PREPARATION OF A SELF-CLEANING GLASS USING SOLUTIONS OF TITANIUM FLUOR COMPLEXES

Ob’єктом дослідження є силікатне скло з наноструктурованним покриттям з оксиду титану (в модифікації анатаза), яке відзначається фотокаталітичною активністю і, як наслідок, набуває здатність до самоочищення у умовах ультрафіолетового опромінювання. Існуючий промисловий метод нанесення такого покриття здійснюється піролітичним способом, але він ефективний для великокамистабільного виробництва, і здійснюється для великооб’ємних виробів з листового флоат-скла. Для виробництва малосерійних, або поштучних виробів, він не використовується. Іншим наносить проблему в якості притаманних покриття з рідкофазних сполук. В першу чергу – золь-гель методом.

Більш дешевим і швидким є метод нанесення покриття з розчинів титанфторкомплексних сполук. Прекурсором використовується гексафтортитанат амонію, але він дорогий. Запропоновано його виготовляти штучним шляхом, відповідно, біфторидним способом.

В ході дослідження використовували біфторид амонію $\text{NH}_4\text{F}_2$ і оксид титану $\text{TiO}_2$, які за запропонованим методом синтезу утворюють $(\text{NH}_4)_2\text{TiF}_6$, його поява підтверджена рентгенофазовим аналізом.

Фторування оксиду титану біфторидом амонію відбувається при температурі, що не перевищує 200 °C. Фторування супроводжувалося виділенням парів води й аміаку.

Отримано фотокаталітичне покриття на зразках флоат-скла шляхом осадження кристалічної фази анатаза з водного розчину $(\text{NH}_4)_2\text{TiF}_6$. Наявність анатаза підтверджена рентгенофазовим аналізом.

1. Introduction

Glass, due to its transparency, is a unique material of modern materials science. However, not all indicators of the properties of glass and products from it remain at the desired level. They can be quite easily improved by surface modification. In this case, the surface layer itself is modified either chemically or physically to a very shallow depth from a few nanometers (nanotechnology) to several micrometers. The incorporation of certain substances into the surface layer of glass causes the emergence of new extreme properties of the glass product. First of all, the appearance of properties associated with quantum optical phenomena. One such extreme modifier is titanium dioxide.

A contemporary urgent scientific problem is the creation of self-cleaning coatings on glass [1]. Glass is self-cleaning or easy to clean with minimal human intervention, which significantly reduces maintenance costs. Currently, several methods for the manufacture of such coatings are known [2].

The main cause of glazing contamination is atmospheric aerosols. They get into the atmosphere as a result of natural processes (erosion, volcanic eruptions, fires), or as a result of human activities (motor vehicles, industrial fuel plants, bitumen, asphalt preparation, garbage burning, cigarette smoke, cooking, especially frying meat). The phenomenon of photoinduced hydrophilicity, discovered in 1997, marked the beginning of the creation of nanostructured transparent coatings for glasses based on titanium dioxide, which exhibit self-cleaning properties under the influence of ultraviolet radiation (UV radiation).

2. The object of research and its technological audit

The object of research is silicate glass with a nanostructured coating of titanium oxide (in the anatase modification), which is noted for its photocatalytic activity and, as a result, acquires the ability to self-clean under ultraviolet irradiation.
Titanium dioxide (TiO₂), in the modification of anatase, has been used as a highly active photocatalytic material and has received great attention in the scientific community over the past two decades [3].

Nanostructured titanium dioxide has a unique photocatalytic property. Its essence lies in the fact that in the volume of a semiconductor particle under the influence of electromagnetic radiation from the UV range of the generated electron–hole pairs, which, when TiO₂ particles reach the surface, enter into redox reactions with molecules adsorbed on it.

