Creation of relief coatings on the surface of silicate materials in the plasma of radio-frequency induction discharge at low pressure

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Abstract. The paper shows the possibility to create relief coatings based on powdered nonmetallic materials (SiO₂ and Al₂O₃) on a silicate substrate in the radio-frequency induction plasma at the low pressure. The features of the structure and properties of the obtained coatings have been studied.

1. Introduction
Nanorelief coatings are currently used to produce materials with great contact angle of wetting values on the "lotus effect" principle. To obtain this result, the combined effect of the surface nanoroughness and its chemical structure should be used. The superhydrophobic properties can only be achieved by the dimensions selecting of the surface relief. Creation of the superhydrophobic coatings on the heterogeneous materials was described in details in the works of L.B. Boinovich [1-3]. It is also known, that silicate and ceramic materials with developed surface are in demand for catalysts carriers' creation. [4].

The study shows investigation in the possibility to obtain the developed surface on the silicate glass by application and thermal fixing of dispersed material under gas radio-frequency induction (RFI) low pressure discharge treatment. Al₂O₃ and SiO₂ powders with different dispersion were used as coating materials.

2. Materials and methods
The household and quartz glass plates, glass fibers and glass microspheres were used as substrates. The powders with different dispersion were used as a coating material: microdispersed SiO₂ with particle dimension 0.5 - 5 μm and nanodispersed SiO₂ with a particle dimension 50 - 300 nm were obtained by the gas-phase method [5], as well as α-Al₂O₃ powder after mechanical dispersion with particles dimension 0.5 - 100 μm. Granular stearic acid was used as an additional non-toxic chemical water-repellent agent.

Experimental RFI plasma set was employed for the powders deposition on the substrate (Fig. 1). Technical parameters of the treatment were the following: ions energy of 30 eV; density of electron current of 25 A/m²; pressure of 60 Pa; plasma-forming gas — Ar and a mixture of Ar-propane (90:10).
The powders were injected into the RFI discharge through the plasmatron together with the working gas.

![Figure 1. The scheme of radio-frequency induction installation](image)

The process of relief coating applying on the substrate included the following steps (Fig. 1):

1. The billet was installed into the operating vacuum chamber 1 of the radio-frequency induction installation above the cut of the quartz plasmatron 2 in the holder 3 at a predetermined height (adjustable by the bracket 4 in the range of 30 - 60 mm).
2. The system was evacuated to a pressure of 10 - 100 Pa.
3. The discharge was ignited and its specific technological parameters were set; the billet was heated above the plasma jet 6 to a temperature of 250 - 300 °C for cleaning, surface activation and internal strains removal.
4. The coating material of the selected fraction was supplied through a powder dispenser 5 with a flow of plasma-forming gas into the working zone through a plasmatron, placed in an inductor 7 with an additional electrode 8.
5. The samples of the catalysts heated in the discharge core to temperatures close to the melting point were thermally deposited on the heated substrate.
6. For additional cleaning and coating fixing the billet was treated in the discharge for 15 - 60 min after the powder supply was stopped.
7. After the discharge was switched off the billet was blown by an inert gas stream.

3. Results and discussion

The coating applying was resulting in the formation of a regular micro-grained relief with the sizes of elements of 0.5 - 1.5 μm. The microscopy results of the flat glasses with coatings are shown in Fig. 2, 3; on glass fabric fibers – in Fig. 4.

![Figure 2. Optical image of Al₂O₃ relief coating, ×2000](image)  
![Figure 3. Optical image of SiO₂ relief coating, ×2000](image)  
![Figure 4. Optical image of glass fiber with SiO₂ coating, ×4000](image)  

The texture, obtained on the glass surface, is characterized by high regularity and granularity. A uniform multimodal relief was formed on glass fiber by agglomerates of particles and individual particles with the details dimensions of 0.5 - 5 μm (Fig. 4).
The possibility to develop the glass microspheres surface is also considered. It was proposed to create a microtexture on the glass spheres (d = 50-500 μm) surface by depositing and fixing silicon dioxide nanoparticles under low pressure RFI plasma treatment. Microspheres and nanoparticles were mixed, according to 1:10 mass ratio, and placed in a hopper for powder feed (item 5, Fig. 1) into the discharge, and caught by a trap filter above the plasmatron cut. The microstructure of the samples was studied by SEM method; the results of the study are shown in Fig. 5. The SiO₂ relief coating with size details of 1-5 μm was formed on the glass microsphere.

![SEM-image of the surface of a glass microsphere with SiO₂ coating, ×500](image)

The results of the created relief on the hydrophobic properties, was investigated by using wetting angle determination method on the KRUSS DSA 30 installation. The results (Fig. 6) demonstrate increased contact angle of wetting on the SiO₂ coating with the stearic acid additionally applied.

![The image of water drop on a glass sample: a – without coating; b – with SiO₂ coating and using of stearic acid](image)

The structure on the surface of silicate glass, created by RFI plasma treatment, enables to strengthen the hydrophobic properties of the surface, in particular, the value of the wetting angle (θ) increased from 37.73° to 154.19°. Therefore, it is advantageous to obtain the superhydrophobic coatings on the silicate materials surface by given technique.

The phase composition of the Al₂O₃ coating was studied by X-ray diffraction method. It was established that with Ar as plasma-forming gas the predominant phase is α-Al₂O₃, whereas in the mixture of Ar-propane gases, the γ-Al₂O₃ phase appears in the coating material (Fig. 7). The X-ray diffraction results demonstrate the following phase composition of the coating: 15% – γ-Al₂O₃, 15% – α-Al₂O₃, 70% – crystalline γ-Al₂O₃. The chemical effect of the plasma was manifested in a significant crystallization of the sample.
4. Conclusion
Overall, the possibility to obtain the relief non-metallic coatings on silicate substrates with different geometry in radio-frequency induction plasma discharge at low pressure has been evidenced with a number of experiments. These coatings can be applied to create catalysts carriers, as well as to impart superhydrophobicity based on the "lotus effect" to silicate materials.

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