Запобігання та ліквідація надзвичайних ситуацій

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MODERN TECHNOLOGIES FOR SOLVING ISSUES OF COLLECTIVE PROTECTION FROM CHEMICALLY HAZARDOUS SUBSTANCES IN THE DEFENSE INDUSTRY

The process of plasma electrolytic oxidation under different conditions and the influence of certain process parameters were studied. It has been established that almost any organic compounds can be oxidized (mineralized) to CO2 and H2O on the surface of TiO2. In order to further capture of chemically hazardous substances, we use a photocatalytic air purification method in which titanium oxides are used as a photocatalyst. Therefore, further work continues on the use of oxide catalysts on titanium alloys and their subsequent installation in existing absorbent filters of the collective protection system for stationary structures and armored vehicles for efficient neutralization of chemically hazardous substances. Further work is being done on the use of oxide catalysts on titanium alloys with the further improvement of the system of collective defense of stationary structures and on armored vehicles for the effective neutralization of hazardous chemicals.

Keywords: *air purification, plasma electrolytic oxidation, photocatalytic method, chemically dangerous substances, titanium oxide, collective protection system, stationary structures, organic compounds.*

Introduction

Formulation of the problem. There are more than 1,5 thousands chemically dangerous objects on the territory of Ukraine, whose activity is related to the production, use, storage and transportation of hazardous chemicals, and more than 22 million people live in the areas of their location. The danger of functioning of these objects of economic activity (chemically dangerous objects) is related to the probability of accidental emissions (spillages) of a large number of hazardous chemical substances outside the objects, because many of them retain 3–15 daily supplies of chemicals [1] (Fig. 1).

Fig. 1. Potentially hazardous facilities in Ukraine

That is why each subsequent emergency situation may be related to the spillage or emission of hazardous chemical substances into the air (hereinafter – HCHS).

Also, the hybrid challenges and the use of weapons of mass destructions by terrorist organizations, the armed conflict in Syria (Fig. 2), during which chemical weapons were used, the aggravation of the situation in the East of Ukraine where a large number of chemically dangerous enterprises are located, the violation of the UN International Convention on the Prohibition of the Use of Chemical Weapons by some states, there is a high likelihood of using sabotage and reconnaissance forces, other illegally formed anti-state formations of committing terrorist acts and sabotage of highly toxic agents to the extent, that makes their combat use for the purpose of defeating manpower (population, troops) impossible [2].

For neutralization of harmful emissions on the prin-ciple of removing toxic impurities, chemical processes are also used along with physical processes, with the help of which the physical properties of impurities can be varied widely (for example, to convert the initial gaseous pollutants into compounds with a high boiling point). In order to facilitate and further capture of chemically dangerous substances, we will use a photocatalytic air purification method, in which titanium oxide is used as a photocatalyst, which can efficiently neutralize (decom-pose) different kinds of toxins at high rates of efficiency over a wide range of temperatures.

Fig. 2. Use of chemical weapons in Syria

Analysis of recent researches and publications. Modern industry, engineering, electronics, medicine, chemical and biological technologies impose different requirements for coatings on metals and alloys. Depending on the composition, coatings protect metal products, devices, structures from the aggressive environment, corrosion and mechanical failure, wear, temperature changes, provide a decorative appearance, improve the adhesion of oils, varnishes, paints, polymers, allow to obtain new properties: dielectric, semiconductor, biocidal, biocompatible, hydrophobic, hydrophilic, ability to luminescence, selective adsorption, catalysis, absorption or reflection of radiation, and many others. Studies aimed at improving known and searching for new methods for surface treatment of metals and alloys are very relevant [3].

Titanium alloys are distinguished by a combination of a number of valuable properties and are promising for use in many branches of modern technology, the high cost of titanium and its alloys in many cases is offset by their capacity for work, and in some cases they are the only material from which it is possible to manufacture equipment or structures capable of operating under certain specific conditions.

However, there are several reasons that limit the use of these materials, in particular, poor antifriction properties that give rise to problems when using titanium alloys in friction pairs, high chemical activity during welding operations and many others, the effective solution of which is possible by modifying the surface. Therefore, the most rational approach is based on the use of galvanochemical technologies for coating of various composition and purpose, among which, with regard to valve metals, conversion and composite are particularly attractive [4].

