V V Sirota1*, S V Zaitsev1, M V Limarenko1 and D S Prochorenkov1
1Belgorod State Technological University named after V. G. Shukhov, Russia, Belgorod, Kostyukova 46

Email: zmas36@mail.ru

Abstract. The article presents the results of a study of the photocatalytic activity of coatings based on titanium dioxide on various structural elements of buildings. Fine-grained lightweight concrete, porcelain stoneware and window glass were used as a base. TiO2 coating was applied by reactive magnetron sputtering. The structure and phase composition of the coatings were investigated by scanning electron microscopy and X-ray phase analysis. The photocatalytic activity of the samples was evaluated according to ISO 27448: 2009 and ISO 10678: 2010. The photocatalytic efficiency of the obtained TiO2 coatings on building materials is shown. The data obtained allow us to make a preliminary assessment of the effectiveness of the application of this method of applying photocatalytic coatings to structural elements of buildings, which will be clarified in the course of future studies.

1. Introduction
Applied research in the field of structural and functional materials with photocatalytic activity has been developed in recent years in various industries, including the construction industry. Photocatalytic concretes and other structural materials can provide not only self-cleaning of the surface, but also contribute to reduce the concentration of pollutants in the air [1]. These building materials have been used in the building industry for several years. Many researchers have noted the effectiveness of the use of the photocatalytic effect in building [2, 3]. TiOx layers are often included in the compositions of light-correcting coatings on window glasses, hardening coatings on glass containers and are the basis for self-cleaning coatings on various technical devices [4]. The magnetron sputtering method has a number of advantages: the ability to obtain dense coatings, the possibility of obtaining a coating with the same thickness over a large area of the product, the ability to vary the structure and phase composition of the coating without significantly changing the rate of deposition and heating of the substrate. In the overwhelming majority of applications of TiOx coatings, an enormous role is played by their structural-phase condition, which depends on the deposition method and process parameters [5-8]. In connection with the above, the purpose of this research was to obtain building elements with photocatalytic activity and to assess their effectiveness.

2. Materials and methods
Float glass, porcelain stoneware and fine-grained lightweight concrete were used as objects of research. Substrates for TiO2 coating were prepared from these materials. The size of the substrates is
50 × 50 × 5 mm. Before applying the coating, the substrates were decreased with alcohol and dried with nitrogen. To remove residual contaminants, the surface of the substrates was clean with argon ions in the chamber of vacuum unit for 10 min at a pressure of 8·10^{-2} Pa and a voltage across the ion source of 2.2 kV. Coatings were deposited on the substrate installing UNICOAT-200 setting with a dual magnetrons system and pulsed power. As an ion source used two titanium plates (Ti -99.99 wt.%) by 154 cm² each. The working gas - Ar (99.999 vol%), the reaction gas - O₂ (99.999 vol%). The working pressure in the chamber is 0.17 ± 0.01 Pa. The volume fraction of the reactive gas (O₂) - 14%. The magnetrons were powered by bipolar pulses with a duration of 50 μs (18 kHz) in the mode of keeping the current at a level of 4 A for each magnetron. The distance from the substrates to the magnetron and the ion source was the same 70 mm. During coating, samples (substrates) were not additionally heated.

The phase composition of the coatings was studied on an ARL9900 Intellipower Workstation diffractometer (ThermoTechno) with Co-Kα radiation (λ = 0.1541744 nm). The phases were identified using the JCPDF database. The morphology of surfaces and chips of the coatings was investigated using a scanning electron microscope (TESCAN MIRA 3 LMU). SEM images were acquired at 5 kV acceleration voltages.

