

O.V. Sanzhak<sup>1</sup>, D.V. Brazhnyk<sup>1</sup>, V.V. Honcharov<sup>2</sup>, V.A. Zazhigalov<sup>1</sup>, F.A. Azimov<sup>1</sup>

## THE PHYSICO-CHEMICAL PROPERTIES OF Ti-CONTAINING STAINLESS STEEL COMPOSITES AND ITS PHOTOACTIVITY

<sup>1</sup> Institute for Sorption and Problems of Endoecology of National Academy of Sciences of Ukraine  
13 General Naumov Str., Kyiv, 03164, Ukraine, E-mail: Sanzhakalena@bigmir.net

<sup>2</sup> State Institution "Lugansk State Medical University"  
32 Budivelnykiv Str., Rubizhne, 93012, Ukraine

The present study aims to obtain the supported Ti-containing catalyst on a surface of stainless steel foil by low temperature ionic implantation method. The geometrical sizes of the implantation chamber allow one to synthesize composites with the maximum size of 30×30 cm. The shape and size of the catalysts provide an opportunity to use obtained samples for removal of harmful substances from both aqueous solutions and gas mixtures. A quantitative estimation of bond strength of the surface layer of the prepared composites was realized by the use of sclerometric method. It is shown that implantation of titanium ions on stainless steel foil provide significant increase in surface layer mechanical strength. The heat treatment of the sample leads to a decrease in this strength, but its value rests higher than that in initial support (stainless steel). The composition of samples surface and the effect of calcination temperature were determined by XRD, SAXS, SEM, AFM, and XPS. It is shown that after ionic implantation nanoscale layer of the implant on the surface of stainless steel was formed. Presence of titanium oxide, nitride and oxynitride was determined by XPS method. The high photocatalytic activity of this catalyst in the process of neutralizing benzene in aqueous solutions under irradiation with visible light, which significantly exceeds its activity under UV-radiation was shown. Increasing the calcination temperature leads to decreasing the samples activity and can be explained by the influence of the ratio between the nitride, oxynitride, and oxide phases of titanium. Exactly the presence of those phases on the surface explains its high activity in the degradation of benzene in aqueous solution under visible light irradiation. Thus, using of the obtained samples in the neutralization of aqueous benzene solutions under visible light irradiation is perspective from ecological point of view.

**Keywords:** stainless steel foil, Ti-containing catalyst, ionic implantation, benzene photodegradation

### INTRODUCTION

Worldwide industrial revolution in the 21st century brought a wide spectrum of problems, mainly contamination of the water with harmful and waste materials, leading to significant adverse effect on the environment and wildlife. Direct disposal of industrial compounds into water makes its unsuitable for drinking and for other purposes. Particularly, non-biodegradable and undesirable chemicals have negative consequences on health of human and aquatic life [1]. Among those chemicals aromatic hydrocarbons (phenol and benzene, particularly) are the most prevailed contamination entering on the environmental with wastewater of paint and varnish, refinery and chemical-recovery industries [2]. Also its can be generated during the decomposition of pesticides, fungicides, and herbicides. Chlorination is the one of the most used method on water-treatment plant. But this stage leads to formation cancerogenic chlorinated substances [3]. The new law about

reception of wastewater to drainage system was implemented since January 2018. Rigid requirements to aromatic hydrocarbonic contents were accepted [4]. The known methods for benzene recovery provide its precipitation or sorption removal by solid sorbents. This operations lead to an increase of the cost of purification treatment [5]. The aromatics photodestruction with the use of heterogeneous catalysts can be the alternative method of benzene removal from water. It is known that titanium dioxide is one of the most studied and active photocatalyst [6]. The main disadvantage of this catalyst is absorption only UV-irradiation (i.e., wavelength < 388 nm) [7]. For the purpose of activity shift to the visible radiation range the intensive researches on TiO<sub>2</sub> doping by various elements including nitrogen are carried out [8–11]. On the other hand, the use of TiO<sub>2</sub> in the form of fine powder is a technological drawback. The use of such form of TiO<sub>2</sub> leads to a problem of spent catalyst removal from the reaction aqueous mixture [12].