The influence of various factors on the photocatalytic activity of titanium dioxide is currently the subject of many studies, due to the importance of this material for environmental catalysis. The photocatalytic effect of titanium dioxide makes it possible to conduct oxidative destruction of most organic pollutants of the environment, as well as many pathogenic bacteria with UV irradiation, at room temperature.

Positive that the use of photocatalysts based on titanium oxide is due to the effect of photocatalytic degradation of organic contaminants to elementary inorganic components. It will open up prospects of using photocatalysts based on titanium dioxide for air purifica-tion.

It is known that when a photon is absorbed by a titanium dioxide with an energy greater than or equal to the width of the band gap, its electron from the valence band can be transferred to the conduction band, thus generating an electronic vacancy – a “hole”. Electrons and “holes” migrate to the catalyst surface where they participate in redox reactions with different types of particles absorbed on the surface. “Holes” can react with water molecules bound to the surface of the catalyst to form hydroxyl radicals and proton or with hydroxyl groups to form hydroxyl radicals OH* (Fig. 3).

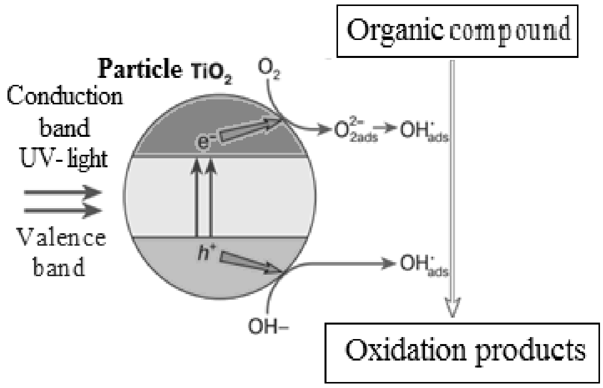

Fig. 3. Scheme of the processes proceeding on a semiconductor particle

Electrons in the reaction with oxygen can generate a superoxide anion radical O_2.The hydroxyl radicals and superoxide anion radicals are supposed to be the main oxidizing agents in photocatalytic oxidation processes. A distinctive feature of TiO_2 nanoparticles is the ability to self-generate active hydroxyl groups on their surface in an aqueous medium, which significantly improves their sorption properties [5].

Plasma electrolytic oxidation (PEO) is also one of the most efficient methods of surface modification, which allows the formation of multifunctional protective and decorative coatings. PEO coating is the result of short-lived micro-discharges on the surface of the material and consists of oxides of the treated metal and components of the electrolyte. Recently PEO coatings have been successfully used as carriers of catalytic materials, however, the possibility of creating in one technological cycle not only the carriers, but also the catalytically active layers remains practically unrealized, since during the coating process by including electrolyte components to their composition, it is possible to create conditions for the formation of simple, complex and mixed oxides and other compounds [6].

The PEO method and the study of their functional properties are undoubtedly promising for the formation of coatings on titanium and its alloys, as well as metal substrates of different kinds [7].

Successful solution of the tasks of choosing the composition and the ratio of components of the electrolyte, as well as optimization of the electrolysis parameters, create prerequisites for the development of coating technology that has an increased service life, chemical resistance to the influence of process media and abrasive wear, elevated tribological characteristics and catalytic activity in heterophase conversions.

It has already been shown that almost all organic compounds can be oxidized (mineralized) to CO_2 and H_2O on the TiO_2 surface. If the compounds contain nitrogen or halogen atom X, HNO_3 and HX will be observed in the reaction products. The only known compound that is resistant to oxidation when it's exposed to light on TiO_2 surface is carbon tetrachloride, but already trichloroethylene is destructed on exposure to light with a quantum yield greater than 1. This is due to the fact that atomic Cl can be formed on TiO_2 surface, which, desorbing from the surface, stimulates the chain process of destruction of trichloroethylene.

In practice, any photocatalytic air purifier includes a porous carrier coated with TiO_2, which is irradiated with light and through which air is blown.

A study of the catalytic properties of coatings with mixed oxides in the oxidation of carbon monoxide was conducted in [8]. The catalytic activity of mixed oxide systems was tested in the oxidation of carbon (II) oxide to carbon (IV) oxide on a laboratory bench in a tubular flow reactor made of silica glass with a coaxially wound heating coil. The reactor temperature was gradually increased from 20 to 450 °C at a rate of 1°C/s during the research. The CO concentration at the inlet and outlet of the reactor was recorded using Dozor signaling-analyzing devices (Fig. 4).

