Investigating interaction of microdischarges with TiO$_2$ surface films in the cell of dielectric barrier discharge

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Abstract. The paper presents the results of studying the interaction of microdischarges in the cell of dielectric barrier discharge (DBD) with enamel-based surface films deposited on a fabric-based laminate. TiO$_2$ powder was added to the surface films. Elemental composition of the surface films was studied in the areas with different level of microdischarges exposure. Before measurement, the samples were bonded onto a 25 mm aluminum specimen with conductive silver paint. The metal was coated with a thin film (13 nm) of carbon using magnetron sputtering method. The observations were carried out using Hitachi SU8000 field-emission scanning electron microscope (FE-SEM). Images were acquired in secondary electron mode at 30 kV accelerating voltage and at working distance 8-15 mm. EDX-SEM investigation and mapping were carried out using Oxford Instruments X-max EDX system. Before measurement, the samples were coated with a thin film (13 nm) of carbon using Cressington 208 carbon coater. The study results showed significant effect of microdischarges in the DBD cell on elemental composition of surface films deposited on the fabric-based laminate surface.

1. Introduction

The importance of studying low-temperature plasma interaction with various materials is related to the fact that it can be used, in particular, for purposeful changes in the physical chemical properties of surface films of materials. For example, comparatively inexpensive photoelectric converters can be developed on the basis of photoelectrodes, which are as a rule dye-sensitized nanoporous TiO$_2$ film [1–8]. In this case, the dielectric barrier discharge is used to improve the effectiveness of energy conversion by photoelectric converters. In particular, it was noted in [2, 3] that the result of DBD treatment is a decrease in oxygen vacancies in the TiO$_2$ surface film, an acceleration of the TiO$_2$ nanoparticles narrowing and also an increase of specific surface area and hydrophilicity of TiO$_2$ surface film. Because of these factors, the dye adsorption on the TiO$_2$ surface film is increased. In addition, the low-temperature nonequilibrium DBD plasma generators are widely used as industrial ozonizers [9–14]. However, the short service life is the main problem of plasma-chemical DBD-based ozone generators. The lifetime of a plasma-chemical ozone generator is mostly determined by the service life of the dielectric barrier. Factors determining the service life of the DBD plasma-chemical generators include the electrical physical characteristics and the surface properties of the dielectric, the design of the electrodes and the plasma-chemical generator discharge cell, as well as the device electric operation mode. Thus, in the discharge cell, the dielectric is very strongly and negatively affected by ozone (a very active element), the high temperature of microdischarge channels, microdischarges and the electric field. Localization of microdischarges presents a special danger for...
the dielectric in the DBD cell resulting in the superheat of the dielectric in the microdischarges localization areas and its breakdown.

One of the possible ways of increasing the service life of dielectric barrier discharge cells is the use of DBD cells with a rotating dielectric [9, 13]. Another method involves using barrier-free discharge cells [14]. A high-voltage pulse power source and a discharge chamber are the basic elements of such setups. To obtain the high-voltage pulses lasting several tens of nanoseconds, a rotating discharger [15] is connected to the output of a high voltage DC source. Another possible way to solve the challenge of increasing the service life of plasma-chemical ozone generators is the development of corona-resistant coatings for deposition on the dielectric surface [16, 17].

Thus, the aim of this research is highly relevant in terms of various practical applications in different technologies.

2. Experimental setup

The experiments were performed at the atmospheric pressure in the DBD cell (figure 1). Fabric-based laminate plates, 10x10 cm in size and 0.5 mm thickness, were exposed to microdischarges. Surface films based on heat-resistant enamel “Zerta” with a small amount of TiO₂ powder were deposited on the one side of the laminate plate. The average film thickness was 0.15 mm.

![Figure 1. Schematic of dielectric barrier discharge cell: 1) flat metal electrodes of rectangular form; 2) surface film; 3) fabric-based laminate plate; 4) high-voltage AC source.](image)

One of the flat rectangular metal electrodes 1 was placed with a gap of 1 mm above the laminate plate 3 (see figure 1) in the experimental setup. On the upper surface of the laminate, the film 2 was deposited. The 50 Hz electric voltage applied to the metal electrodes 1 in the DBD cell could cause electrical breakdown of the fabric-based laminate without the film after 30 minutes on average. The voltage effective value was equal to 7 kV. During the experiments the laminate without the film coating was replaced with the laminate of the same dimensions, but with the enamel-based film coating (enamel “Zerta”). During the experiments, the laminate with surface film was exposed to the microdischarge until the electrical breakdown. The exposure of the laminate with the surface film to the microdischarge action was more than 4 hours until the electrical breakdown.

