

UDC 621.357

**Fe/TiO<sub>2</sub> COMPOSITE COATINGS: ELECTRODEPOSITION AND APPLICATION FOR PHOTO-CATALYTIC DYE DEGRADATION**

TSURKAN A.V., VASIL'EVA E.A., PROTSENKO V.S., DANILOV F.I.  
*Ukrainian State University of Chemical Technology*  
*annaturkan@ukr.net*

The electrodeposition of iron-titania composite coatings from a methanesulfonate plating bath is studied in this work. The TiO<sub>2</sub> content in deposits is shown to increase with increasing titania concentration in suspension electrolyte and decreasing cathode current density. The kinetics of composite Fe/TiO<sub>2</sub> electrodeposition obeys the model proposed by Guglielmi. The photo-catalytic activity of synthesized Fe/TiO<sub>2</sub> composite electrochemical coatings was estimated in the model reaction of decomposition of Methyl Orange dye in an alkaline solution. The use of the Fe/TiO<sub>2</sub> composite electroplated films as a photo-catalyst allows accelerating the decomposition of Methyl Orange dye in aqueous media under the action of UV radiation.

Developing novel catalytic materials for the decontamination of wastewaters containing various organic pollutants is an important task of modern chemistry and chemical engineering [1]. In this context, TiO<sub>2</sub> may be considered as the most efficient and environmentally friendly photo-catalyst, and it has been widely used for photo-degradation of various pollutants [2]. In particular, titania is very effective in photo-catalytic decomposition of various organic dyes in wastewaters [3]. In this respect, one of unsolved problems is the development of convenient supports for the TiO<sub>2</sub> photo-catalyst, because the use of powdered titania for wastewater treatment involves evident implementation impediments. We think that the electrodeposition of composite coatings in which TiO<sub>2</sub> particles are uniformly distributed in a metal matrix allows successfully solving the problem concerned [4].

From our point of view, composite coatings containing TiO<sub>2</sub> particles entrapped into electrodeposited iron matrix attract considerable attention, because Fe and its compounds are particularly cheap, available and low-toxic. In this study we used methanesulfonate plating baths for iron matrix electrodeposition [4-6]. Methanesulfonate plating baths based on methanesulfonic acid CH<sub>3</sub>SO<sub>3</sub>H (MSA) are known to be an attractive alternative to ordinary electroplating baths because MSA is regarded as a "green acid" due to its environmental advantages [7].

### Research Methodology

All solutions were prepared using double distilled water and reagent grade chemicals. Iron (II) methanesulfonate was synthesized by the procedure reported in detail elsewhere [7]. The pH value of the plating bath was controlled through a common potentiometric method and adjusted to the required value by adding either  $\text{Na}_2\text{CO}_3$  or MSA solutions. To obtain composite coatings, a weighed portion of  $\text{TiO}_2$  nano-powder (Degussa P 25, Evonik; the average particle size 25 nm) was introduced into the electroplating bath. Before electrodeposition, the plating bath was stirred for 1 h by mechanical agitator and then ultrasonically treated with a UZDN-A ultrasonic disperser to reach uniform distribution of colloidal particles in the bath. The electrodeposition of  $\text{Fe/TiO}_2$  composite coatings was performed under the conditions of a continuous bath agitation with a magnetic stirrer (ca.  $60 \text{ rev min}^{-1}$ ).

Electrodeposition was performed at a steady current density in a usual thermostated glass cell (298 K) for 20 min. Iron-titania films were deposited on the mild steel plates fixed in a plastic holder. Prior to each experiment, the sample surface was treated with magnesium oxide, etched for several minutes in 1:1 (vol.) HCl solution and then thoroughly rinsed with double distilled water. The electrolysis was carried out with anodes made from mild steel.