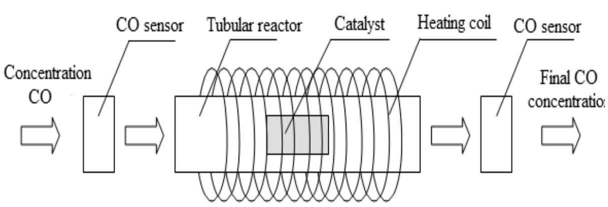

Fig. 4. Scheme of the bench for catalytic oxidation of carbon (II) oxide

The catalytic activity of coatings with manganese-, nickel-, cobalt- and iron-based mixed oxides was tested, which showed that the ignition temperature T_i corresponding to the beginning of the effective catalyst operation for the synthesized oxide systems is within the range of 250–270°C, and on platinum is slightly below 200°C (Fig. 5).

The results showed that the system TinOm•MnxOy was the most effecticient one among the mixed oxide coatings where complete conversion is achieved at 400 C (T_i 250 °C). Oxide systems TinOm•CoxOy, TinOm•NiO, TinOm•FexOy at 420°C provide a degree of CO conversion of 68 %, 57 % and 46 % respectively. Complete conversion of carbon monoxide on these materials is achieved at higher temperatures (Table 1).

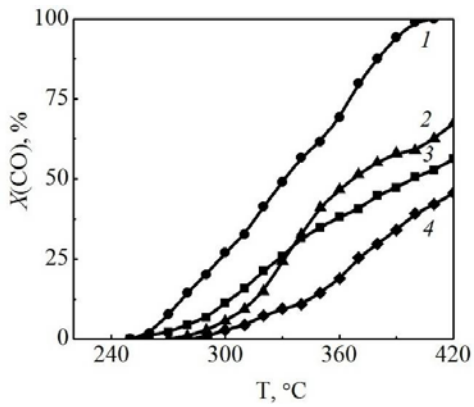

Fig. 5. Thermograms of the degree of conversion of carbon (II) oxide on mixed oxide coatings:
1 – TinOm·MnxOy; 2 – TinOm·CoxOy;
3 – TinOm·NiO; 4 – TinOm·FexOy

Table 1

Characteristics of the coatings with mixed oxides

Electrode material	Content of the active component ω,% wt.	Degree of conversion X, %	Ignition temperature T_i, °C
Pt [117]	100	100	200
Ptexp	100		
Ti_nO_m Mn_xO_y	ω(Mn) = 7,5	100	250
Ti_nO_m Co_xO_y	ω(Co) = 7,7	68	280
Ti_nO_m NiO	ω(Ni) = 3,2	57	270
Ti_nO_m Fe_xO_y	ω(Fe) = 5,2	46	290

The purpose of research. It has been established that there are no absorbent filters that can protect against all types of HCHS, and the time of action in insulating gas masks may not be sufficient in places of possible contamination [9]. For this purpose, it is necessary to improve the collective protection systems, stationary and in armored vehicles, using oxide catalysts based on titanium alloys with their subsequent installation in existing absorbent filters for efficient neutralization of HCHS.

When a personnel enters a cloud of contaminated air, in case of destruction of chemically dangerous objects, which contains toxic chemical compounds that are formed in large quantities in industrial processes or with the use of hazardous chemical substances, a collective protection system, which protects by installing a mesh coated with titanium oxide, will be activated (Fig. 6).

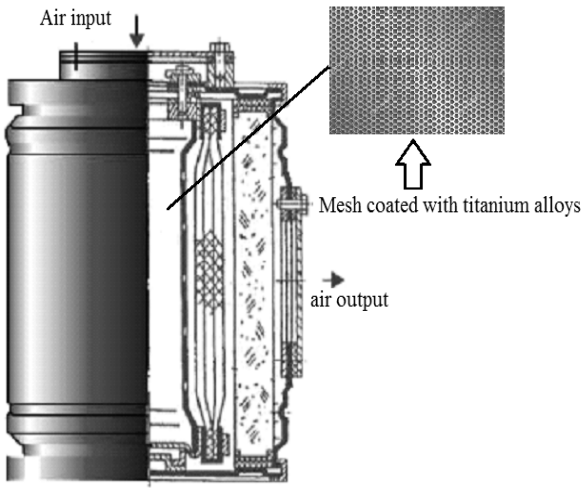

Fig. 6. Installation of mesh coated with titanium dioxide in the collective protection system