The intrinsic photocatalytic activity of the coatings was evaluated in accordance with ISO 10678:2010 by the relative decrease in the concentration of the indicator. Indicator - methylene blue. It decomposes in aqueous solution in the presence of a photocatalytically active surface and UV irradiation in the range of 320-400 nm. The samples were kept in a solution of indicator with a concentration of 2 μmol/l in the dark for 12 h for adsorption saturation of the surface. After exposure in the dark produced solution photometry at a wavelength of 664 nm and taking into account the optical thickness of the cuvette of 20.11 mm in a spectrophotometer SF-56. Then, the samples in solution were irradiated with UV radiation. During irradiation, the solutions were stirred every 20 min. Evaluation of photocatalytic activity was carried out every hour for a relative decrease in the optical density of the solution for 10 h exposure.

3. Results and discussion

All types of substrates were coated with TiO₂ under the same conditions for an hour. This makes it possible to compare the composition, structure, and photocatalytic properties of coatings formed on the surface of the materials under study. The synthesized phases were identified by comparing the X-ray diffraction patterns before and after the formation of the titanium dioxide layer for the same samples by the difference curve (figure 1). The difference curve is the diffractograms of the applied coating. We failed to find crystalline phases in titanium oxide films in concrete samples (figure 1 a). The peaks on the difference curve are exactly the same as those of the original material. This may be due to the growth of titanium oxide crystallites in the direction of orientation of mineral crystals on the concrete surface. On porcelain stoneware, in addition to X-ray amorphous phases, anatase was found by the main reflections at 29.5°, 43.9° and 63.0° (figure 1 b). Rutile was identified in the coating on float glass (figure 1 c), the formation of which may be associated with the features of the glass structure and its surface.

*Figure 1. X-ray diffraction patterns of TiO₂ coatings on concrete (a), porcelain stoneware (b) and float glass (c).*
The structure and texture of the films were evaluative from photographs obtained with a high-resolution scanning electron microscope TESCAN MIRA 3 LMU. The thickness of the synthesized coatings was estimated by SEM-images of transverse chips (figure 2).

Table 1 shows the average thicknesses of the synthesized titanium oxide coatings on the surface of the substrates.

| Fine-grained lightweight concrete | Porcelain stoneware | Float glass |
|----------------------------------|---------------------|-------------|
| Average thickness of the coating, nm | 1000 | 900 | 700 |

On the surface of a concrete substrate, the structure of the coating is porous, which is explained by the peculiarities and composition of the substrate. Different forms of cement stone crystals and their mutual arrangement lead to the growth of titanium oxide crystallites in different directions, which leads to the formation of nano- and microporosity in the synthesized film. When using denser materials such as porcelain stoneware and glass as a substrate, the formed structure of the coating is completely different (Figures 2 b and 2 c). The flat and smooth surface of these materials contributes to the formation of a dense titanium oxide structure. The crystallite size is much larger here, especially in the case of porcelain stoneware (Figure 2b), which give single reflections on the diffractograms (Figure 1 b). From the SEM images of transverse chips (figures 2 b and 2 c), it can be seen that the coating consists of two layers - the amorphous lower (transitional) and the crystalline upper (main). The thickness of the transition layer on porcelain stoneware is approximately half of the entire coating, i.e. about 400-500 nm. A different picture on glass - here the transition layer makes up about a quarter of the entire coating, i.e. about 150 nm.

Table 2. Photocatalytic activity of TiO₂ coatings obtained by magnetron sputtering on the surface of the studied substrates by the degradation of methylene blue dye.

| Photocatalytic activity of titanium oxide coatings EDBM, μmol/(m²·h) | Fine-grained lightweight concrete | Porcelain stoneware | Float glass |
|---------------------------------------------------------------------|----------------------------------|---------------------|-------------|
|                                                                     | 10.6                             | 5.19                | 1.12        |
The photocatalytic activity values for the obtained materials, calculated in accordance with ISO 10678:2010 and shown in Table 2. The value of the photocatalytic activity for TiO$_2$ coatings on fine-grained concrete is overestimated. The reason lies in their porosity and high adsorption capacity. However, the value obtained on porcelain stoneware 5.19 µmol/(m$^2$·h) is consistent with the photocatalytic activity for Pilkington Aktiv (TM) glasses of 7 µmol/(m$^2$·h) [9].

