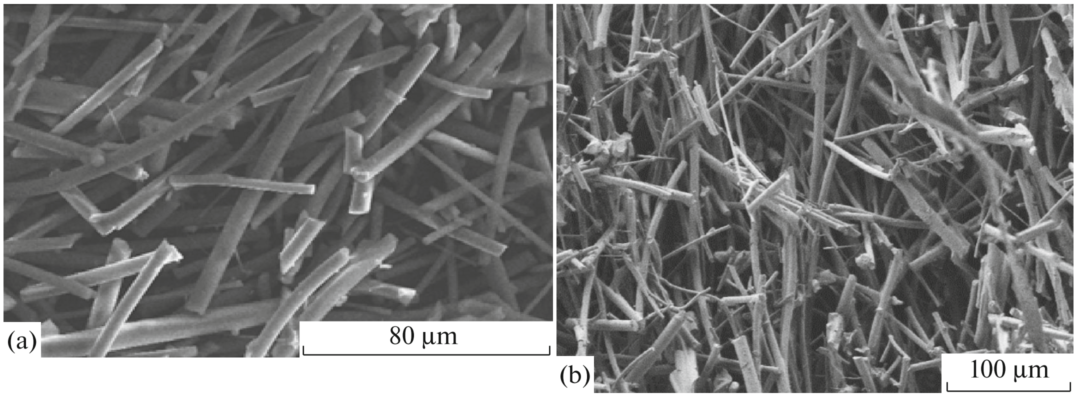

Fig. 3. SEM micrographs (a) in the plane and (b) on the end face of a sample.

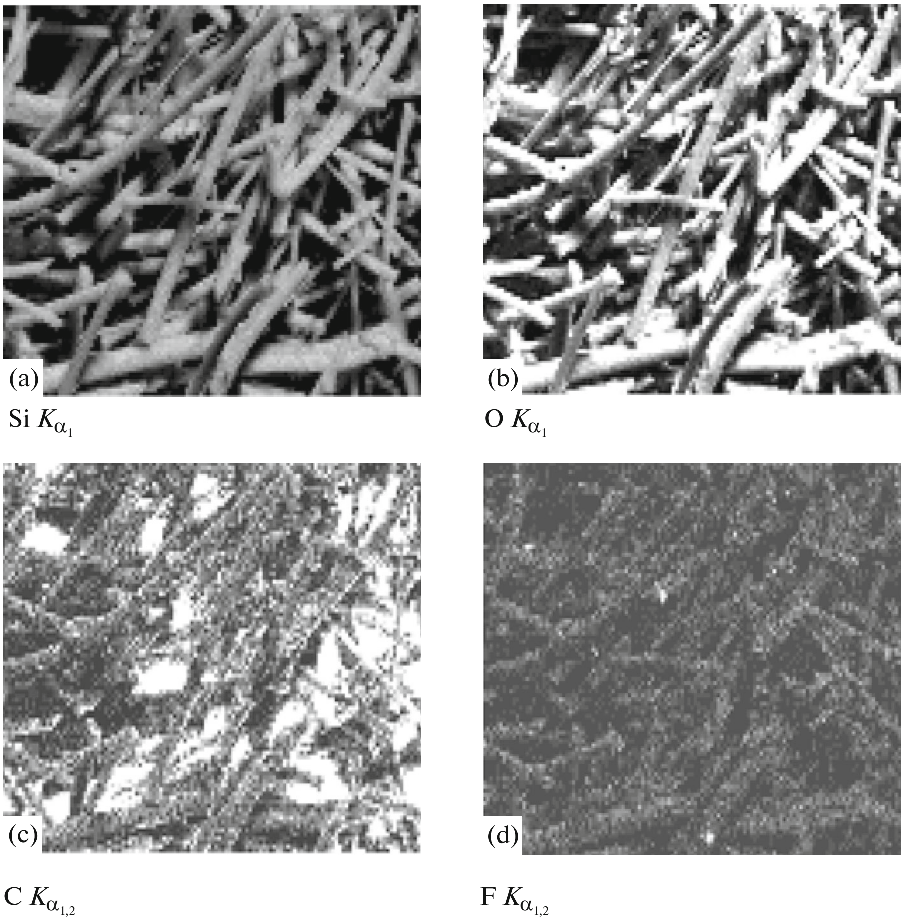

Fig. 4. Element X-ray maps of hydrophobized TZMK-10 plates: (a) silicon, (b) oxygen, (c) carbon, (d) fluorine.

onto the sample surface. Element X-ray maps were obtained as averages over 200 scans.

The contact angle was determined through digital processing of an image of a water droplet using a setup described by Emelyanenko and Boinovich [28]. We examined both sides of a flat sample at different points and evaluated the average contact angle. For each position of the water droplet, the average angle was determined using ten sequential images. To remove water-soluble contaminants, the sample was prewashed in water for 5 min using a Grad 13-35 ultrasonic bath.