The solve of this problem may be related to the use of various supported TiO<sub>2</sub>-containing catalysts [13, 14]. The known supported catalysts have a number of disadvantages the causes of which are also primarily complicated methods of their synthesis and difficulties with preparation of the durable and stable TiO<sub>2</sub> coatings. Therefore, the photocatalysts deposited on supports are promising and for the preparation of the supported samples both mechanically strong granules and hard flat profile composites can be used. In the paper the results of the ionic implantation method use for the preparation of TiO<sub>2</sub>-containing photocatalyst on the base of stainless steel foil as a support are reported.

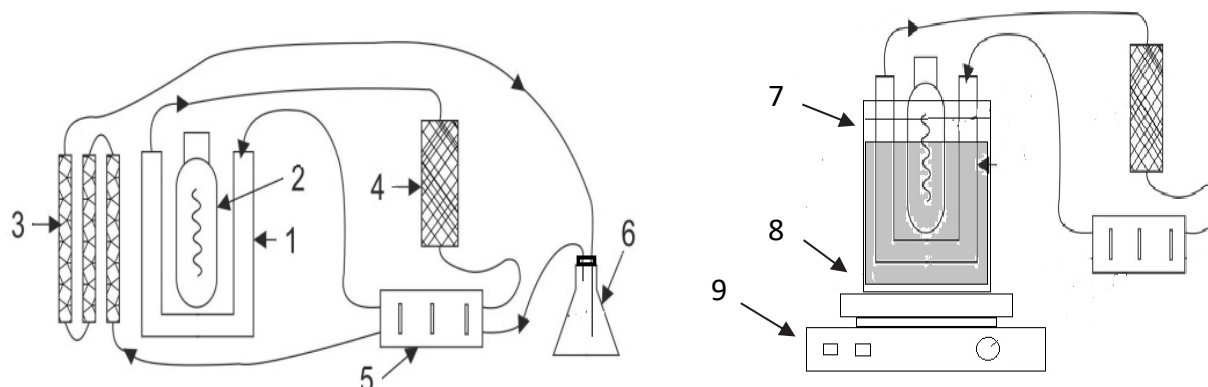
#### MATERIALS AND METHODS

Synthesis of Ti-containing composites supported on stainless steel (SS) AISI 321H (thickness 80 μm) was carried out by ionic implantation method described in [15]. Metallic Ti was used as an implant. The cathode sputtering of the target (Ti) was carried out by N<sub>2</sub> ions. The energy of implantation was 20 keV at a fluence of 5×10<sup>17</sup> ions/cm<sup>2</sup>. The camera for implantation allows one receiving samples with the maximum linear sizes 30×30 cm. The prepared Ti-containing foils (Ti/SS) were calcinated in air at the temperature range of 200–600 °C and determined as Ti/SS/T °C. X-ray diffraction (XRD) patterns were obtained with a Philips PW 1830 diffractometer (monochromatic CuK<sub>α</sub> – radiation). Phase composition of the surface layer was studied by

the method of low-angle X-ray scattering (SAXS) with a 2D X-ray Rigaku (Dmax rapid). The surface morphology of the samples was studied by atomic force microscopy (AFM) with a Nanoscope Multi Mode V and by scanning electronic microscopy with a «Hitachi S-400» (SEM). The surface composition of the samples was obtained by X-ray photoelectron spectroscopy (XPS) with a SES R 4000 (Gammadata Scienta) instrument. Distribution of elements through the depth of composite was carried out by the XPS method (a VG Scientific ESCA-3) by step-by-step removal of surface layers (argon bombing).

The quantitative estimation of the bond strength of the surface layer of the prepared composites was realized by sclerometric method [16].

The activity of synthesized samples was determined in the reaction of photodegradation of benzene in aqueous solution (50 threshold limit values (TLV)). The study was carried out in a cylindrical reactor (diameter was equal to 9 cm) with wall-placed catalyst (synthesized composite) which has height equal to 10 cm (implantation of titanium was effected on both sides of the foil). The thermostatically controlled radiation source was immersed into the reactor. The design of the reactor, the shape and size of the catalysts provide an opportunity to use received samples for removal of harmful substances from both aqueous solutions and gas mixtures (Fig. 1).