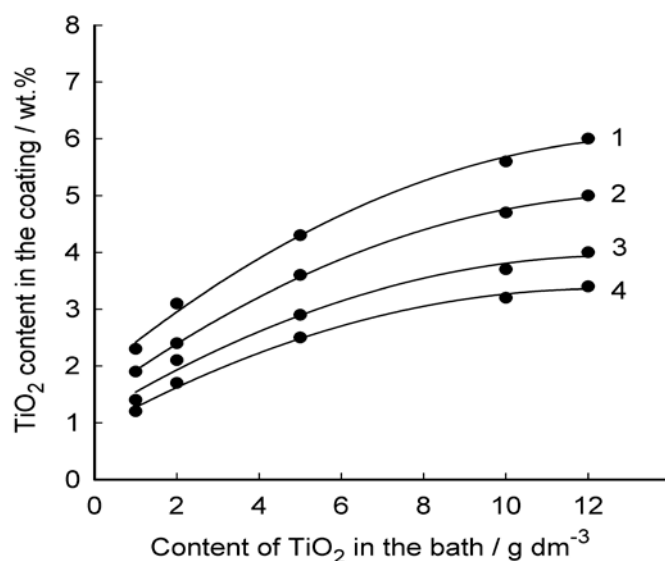
The photo-catalytic properties of the  $\text{Fe/TiO}_2$  composites were evaluated by studying the kinetics of decomposition of Methyl Orange (MO) dye under the action of UV radiation in an aqueous alkali solution (0.1 M NaOH). A UV lamp with the effective spectral range of 180 to 275 nm was used. The lamp was arranged over the MO solution at a distance of 10 cm from its surface. In the course of photo-catalytic decomposition, the MO solution was continuously stirred with a magnetic stirrer. The MO concentration was determined photo-metrically. Steel plates with the electrodeposited  $\text{Fe/TiO}_2$  coating were fixed at a depth of 2 mm in the solution parallel to its surface (at an angle of  $90^\circ$  to the UV beam).

### Results and Discussion

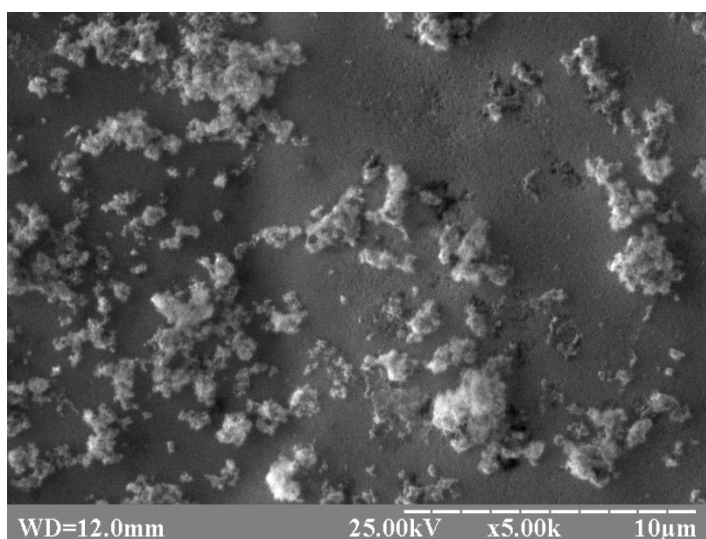
Fig. 1 shows that the amount of the  $\text{TiO}_2$  particles in the coatings increases with an increase in titania concentrations in the electrolyte and with a decrease in the current density.

According to this concept, the particles inclusion in the metallic matrix occurs in two consecutive steps of adsorption. The model involves Langmuir adsorption of particles. In the first step, called a "loose adsorption", the ion-coated particles are reversibly adsorbed on the cathode surface and yield a high degree of coverage. The second step is

a "strong adsorption" of particles. The reduction of metal ions adsorbed on the particles creates the circumstances of an irreversible strong adsorption. Further, the particles are engulfed by the overgrowing of a metallic matrix.



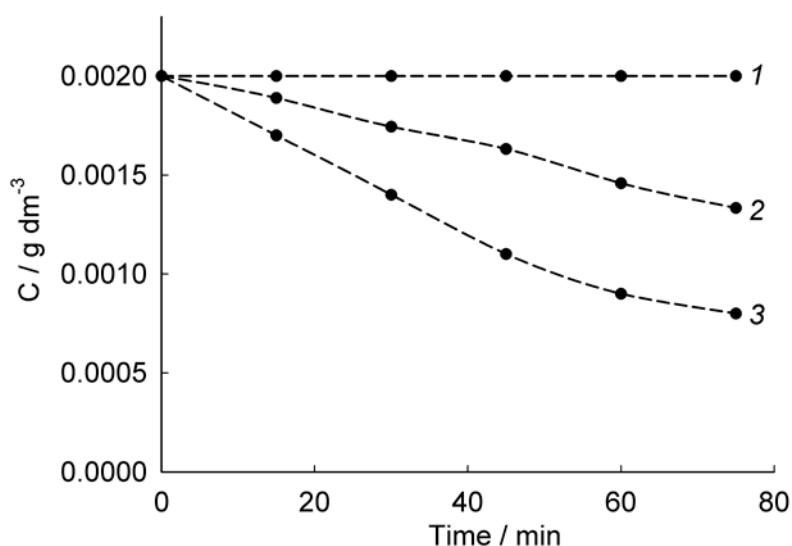
**Figure 1.** Effect of titania concentration in the bath on TiO<sub>2</sub> in coatings at various current densities, A dm<sup>-2</sup>: (1) 5, (2) 10, (3) 15, (4) 20