Titanium dioxide is an n-type semiconductor. The band gap for anatase and rutile is 3.2 eV and 3.9 eV, respectively [4]. Photocatalytic reactions are initiated when photons are absorbed with energy equal to or greater than the band gap. This leads to the transition of an electron from the semiconductor valence band to the conduction band gap. This leads to the transition of an electron from the semiconductor valence band to the conduction band with the formation of an electron-hole pair. The highest catalytic activity in such processes is expressed by the anatase modification. The optimal particle size of TiO₂ for catalytic activity in such processes is expressed by the volume of a semiconductor particle under the influence of electromagnetic radiation from the UV range of the range from 15 to 110 nm.

Titanium dioxide is used to create gas sensors [5], in medicine as biocompatible and antibacterial coatings [6]. It acts as a catalyst in the processes of oxidation of halogenorganic compounds [7] and reduction of nitrogen oxides [8].

The well-known method of applying a self-cleaning coating based on anatase by pyrolysis from a vapor–gas phase is effective for large-tonnage production of flat glass by the float method. For the production of small-scale, or piece products, products of complex configuration, and especially hollow, it is not advisable. In the case there are methods of coating from the liquid phase. First of all, the sol-gel method. The classical such method requires titanium alkoxides, which are of high cost, as precursors. Cheaper and more flexible is the method of coating from solutions of titanium fluoride complex compounds. Ammonium hexafluorotitanate is used as a precursor, but it is expensive. The paper proposes to modify the chain of chemical transformations, namely: to use the cheaper and more affordable ones as primary precursors. It is proposed to use anatase-based coatings. Since the known method in which (NH₄)₂TiF₆ is used as a precursor for liquid-phase deposition is not rational due to the high cost of this substance.

3. The aim and objectives of research

The aim of research is development of a new method for preparing precursors for applying an anatase-based nanostructured self-cleaning coating on glass.

To achieve this aim, it is necessary to complete the following objectives:

1. To propose other, less valuable and more affordable precursors for the implementation of the technological process, in the chain of which (NH₄)₂TiF₆ becomes an intermediate substance, as well as appropriate laboratory equipment and set the synthesis parameters of (NH₄)₂TiF₆.

2. To assess the perfection of the synthesis reactions by the method of X-ray phase analysis of the synthesized substance.

3. To coat silicate glass and make sure that the coating is nanostructured anatase.

4. To ascertain the presence of photocatalytic activity of the glass surface by spectrophotometry of the sample in the UV range and by measuring the contact angle.

4. Research of existing solutions of the problem

Today, there are many methods and technologies for producing TiO₂ nanoparticles with various morphologies [9]. They obey two main directions: high-temperature synthesis from the gas phase and low-temperature synthesis from the liquid phase.

According to the first direction, the most common is the method of pyrolysis in the gas phase. To obtain TiO₂ by high-temperature decomposition, gaseous halides [10] or titanium alcohohates that are volatile at elevated temperatures are used as gaseous precursors. In the presence of water vapor, titanium tetrachloride vapor can be hydrolyzed to form finely dispersed TiO₂ nanoparticles [11]. Depending on the processes of formation of TiO₂ by chemical reactions, the methods of chemical and physical deposition are distinguished.

An example of chemical vapor deposition is the preparation of TiO₂nanocrystalline films of pyrolysis of titanium (IV) tetraisopropoxide in a gas mixture of helium and oxygen [12]. By physical deposition of titanium metal upon heating in vacuum followed by oxidation with gaseous oxygen, TiO₂ crystals can be obtained on the surface of various materials [13].

Low-temperature synthesis from the liquid phase is carried out by various methods, among which the following are most common.

The hydrothermal synthesis method is based on the ability of water and aqueous solutions to dissolve substances that are practically insoluble under normal conditions at high temperature (up to 500 °C) and pressure (10–80 MPa). Using the hydrothermal synthesis method, various modifications of TiO₂ can be obtained [14].

Solvothermal synthesis is carried out in organic solvents having a higher boiling point. Such a synthesis of TiO₂ nanoparticles in nonaqueous media at a higher temperature makes it possible to obtain more dispersed titanium dioxide nanoparticles [15].