**Fig. 1.** The photocatalytic installation (left – for gaseous mixtures and right – for aqueous solutions): 1 – cooling jacket, 2 – irradiation source (UV- or VIS-lamp), 3 – system of the catalyst filled quartz tubes connected in series, 4 – cooling water, 5 – peristaltic pump, 6 – gas mixture with pollutant, 7 – aqueous solution with pollutant, 8 – stainless steel foil, 9 – magnetic stirrer

The high pressure mercury or sodium lamps were used as a source of radiation. The reaction products were analyzed with a SelmiChrom-2 gas chromatograph equipped with a FID on a stainless steel column (length 1 m, diameter 3 mm) filled with Porapak Q.

## RESULTS AND DISCUSSION

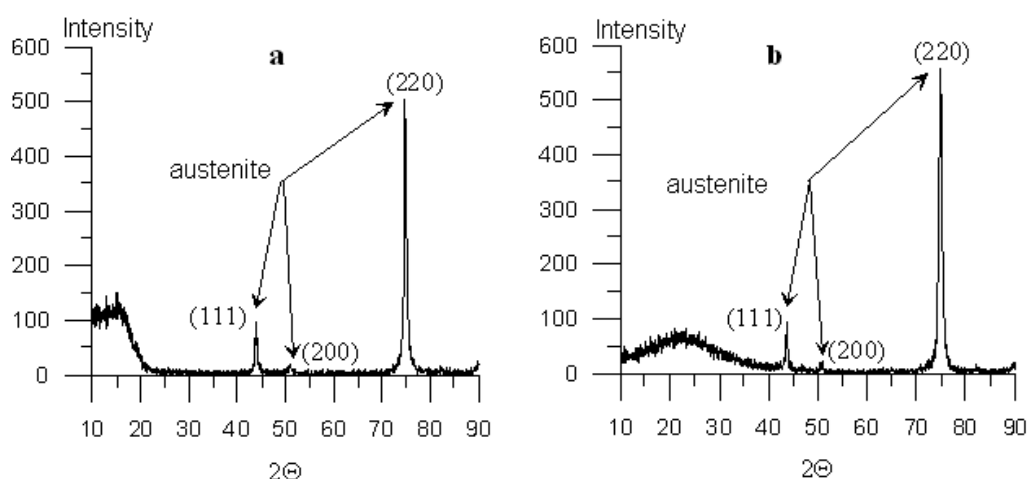
The mechanical strength of the active components surface layer and the composite is one of important properties of catalysts used in aqueous solution for their utilization on practice. The data presented in Table 1 show that implantation of titanium ions into stainless steel foil provide a significant increase in surface layer mechanical strength. The heat treatment of the sample leads to a decrease in this strength,

but its value rests higher than that in initial support (stainless steel). Thus it is possible to claim that the ionic implantation method allows receiving mechanically strong layer of active component on the support surface with strength which is practically not influenced by heat treatment and mechanical deformation. It actually permits us to use prepared composites in reactors of various shapes and size.

An analysis of synthesized samples by XRD method (Fig. 2) shows that they contain only the reflexes of the planes (111), (200), and (220) of the austenite phases, which can be referred to the stainless steel [17]. The heat treatment of the samples (up to 600 °C) does not change the structural state of the surface.

**Table 1.** The samples' mechanical strength

Sample	The value of mechanical strength, GPa
SS	1.7
Ti/SS	5.3
Ti/SS/300 °C	5.4
Ti/SS/500 °C	5.2
Ti/SS/600 °C	5.1



**Fig. 2.** XRD patterns of the catalyst supported on stainless steel: *a* – Ti/SS; *b* – Ti/SS/600 °C

The absence of the reflexes of implanted titanium or its compounds may indicate their amorphous state or a low concentration in the surface layer of the composite. Therefore, the samples were studied by SAXS method (Fig. 3).

An analysis of obtained results shows that in this case there are only austenite phase reflexes on XRD and SAXS patterns. Nevertheless, it should

be noted that implantation of titanium ions leads to low-angle shift of all reflexes of austenite that can be seen from the given example of a reflex from plane (111). This fact can indicate the implant ions incorporation into a support lattice and its corresponding broadening.