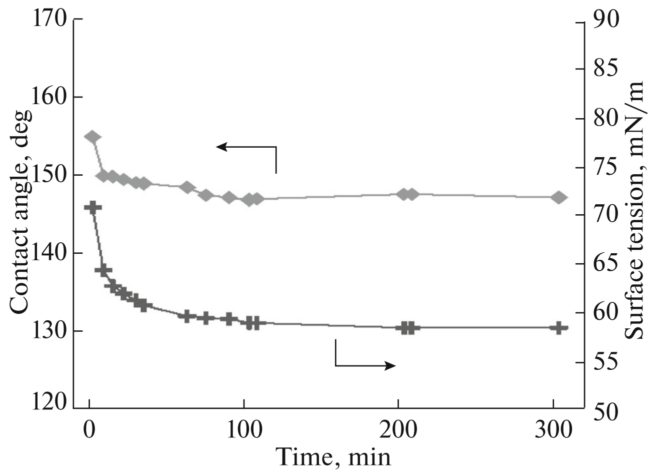

Fig. 5. Evolution of the contact angle and surface tension during long-term contact of a hydrophobized porous silica sample with water.

RESULTS AND DISCUSSION

The micrographs in Fig. 3 demonstrate that the samples under investigation consist of rods 50–200 μm in length and 1 to 10 μm in diameter, oriented preferentially in the plane of the sample. The rods touch each other, being secured at these places, and some of them form parallel bound structures (double fiber). The binding ensures rigidity of the sample and determines its macroscopic shape. The sample is characterized by high porosity (Fig. 3) and contains pores up to 100 μm in size.

Element X-ray mapping allows one to visualize the spatial distribution of individual chemical elements, as illustrated in Fig. 4. In our case, it is of importance because the method offers the possibility of assessing the nature of the fluoroalkane coating on oxide fibers. The silicon and oxygen X-ray maps have better resolution than do the carbon and fluorine X-ray maps, which is the result of the small thickness of the fluoroalkane layer. The constituent elements of the fluoroalkane are evenly distributed over the fibers both in the surface layer and in the bulk (the latter was inferred from analysis of cross sections). The identical observabilities of images of the rods in the top and deeper (bulk) layers in terms of the constituent elements of the fluoropolymers suggest that these elements penetrate the bulk of the sample. The contours of the fibers in the oxygen and silicon X-ray maps are identical to those in the carbon and fluorine X-ray maps, which is due to the fact that the fibers have homogeneous fluoroalkane coatings.

The chemical composition of the sample was determined to be 28.76% silicon, 70.62% oxygen, 7.49% carbon, and 0.30% fluorine. The relationship between the first two elements is close to that stemming from the chemical formula SiO_2, even though the oxygen content is slightly increased, but it is not clear why the carbon content is 20 times the fluorine content, whereas it should be at least a factor of 2 lower. Analysis of the as-prepared (unprocessed) sample showed that it contained 12.76% carbon, without fluorine. Most likely, carbon originated from the organic compounds used in the preparation of the starting porous material.

As mentioned above, the material instantaneously sorbs a water droplet. When placed in water, it sinks to the bottom of the vessel; in other words, the material is hydrophilic. After processing, it does not sink in water, floating on its surface for a long time, which suggests that it has passed into a hydrophobic state. We performed quantitative studies of the wetting of the hydrophobized sample.

Since the surface of the sample has considerable macroscopic roughness, the measured contact angle varies strongly from region to region. In specially selected regions, the angle reaches 155° (Fig. 5), which corresponds to one of the signs of the superhydrophobic state [15]. The average contact angle is almost the same on the two sides of the sample: 142.9° ± 3.5° and 142.1° ± 4.9°. No water droplet roll off was observed on either side of the sample, which is attributable to a mixed, homogeneous/heterogeneous wetting regime. It seems likely that the texture of the sample, formed when the sample was produced, does not meet the surface profile multimodality condition. One important characteristic of surface wettability is the evolution of the contact angle and surface tension on the water/vapor interface during long-term contact of a droplet with the material under investigation under saturated water vapor conditions [29]. The time dependences of these parameters are presented in Fig. 5 for a region with the maximum contact angle. Three distinct portions can be distinguished. During the first 10 min, the contact angle decreases from 155° to 150°. In the interval 10 to 100 min, the contact angle varies more slowly, decreasing to 146°. Next, there is a plateau throughout the time interval of the measurements (up to 300 min). On the whole, the contact angle decreased by 9° in 5 h of contact. A similar trend is exhibited by surface tension.

The observed variation in the contact angle can be accounted for under the assumption that, when the fibers are in contact with water, partial fluoroalkane desorption from their surface occurs (the first two steps). Moreover, fluoroalkane migration from the SiO_2/droplet interface to the droplet/air surface leads to a reduction in the surface tension of the droplet.

CONCLUSIONS

We have for the first time tested a process for depositing hydrophobic fluoroalkane coatings onto silica fibers in a porous material using fluoroalkane dissolution in SC carbon dioxide. We have found processing conditions that allow us to produce thin, homogeneous fluoroalkane coatings not only on the fibers in the outer layer but also in the bulk of the material, ensuring effective hydrophobicity not only of the surface layer but of the entire material.

We have identified the key morphological features of the material and fluoroalkane coatings, which have been shown to be continuous. The wettability parameters of the hydrophobized material have been shown to vary over time because of the interaction between the fluoroalkane coating and water, but the material is stably in a highly hydrophobic state. The proposed processing significantly improves the performance parameters of the material, extending its potential application field.

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