One of the most popular methods for the preparation of TiO₂ nanosized particles is the hydrolysis of titanium-bearing precursors, for example, TiCl₄, titanium alkoxides, or titanyl sulfate.

The sol-gel method, widely used for the synthesis of glass and ceramics, has also been adapted to produce various coatings based on nanostructured TiO₂. Nanosized TiO₂ particles are synthesized by the sol-gel method using hydrolysis of titanium precursors. For the synthesis of TiO₂ with titanium alkoxides, the most effective titanium tetraisopropoxide and titanium tetrabutoxide.

The sol-gel method has been successfully used for the manufacture of silica, titanium, or composite (hybrid) coatings [16]. The synthesis technique of TiO₂ allows the formation of the anatase phase even at low temperatures [17], especially when titanium tetraisopropoxide is used as alkoxides, and the acid acts as an electrostatic stabilizer and hydrolysis catalyst [18].

The technologies for producing TiO₂ nanoparticles obey two principal directions.

The first direction is the production of nanopowders, as such. In the state of lyosols or aerosols, they are used as highly effective cleaners of water or gas environments. The vast majority of scientific papers are devoted to this particular area.
The second direction is the production of nanocoatings on various materials.

The self-purification phenomenon, which is considered in this work, occurs on the basis of a combination of two effects: the photoinduced properties of a thin film of TiO2, namely: photocatalytic activity leads to degradation of organic substances, superhydrophilicity provides high surface wetness.

The self-cleaning effect of glass occurs with the participation of water (rain, service flushing) [19].

However, atmospheric aerosol pollution is not the only problem. An additional problem is the condensation of moisture, which settles on the cold surface of the glass. Condensation on glass surfaces can be minimized to a certain extent [20]. The combined effect of these two effects eliminates fogging of the glass. A thin transparent film of boric acid, which readily reacts with F− ions as follows:

\[ \text{HBF}_2(\text{OH})_2 + \text{HBF}_3(\text{OH}) + \text{H}_2\text{O} \rightarrow \text{HBF}_4 + \text{HBF}_2(\text{OH})_2 + \text{H}_2\text{O} \]

At the same time, the F− ions in [TiF6]2− are gradually replaced by OH− ions. Finally, [TiF6]2− turns into [Ti(OH)6]2−. So, thin films of titanium oxide are formed on the substrate during dehydration of the [Ti(OH)6]2− species formed as a result of the hydrolysis of [TiF6]2−.

The final equation will take the form:

\[ 2(\text{NH}_4)_2\text{TiF}_6 + 3\text{H}_2\text{BO}_3 = 3\text{HBF}_4 + 2\text{TiO}_2 + 4\text{NH}_3 + 5\text{H}_2\text{O}. \]

According to the well-known scheme for the implementation of chemical transformations, the precursor is ammonium hexafluorotitanate, the substance is quite expensive and scarce.

It is proposed in the work to obtain it artificially, using the bifluoride method.

The physicochemical basis of the process of fluorination of ammonium bifluoride is that TiO2, when reacted with NH4HF2, (NH4)2TiF6, which becomes a precursor in the reagent-phase deposition scheme.

Processing of titanium oxide with ammonium bifluoride is easy to do: fluorination occurs at a temperature not exceeding 200 °C, by-products (water and ammonia vapors) do not contain fluoride, ensures the environmental safety of the process.

The interaction of titanium oxide with ammonium bifluoride occurs with the formation of ammonium fluoride or oxofluorotitanates. Fluorination is accompanied by the release of only water vapor and ammonia by reaction:

\[ \text{TiO}_2 + 3\text{NH}_4\text{HF}_2 = (\text{NH}_4)_2\text{TiF}_6 + \text{NH}_3 + 2\text{H}_2\text{O}. \]

The output reagents were solved in an equimolar ratio (1:3), ground and mixed in a porcelain mortar.