The obtained results demonstrate that after ionic implantation on a support surface titanium

amorphous structure are formed or concentration of its crystal particles is so small that is out of detection limits by these research techniques.

According to the AFM data titanium implantation leads to smoothing of a relief of

initial support surface, but at the same time new narrower surface defects (depth of 200–400 nm) are formed that causes its larger inhomogeneity (Fig. 4).

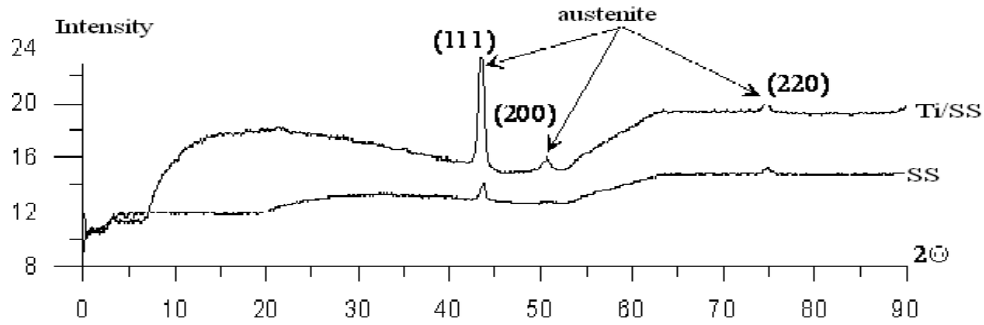


Fig. 3. SAXS patterns of the catalyst supported on stainless steel

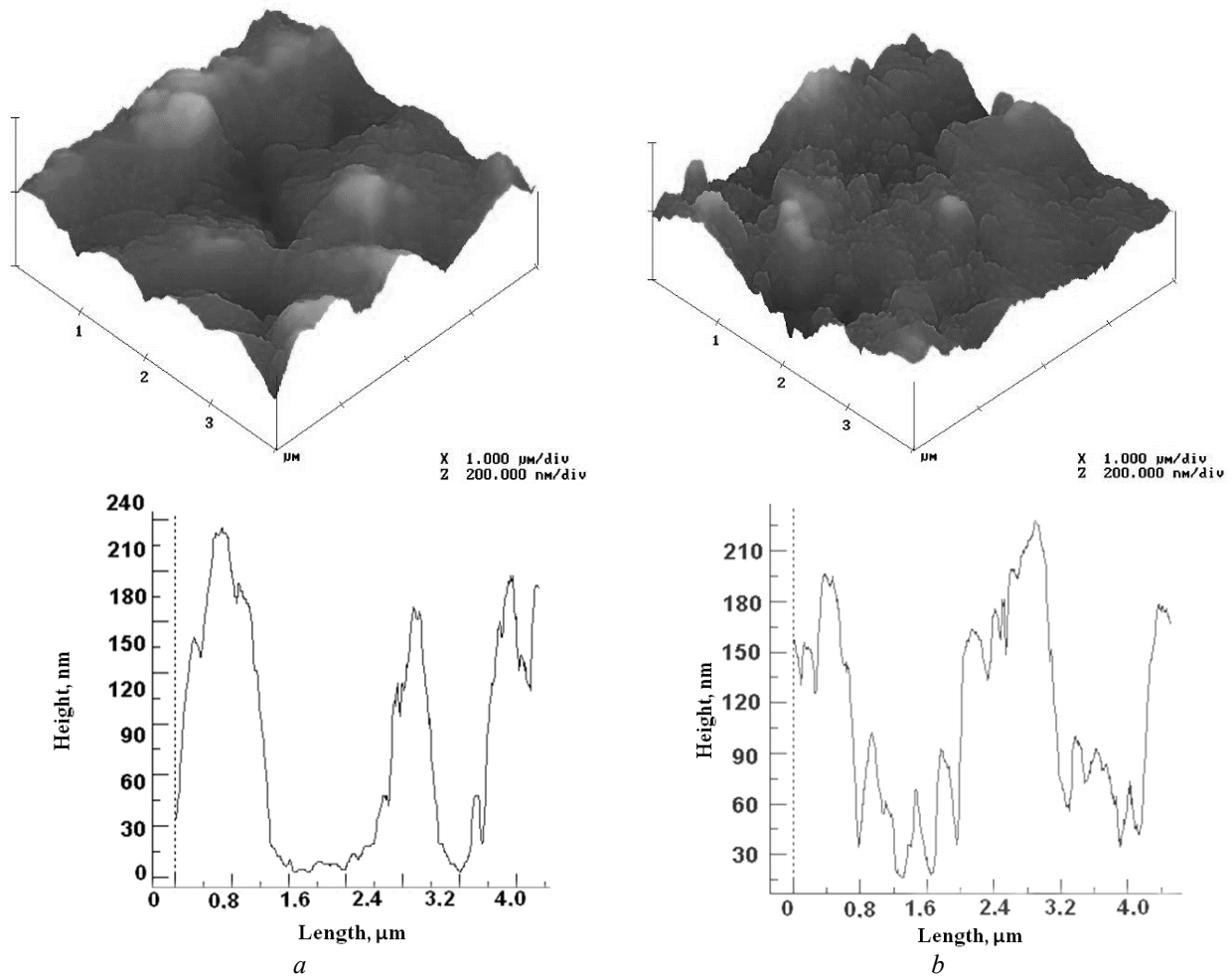


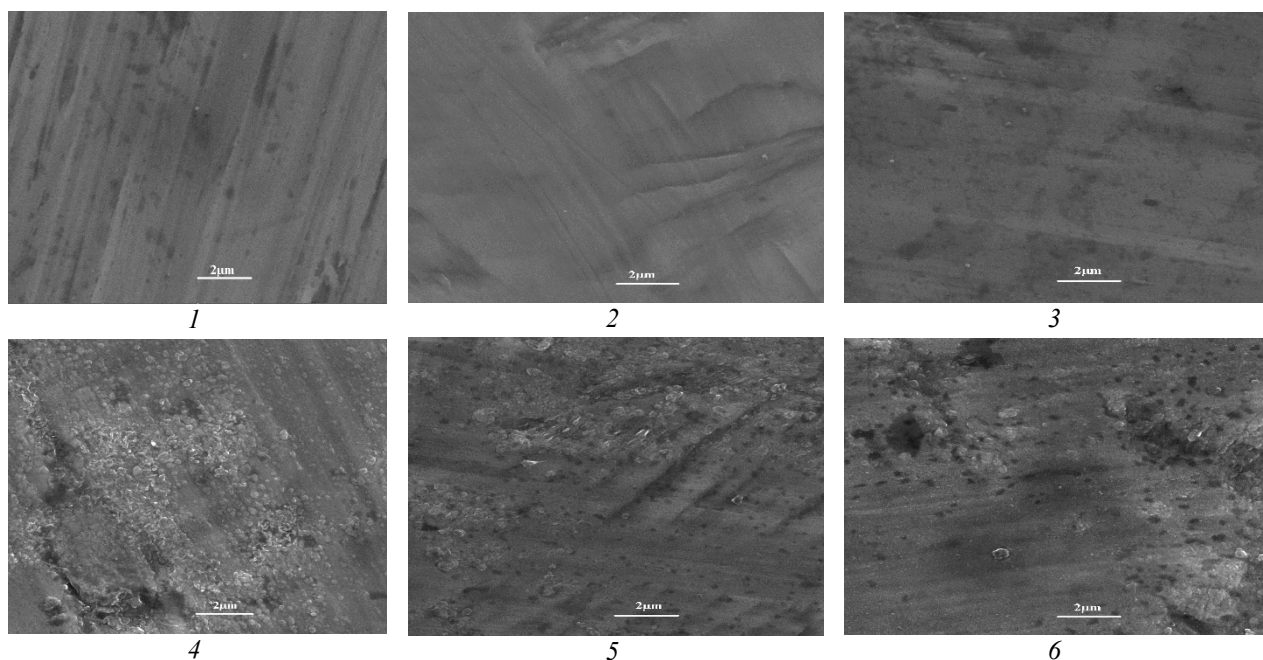
Fig. 4. Morphology of the samples surface (AFM): a – Ti/SS, b – Ti/SS/600 °C

The head treatment of the sample is followed by new peaks formation in the existing hollows. As a result, an insignificant change of surface irregularities with its rather big average roughness is observed.