The heat-resistant enamel “Zerta” is a suspension of aluminum powder or black heat-resistant pigment, polyphenylsiloxane resin, talcum micropowder in the solution of toluene and butyl acetate. The quantitative composition of the enamel is as follows: polyphenylsiloxane resin – 50%, heat-resistant pigment (of different colors) – 15%, talcum micropowder – 10%, butyl acetate – 5%, toluene – 20%.

Target-oriented approach was utilized for the optimization of the analytic measurements [18]. Before measurement, the samples were bonded to a 25 mm aluminum specimen with a conductive silver paint. The metal was coated with a thin film (13 nm) of carbon using magnetron sputtering method as described previously [19]. The observations were carried out using Hitachi SU8000 field-emission scanning electron microscope (FE-SEM). Images were acquired in secondary electron mode at 30 kV accelerating voltage and at 8-15 mm working distance. Morphology of the samples was studied taking into account possible influence of metal coating on the surface [19].
EDX-SEM studies and mapping were carried out using Oxford Instruments X-max EDX system. Before the measurement, the samples were coated with a thin film (13 nm) of carbon using Cressington 208 carbon coater.

3. Results and discussion

Figure 2 FE-SEM contains images of the film prepared on the basis of the heat-resistant enamel “Zerta” of yellow color with a small amount of TiO₂ powder and deposited on the fabric-based laminate surface. Images (a) – (c) in figure 2 were obtained in the immediate vicinity of the electrical breakdown zone of a fabric-based laminate with a film coating, and images (d) – (f) were obtained at a distance of 1 cm from this zone. The boundary of the electric breakdown zone is visible at the top of image (a) in figure 2. Moving further away from the zone of electrical breakdown of the film-coated fabric-based laminate, microstructures with more distinct boundaries are observed. In addition, at a distance from the electric breakdown zone, both large and small formations with clear boundaries are present. This can be seen by comparing images (a) – (c) with (d) – (f) in figure 2. Sufficiently large formations with less clear boundaries prevail in the immediate vicinity of the electrical breakdown zone on the laminate surface (figure 2, (b), (c)). This is a result of both the influence of a higher average temperature near the electrical breakdown zone on the laminate surface, and the effect of the electric field, microdischarges, and also of very chemically active ozone.

In the images (figure 2, (b) and (e)), shallow pits are visible. They emerged as a result of the action of microdischarges on the surface film. It should be noted that during the experiments in the DBD cell (schematic in figure 1), most of the surface film was exposed to different degrees of microdischarges action. However, in the vicinity of electrical breakdown zone of dielectric, the level of the effect the electric field and microdischarges had on the surface film was much higher.

The analysis of the element composition of the surface film showed that the proportion of oxygen atoms is lower in the vicinity of the electric breakdown zone of dielectric. This share varies from 60% to 65%. Although individual areas with an increased oxygen content of up to 82% in the vicinity of the electric breakdown zone were observed. At a distance of 1 cm from the electrical breakdown zone of film-coated laminate, the proportion of oxygen atoms varies from 73% to 76% on average. The straightforward correlation between the titanium atoms share and the extent of the microdischarges action on the surface film was not established. The share of titanium atoms varies from 0.4% to 2.8% in the vicinity of the electric breakdown zone of dielectric. The same parameter at a distance of 1 cm from the electrical breakdown zone of the film-coated laminate varied from 1.1% to 3.5%. However, it can be argued that in the areas of the surface film exposed to more intense action of microdischarges, the share of titanium atoms is on average smaller in comparison with the case of less intense microdischarges action.

The significant variation in the share of different atoms in the surface film can be attributed to the statistical nature of emergence of individual microdischarges on different areas of film on the laminate surface in the DBD cell (figure 1). Electrical breakdown of dielectric, as a rule, occurs in that zone, where there is some defect, i.e. the surface properties in this local microzone differ substantially from the average surface properties. As a result, microdischarges occur more often in local micro-zones with defects on the dielectric surface. As a consequence, in such micro-zones the local temperature becomes higher than the average surface temperature. Consequently, a higher average temperature in the electrical breakdown zone, a longer exposure to the electric field and microdischarges, which have a statistical nature, lead to significant differences in the element composition of the surface film at various points.
Figure 2. FE-SEM images of a film deposited on the surface of a fabric-based laminate: in the vicinity of the zone of its electrical breakdown (left) and about at 1 cm distance from this point (right).

4. Conclusion
Thus, the study results show a significant effect of micro discharges in the dielectric barrier discharge cell on the elemental composition of surface films, deposited on the fabric-based laminate surface.

Acknowledgments
Electron microscopy characterization was performed in the Department of Structural Studies of Zelinsky Institute of Organic Chemistry, Moscow.

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