To carry out such synthesis, a laboratory unit is assembled (Fig. 1). The unit is a vertical muffle electric furnace, in which there is a fluoroplastic glass with a twisting lid, in the opening of which a return air cooler is inserted, prevents premature removal of water. Ammonia is predominantly released, shifts the equilibrium to the right (work under the hood). The temperature in the furnace cavity is controlled by a chromel-alumel thermocouple (CA-thermocouple). The temperature is maintained at 170±10 °C. Processing time is 5–6 hours.

After the end of the process, the reaction products are a semi-dry paste-like mass, well soluble in water. The
resulting solution is filtered. The filtrate is evaporated and hung. The resulting powder is subsequently used to carry out reaction (3). For this, a solution of 0.1 M (NH₄)₂TiF₆ and 0.3 M H₃BO₃ is prepared. A glass product (plate) is immersed in the glass and an exposure time of 10 hours is carried out [23–25]. As a result, the glass is covered with a film of titanium oxide.

Fig. 1. Scheme of the unit for the synthesis of ammonium hexafluorotitanate: 1 – shaft furnace; 2 – muffle; 3 – heater spiral; 4 – fluoroplastic glass with a lid; 5 – reflux condenser; 6 – measuring device; 7 – CA thermocouple

Fig. 2 shows a diagram of technological operations. All intermediates and final products are subjected to X-ray phase analysis.

Fig. 3 shows the results of X-ray phase analysis (XRD) of primary titanium oxide, first it is in the modification of rutile and subsequent intermediate solutions.

The results convincingly show the feasibility of the proposed method for producing ammonium hexafluorotitanate (Fig. 3, diffraction patterns 2).

There is an assumption that adverse reactions also occur with the formation of ammonium oxofluorotitanate:

\[ \text{TiO}_2 + 3\text{NH}_4\text{HF}_2 = (\text{NH}_4)\text{Ti}(\text{O}_2)\text{F}_5 + \text{HF}. \]  

Precipitation obtained on glass is also subjected to X-ray phase analysis. The crystalline phase of anatase is already observed during low-temperature precipitation from the mother liquor. Glass with this coating already produces photocatalytic activity.

As follows from the diagram in Fig. 4, the intensity of reflexes increases with increasing temperature. However, at temperatures above 800 °C, anatase turns into rutile.

The criterion for the presence of a photocatalytic coating of anatase on glass is the interaction of this coating with ultraviolet radiation. To state this fact, spectral studies are performed (Fig. 5).

As a prototype, a quartz glass plate 2 mm thick is used. The use of quartz glass is dictated by the necessary condition for transparency in the UV range. For uncoated glass (Fig. 5, curve 1), a fairly high transparency is observed in the range 200–400 nm.

Fig. 3. X-ray phase analysis of the initial powder of titanium oxide and subsequent intermediate substances obtained in solutions: 1 – output titanium dioxide (rutile); 2 – products of its interaction TiO₂ with (NH₄)HF₂; 3 – mother liquor for the anatase deposition

Fig. 2. Scheme of technological operations and transformations
For coated glass (Fig. 5, curve 2), there is a complete absorption of radiation in the range 200–300 nm and a significant decrease in transparency in the range 300–400 nm. For clarity, the interdependence of the band gap on the wavelength is shown (Fig. 5, curve 3). As follows from Fig. 5, the high transparency of the coated glass is restored after about 380 nm, which corresponds to an anatase gap of 3.2 eV.

7. SWOT analysis of research results

Strengths. An alternative technology for applying a self-cleaning coating to glass is proposed. At that time, it was known that instead of the expensive precursor (NH₄)₂TiF₆, much cheaper reagents were used as precursors in the technological scheme of transformations: TiO₂ and NH₄HF₂.

The synthesis of (NH₄)₂TiF₆, which becomes an intermediate product, is carried out at relatively low temperatures (not more than 200 °C) and without the release of toxic fluorinated substances. This complies with the principles of energy conservation and environmental safety of the process.