The optimal method of air purification from HCHS is photocatalytic air purification, where titanium dioxide is used as a photocatalyst, which can efficiently neutralize (decompose) different kinds of toxins at high rates of efficiency over a wide range of temperatures [10]. Researches of the catalytic properties of coatings with mixed oxides will be conducted in the reactions of oxidation of sulfur dioxide, ammonia, chlorine and carbon monoxide.

Conclusion

Solving the issue of protection of armored vehicles and stationary structures from contemporary risks that arise in the world, with the help of photocatalytic purification of gases, in which titanium oxide is used as a photocatalyst, is a promising direction of development in the defense field of the state. Therefore, the installation of mesh coated with titanium oxide in the absorbent filters of the filter-ventilator units for armored vehicles and stationary objects is considered in the future.

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СУЧАСНІ ТЕХНОЛОГІЇ ВИРІШЕННЯ ПРОБЛЕМ КОЛЕКТИВНОГО ЗАХИСТУ ВІД ХІМІЧНО-НЕБЕЗПЕЧНИХ РЕЧОВИН В ОБОРОННІЙ ПРОМИСЛОВОСТІ

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Досліджено процес плазмового електролітичного оксидування при різних умовах та впливу визначених параметрах процесу. Встановлено, що на поверхні TiO2 можуть бути окислені (мінералізовані) до CO2 і H2O практично будь-які органічні сполуки. Тому потребують вдосконалення існуючі системи колективного захисту, як стаціонарні так і на бронетехніці шляхом застосування способу фотокаталітичної деструкції токсикантів із використанням в ролі каталітичного матеріалу оксидів титану, нанесених на поруваті або мережеві носії, з подальшим їх встановленням в конструкцію систем колективного захисту решітки (сітки) з нанесеним шаром каталітичного матеріалу, що буде нейтралізувати різні види небезпечних хімічних речовин за рахунок фотокаталітичного очищення повітря оксидами титану. Триває подальша робота щодо використання оксидних каталізаторів на сплавах титану з подальшим вдосконаленням системи колективного захисту стаціонарних споруд та на бронетехніці для ефективної нейтралізації небезпечних хімічних речовин.

Ключові слова: *очищення повітря, плазмено-електролітичне оксидування, фотокаталітичний метод, хімічно-небезпечні речовини, оксид титану, система колективного захисту, стаціонарні споруди, органічні сполуки*

СОВРЕМЕННЫЕ ТЕХНОЛОГИИ РЕШЕНИЯ ПРОБЛЕМ КОЛЛЕКТИВНОЙ ЗАЩИТЫ ОТ ХИМИЧЕСКИ-ОПАСНЫХ ВЕЩЕСТВ В ОБОРОННОЙ ПРОМЫШЛЕННОСТИ

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Исследован процесс плазменного электролитического оксидирования при различных условиях и влияния определенных параметрах процесса. Установлено, что на поверхности TiO2 могут быть окислены (минерализованы) до CO2 и H2O практически любые органические соединения. Поэтому нуждаются в совершенствовании существующие системы коллективной защиты, как стационарные так и на бронетехнике путем применения способа фотокаталитической деструкции токсикантов с использованием в качестве каталитического материала оксидов титана, нанесенных на пористые или сетевые носители, с последующим их установкой в конструкцию систем коллективной защиты решетки (сетки) с нанесенным слоем каталитического материала, который будет нейтрализовать различные виды опасных химических веществ за счет фотокаталитической очистки воздуха оксидами титана. Продолжается дальнейшая работа по использованию оксидных катализаторов на сплавах титана с дальнейшим совершенствованием системы коллективной защиты стационарных сооружений и на бронетехнике для эффективной нейтрализации опасных химических веществ.

Ключевые слова: *очистка воздуха, плазменно-электролитическое оксидирование, фотокаталитический метод, химически опасные вещества, оксид титана, система коллективной защиты, стационарные сооружения, органические соединения.*