The SEM data (Fig. 5) demonstrate that in samples calcinated at 200 and 300 °C the surface irregularities, characteristic for initial support, are observed. It may indicate formation of a nanoscale layer of implanted titanium on the support surface.

It is also possible to note an emergence of new surface defects that has good accordance with the results obtained by AFM data. An increase of the treatment temperature leads to the subsequent agglomeration of the part of supported titanium layer with formation of new spherical particles.

Results of the XPS characterization of the prepared composites are summarized in Table 2. The obtained data show that the ionic implantation of titanium leads to formation of titanium nitride (the peaks of electrons with binding energies:  $Ti2p_{3/2}$  – 460.3 eV,  $N1s$  – 396.1 eV) and titanium oxynitride (the peaks of electrons with binding energies:  $Ti2p_{3/2}$  – 457.9 eV,  $N1s$  – 400.0 eV,  $O1s$  – 527.6 eV) on the sample surface. After sample heat treatment the peaks which can indicate the existence in surface of the composite both oxynitride of the titanium (BE  $Ti2p_{3/2}$  = 458.1,  $N1s$  = 400.4,  $O1s$  = 528.0 eV) and its oxide (BE  $Ti2p_{3/2}$  = 459.1,  $O1s$  = 529.7 eV) are identified. These results permit us to assume that heat treatment leads to oxidation of titanium nitride to its oxynitride, and titanium oxynitride to  $TiO_2$ .



**Fig. 5.** SEM images of the samples: 1 – Ti/SS; 2 – Ti/SS/200 °C; 3 – Ti/SS/300 °C; 4 – Ti/SS/400 °C; 5 – Ti/SS/500 °C; 6 – Ti/SS/600 °C

**Table 2.** The surface composition of the samples

Sample	Binding energy, eV		
	O1s	Ti2p <sub>3/2</sub>	N1s
Ti/SS	527.6; 529.7; 531.6; 532.9; 535.8	457.9; 460.3	396.1; 398.2; 400.0
Ti/SS/600 °C	528.0; 529.7; 531.4	458.1; 459.1	400.4

The XPS method with the removal of surface layers (surface bombing by argon) was used for the study of implant incorporation depth in the support and the determination of its surface layer thickness (Fig. 6). The obtained results show that thickness of the implant layer on support surface is about 80 nm and depth of titanium intrusion in foil near 30 nm. It permits to assume that the formation of an intermediate layer with implant introduced in stainless steel determines the high mechanical strength of the composite.

The activity of the synthesized samples was investigated in reaction of photodegradation of benzene in aqueous solution (Fig. 7). The presented results show that the activity of

practically all synthesized samples at visible light irradiation is significantly higher than at UV irradiation (conversion up to 25 and 7 %, respectively). In the case of UV-irradiation the most active catalyst is the initial implanted sample Ti/SS. The heat treatment reduces the catalyst photoactivity. This fact can be related to the existence of surface initial implanted sample of the titanium oxynitride and its nitride. It is known [19–21] that titanium oxynitride demonstrates high activity in photocatalytic processes. The heat treatment leads to TiO<sub>2</sub> phase formation and it has negative effect on samples properties.