The yield of the reaction for producing (NH₄)₂TiF₆ is quite high (not less than 95%). This product is readily soluble in water. The precipitate obtained after filtering its solution and drying is subjected to x-ray phase analysis, which confirmed the presence of this particular product with a possible admixture of oxofluorotitanate, which is not an obstacle to coating the glass.

The photocatalytic coating is applied to glass by immersion of a glass sample in a solution of (NH₄)₂TiF₆ and H₂BO₃ at room temperature and a holding time of several hours. Nanostructured anatase coatings are formed on the glass. Further heat treatment of the glass samples is advisable. X-ray phase analysis showed an increase in the content of nanostructured anatase to temperatures of about 750 °C. The size of the crystallites calculated by the Scherrer formula is 15–20 nm. At higher temperatures, there is a risk of the conversion of anatase to rutile, which is not desirable.

The presence of the photocatalytic properties of the coating and, as a consequence, the self-cleaning properties of the glass are investigated indirectly: by the spectral method and by measuring the contact angle of water wetting on the glass. A spectral study shows the disappearance of the transparency of quartz glass with this coating in the UV range of 200÷400 nm. The contact angle of glass wetting decreased to 2÷3°.

Weaknesses. However, the main characteristic, namely, the ability to self-cleanse is not investigated in the work. Since the work speaks of self-cleaning glazing from atmospheric pollutants, such an experiment will require a long time, modeling the effects of various pollutants, various degrees of moisture of the glass, and the like. The authors proceed from the following axiomatic statement: «superhydrophilicity» is a mandatory attribute of the self-cleaning ability of glass.

Opportunities. In recent years, fluoride technologies have begun to be intensively used in various sectors of the chemical industry. They allow to get high purity substances. Ammonium bifluoride NH₄HF₂ is used as the main reagent for fluorination. Of relatively great importance is its relatively low cost (5 USD per 1 kg). Important is the fact that ammonium bifluoride is a by-product of many fluoride plants. Titanium dioxide is also widely used in industry due to its relatively low cost (8 USD per 1 kg), chemical stability, and non-toxicity to living organisms. Given that the estimated market value of 1 kg of ammonium hexafluorotitanate is 800 USD, it is possible to predict the reduction in the cost of applying this coating by several tens of times.

Threats. Self-cleaning glass has an effective function only in conditions of periodic wetting by atmospheric precipitation. Otherwise, for example, indoors, in car tunnels, such glass will require additional periodic maintenance (washing), greatly simplified compared to ordinary glass.
8. Conclusions

1. Instead of the expensive precursor \((\text{NH}_4)_2\text{TiF}_6\), significantly cheaper reagents \(\text{TiO}_2\) and \(\text{NH}_2\text{HF}_2\) are proposed as precursors in the technological scheme of transformations. To carry out such synthesis, a laboratory setup is proposed, which is a vertical muffle electric furnace with a fluoroplastic vessel in which the synthesis of \((\text{NH}_4)_2\text{TiF}_6\) takes place. The temperature is maintained at 170±10 °C. Processing time 5–6 hours.

2. It is found that the yield of the desired product of the synthesis reaction is at least 95 %. As a result of the synthesis, it is precisely \((\text{NH}_4)_2\text{TiF}_6\) that is formed, which is confirmed by X-ray phase analysis. In addition, ammonium oxofluorotitanate is also likely to form, which is not an obstacle to coating with Anatase.

3. Coated silicate glass from an aqueous solution of \((\text{NH}_4)_2\text{TiF}_6\) and \(\text{H}_2\text{BO}_3\). It is found that the crystalline phase of anatase forms immediately after precipitation at room temperature. Further heating of the coated glass to temperatures of about 800 °C is advisable, since the crystalline phase of anatase accumulates. The size of crystalline clusters is estimated by the Scherrer formula at 15

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