In accordance with the Langmuir-Hinshelwood kinetic model, the rate constants of the photocatalytic reaction of methylene blue degradation on TiO$_2$ coatings are calculated. Kinetic constants for all samples are presented in Table 3.

**Table 3.** Rate constants of the photocatalytic reaction for TiO$_2$ coatings obtained by magnetron sputtering on the surface of the studied substrates by the degradation of methylene blue dye.

|                      | Fine-grained lightweight concrete | Porcelain stoneware | Float glass |
|----------------------|----------------------------------|---------------------|-------------|
| k, h$^{-1}$          | 0.1825                           | 0.0196              | 0.0044      |

The obtained values of the rate constants of the photocatalytic reaction agree with the previously presented results. Photocatalytically active materials (porcelain stoneware, fine-grained concrete with titanium oxide coatings) have values comparable to the results obtained by other researchers [10].

It should be noted that the modified porcelain stoneware is characterized by a decrease in the contact angle of wetting by water drops after ultraviolet irradiation of the surface for 24 hours (figure 3). This is the effect of photoinduced hydrophilicity, which was noted by other researchers on the surface of photocatalytically active materials [11].

**Figure 3.** Change in the contact angle of water wetting of the surface of a TiO$_2$ coating on porcelain stoneware as a result of exposure to ultraviolet radiation: without UV treatment (a), after UV treatment (b).

Such a large decrease in the contact angle from 74° to 20° is determined by the formation on the surface of the porcelain stoneware of anatase coating TiO$_2$. A similar effect, but to a much lesser extent, is observed on TiO$_2$ coatings on window glass (figure 4). Here, the decrease in the contact angle is 23° - from 74° to 51°.

**Figure 4.** Changes in the contact angle of water wetting of the surface of a TiO$_2$ coating on glass as a result of UV irradiation without UV treatment (a), after UV treatment (b).

**4. Summary**

The creation of photocatalytically active structural elements of buildings by the method of reactive magnetron sputtering is quite reasonable and technically feasible. The photocatalytic activity of the
TiO$_2$ coating samples obtained in this work turned out to be comparable with the results of other researchers and industrial samples. One may conclude that the obtained experimental samples is a promising material for use in construction.

5. References

[1] Janus M, Zajac K 2016. Concretes with Photocatalytic Activity (London: IntechOpen) p 141
[2] Witkowski H, Jackiewicz-Rek W, Chilmon K, Jarosławski J, Tryfon-Bojarska A. and Gasinski A. 2019 Appl. Sci. 9 1735
[3] Yang L, Hakki A, Wang F, Macphee D E 2018 Appl. Catal. B. 222 200.
[4] Diebold U. 2003 Surf. Sci. Rep. 43 53.
[5] Nartsev V M, Atkarskaya A B, Zaïtsev S V, Osipenko N V, Prokhorenkov D S, and Evtushenko E I 2016 J. Opt. Technol. 83(4) 263.
[6] Mráz S, Schneider J M 2011 J. Appl. Phys. 109 id 023512 6 p.
[7] Mukherjee S K, Nebatti A, Mohtascham F 2014 Thin Solid Films 558 443.
[8] Pansila P, Wititnun N, Chaiyakun S 2012 Procedia Eng. 32 862.
[9] Navabpour P, Ostovarpour S, Tattershall C 014 Coatings 2(4) 433.
[10] Bannier E, Darut G, Sánchez E, Denoirjean A, Bordes M C, Salvador M D, Rayón E, Ageorges H 2011 Surf. Coat. Tech. 206(2-3) 378.
[11] Shibuya M, Miyauchi M 2009 Adv. Mater. 21 1373.

Acknowledgments

The work was carried out within the framework of the State Assignment of the Ministry of Education and Science of the Russian Federation, project No. 0625-2020-0011. The study was carried out equipment of the Center of Advanced Technologies, Belgorod State Technological University named after V.G. Shoukhov.