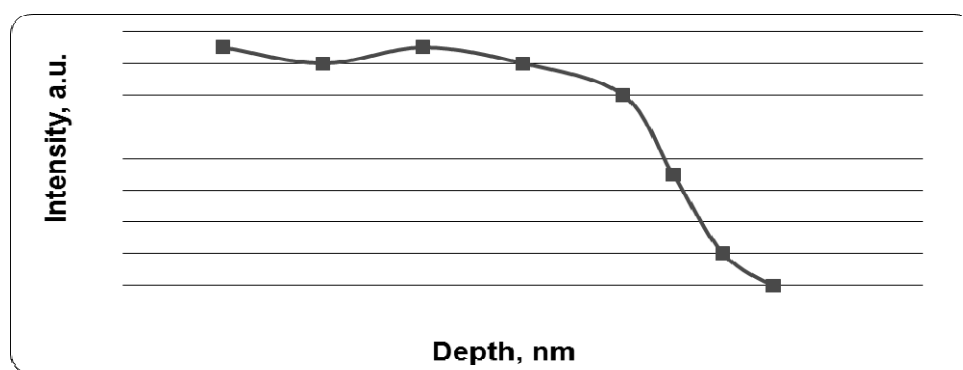


Fig. 6. Titanium implantation depth

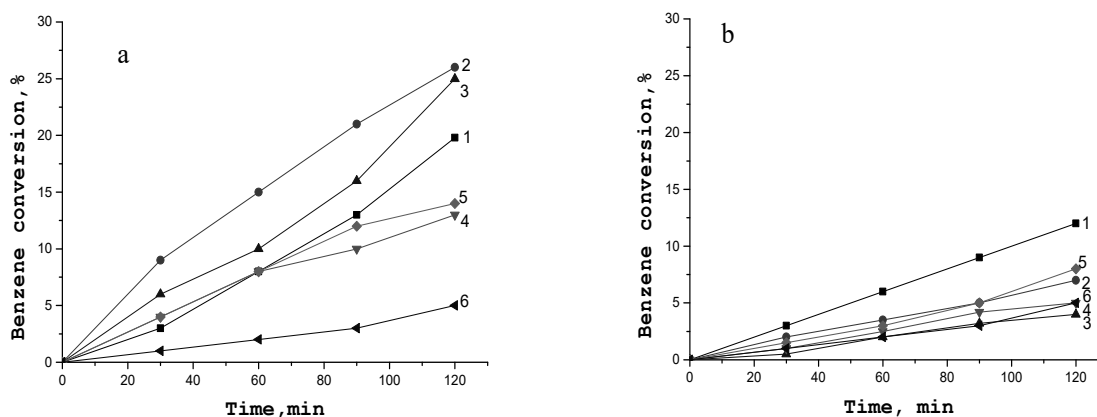


Fig. 7. Photodegradation of aqueous benzene solution: *a* – visible light irradiation, *b* – UV irradiation; 1 – Ti/SS; 2 – Ti/SS/200 °C; 3 – Ti/SS/300 °C; 4 – Ti/SS/400 °C; 5 – Ti/SS/500 °C; 6 – Ti/SS/600 °C

It should be noted that at visible light irradiation samples after treatment at 200 and 300 °C have the maximum activity (26 and 25 %, respectively). Increase of temperature treatment leads to decrease in the samples activity. Those kinds of changes in samples activity can be explained by the influence of

temperature on the ratios between nitride, oxynitride and oxide phases of the titanium.

It is possible to propose a hypothesis that the high activity of the synthesized samples is caused by presence of titanium nitride and oxynitride on the support surface.

## CONCLUSIONS

It is shown that as a result of ionic implantation of Ti on the surface of a stainless steel nanoscale layer of the implant in the form of amorphous composition consisting of oxide, titanium nitride and titanium oxynitride are formed.

A hypothesis of active phases on the surface of support, which ensures its high activity in the

reaction of photodegradation of benzene in aqueous solution under visible light irradiation is proposed.

A perspective is shown of practice use of the obtained samples in the process of removal of benzene from its aqueous solutions with visible light irradiation, which today is very important from the ecological point of view.

## Фізико–хімічні властивості Ті–вмісних нанесених на нержавіючу сталь композитів

О.В. Санжак, Д.В. Бражник, В.В. Гончаров, В.О. Зажигалов, Ф.А. Азімов

*Институт сорбції та проблем ендоекології Національної академії наук України  
вул. Наумова, 13, Київ, 03164, Україна, Sanzhakalena@bigmir.net  
Державний заклад “Луганський Державний Медичний Університет”  
вул. Будівельників, 32, Рубіжне, Луганська обл., 93012, Україна*

*Методом іонної імплантації синтезовано нанесений Ті-вмісний каталізатор на поверхні нержавіючої сталі. Геометричні розміри камери для імплантації дозволяють синтезувати композити з максимальним розміром 30×30 см. Форма і розміри дозволяють використовувати отримані зразки для видалення шкідливих речовин як з водних розчинів, так із газових сумішей. Показано, що в результаті імплантації іонів Ті відбувається досить значне збільшення механічної міцності поверхневого шару. Після термічної обробки вона децю спадає, але все одно залишається більшою, ніж міцність самого носія – нержавіючої сталі. Фізико-хімічними методами (РФА, АСМ, СЕМ та РФЕС) охарактеризовано склад поверхні нанесеного каталізатора та вплив на нього термічної обробки зразка. Показано, що в результаті іонної імплантації Ті на поверхні нержавіючої сталі формується нанорозмірний шар імплантату, у вигляді рентгеноаморфної композиції, яка складається з оксиду, нітриду та оксинітриду титану. Показана висока фотокаталітична активність цього каталізатора в процесі знешкодження бензолу у водних стоках при опроміненні видимим світлом, яка значно перевищує його активність в УФ-діапазоні. Підвищення температури обробки веде до зниження активності зразків. Подібні зміни фотоактивності зразків можуть бути пояснені впливом температури на співвідношення між нітридною, оксинітридною та оксидною фазами титану. При цьому кількість останньої зростає при збільшенні температури обробки. Висловлено гіпотезу про активні фази на поверхні носія, які забезпечують його високу активність в реакції фотодеструкції водного розчину бензолу при опроміненні видимим світлом. Таким чином, показано перспективність та практичність використання одержаних зразків в процесі видалення бензолу з його водних розчинів у видимому спектрі випромінювання, що є надзвичайно актуальним з екологічної точки зору.*

**Ключові слова:** фольга з нержавіючої сталі, іонна імплантація титану, фотодеградація бензолу

## Физико–химические свойства Ti – содержащих нанесенных на нержавеющую сталь композитов

Е.В. Санжак, Д.В. Бражник, В.В. Гончаров, В.А. Зажигалов, Ф.А. Азимов

Институт сорбции и проблем эндоэкологии Национальной академии наук Украины  
ул. Наумова, 13, Киев, 03164, Украина, Sanzhakalena@bigmir.net  
Государственное учреждение “Луганский государственный медицинский университет”  
ул. Строителей, 32, Рубежное, Луганская обл., 93012, Украина

Методом ионной имплантации синтезирован нанесенный Ti-содержащий катализатор на поверхности нержавеющей стали. Геометрические размеры камеры для имплантации позволяют синтезировать композиты с максимальным размером 30×30 см. Форма и размеры позволяют использовать полученные образцы для удаления вредных веществ как из водных растворов, так и из газовых смесей. Показано, что в результате имплантации ионов Ti наблюдается значительное увеличение механической прочности поверхностного слоя. После термической обработки она немного падает, но все равно остается выше, чем прочность самого носителя – нержавеющей стали. Физико-химическими методами (РФА, АСМ, СЭМ та РФЭС) охарактеризован состав поверхности нанесенного катализатора и влияние на него термической обработки. Показано, что в результате ионной имплантации Ti на поверхность нержавеющей стали формируется наноразмерный слой имплантата, в виде рентгеноаморфной композиции, которая состоит из оксида, нитрида и оксинитрида титана. Показана высокая фотокаталитическая активность этого катализатора в процессе удаления бензола из сточных вод при облучении видимым светом, которая значительно превышает его активность в УФ-диапазоне. Повышение температуры обработки ведет к уменьшению активности образцов. Подобные изменения фотоактивности образцов можно объяснить влиянием температуры на соотношение между нитридной, оксинитридной и оксидной фазами титана. При этом количество последней растет при увеличении температуры обработки. Предложена гипотеза об активных фазах на поверхности носителя, которые обеспечивают его высокую активность в реакции фотодеструкции водного раствора бензола при облучении видимым светом. Таким образом, показана перспективность и практическая использования полученных образцов в процессе удаления бензола из его водных растворов в видимом спектре излучения, что чрезвычайно актуально с экологической точки зрения.

**Ключевые слова:** фольга из нержавеющей стали, ионная имплантация титана, фотодеградация бензола

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