**Figure 2.** SEM image of Fe/TiO<sub>2</sub> (5% wt.) coating electrodeposited from methanesulfonate bath at 10 A dm<sup>-2</sup>

SEM images of Fe/TiO<sub>2</sub> coating deposited from methanesulfonate baths show that the surface contains flakelike particles of agglomerated TiO<sub>2</sub> with an average size of about several micrometers (Fig. 2). The EDS analysis revealed that the surface areas corresponding to flakelike particles in SEM photos consist essentially of titanium and oxygen in a ratio practically equal to the stoichiometric composition

of TiO<sub>2</sub>. This means that the aggregation of TiO<sub>2</sub> nano-powder occurs in methanesulfonate solutions. These findings are fully conformed by the results of sedimentometric analysis. The coarsening of the particles results in their enhanced sedimentation and subsequent phase separation. This is why the electrochemical synthesis of the Fe/TiO<sub>2</sub> composites was carried out under the conditions of a continuous bath agitation with a magnetic stirrer.



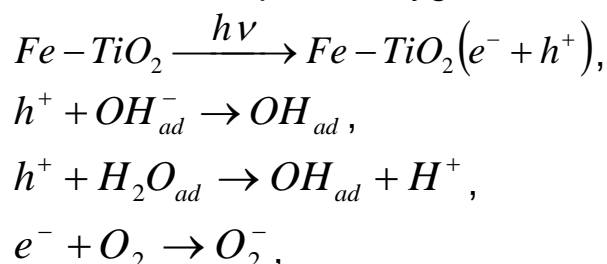
**Figure 3.** Time dependences of MO concentration (1) in the dark, (2) under UV irradiation without catalyst, and (3) under UV irradiation in the presence of Fe/TiO<sub>2</sub> catalyst (10% wt. TiO<sub>2</sub>)

The photocatalytic activity of Fe/TiO<sub>2</sub> composite electrochemical coatings was evaluated in this study in the model reaction of decomposition of MO dye in alkaline solution [9].

Without the action of UV irradiation, Methyl Orange dye does not undergo spontaneous decomposition (Fig. 3). The photocatalytic decomposition of the dye under

the action of UV radiation is appreciably accelerated in the presence of a catalyst, Fe/TiO<sub>2</sub> catalyst. It was stated that the kinetic curves plotted in the coordinates "logarithm of MO concentration versus time" are straight lines, this suggests the pseudo-first reaction order. The formal rate constants were shown to be 0.0054 and 0.0135 min<sup>-1</sup> for the photocatalytic decomposition without catalyst and in the presence of the iron/titania catalyst, respectively.

According to the modern notion of the mechanism of the photocatalytic action of titania in the dye decomposition [9], the following processes occur on the TiO<sub>2</sub> surface under the action of UV radiation in a medium containing dissolved atmospheric oxygen:



where  $h^+$  are positively charged holes generated on the catalyst surface.

The MO molecules decompose under the action of the generated hydroxyl radicals forming CO<sub>2</sub> and H<sub>2</sub>O as final decomposition products [9].

## Conclusions

1. Fe/TiO<sub>2</sub> composite coatings can be synthesized by electrodeposition method from an environmentally friendly methanesulfonate iron plating bath containing titania nano-powder. The content of TiO<sub>2</sub> particles in the coatings is shown to increase with increasing titania concentrations in the electrolyte and decreasing the cathodic current density.

2. The use of the Fe/TiO<sub>2</sub> composite electroplated coating as the catalyst allows accelerating the decomposition of Methyl Orange in aqueous solution under the action of UV radiation. Thus, these photocatalysts seem to be promising in waste-water treatment processes.

## References

- [1] Brillas E., Martínez-Huitleb C.A., Decontamination of wastewaters containing synthetic organic dyes by electrochemical methods. An updated review, *Appl. Catal. B: Environ.*, 166-167, 603-643, (2015).
- [2] Chen X., Mao S.S., Titanium dioxide nanomaterials: synthesis, properties, modifications, and applications, *Chem. Rev.*, 107, 2891-2959, (2007).
- [3] Lachheb H., Puzenat E., Houas A., Ksibi M., Elaloui E., Guillard C., Herrmann J.-M., Photocatalytic degradation of various types of dyes (Alizarin S, Crocein Orange G, Methyl Red, Congo Red, Methylene Blue) in water by UV-irradiated titania, *Appl. Catal. B: Environ.*, 39, 75-90, (2002).
- [4] Protsenko V.S., Vasil'eva E.A., Smenova I.V., Danilov F.I. Electrodeposition of iron/titania composite coatings from methanesulfonate electrolyte, *Russ. J. Appl. Chem.*, 87, 283-288, (2014).
- [5] Protsenko V.S., Vasil'eva E.A., Smenova I.V., Baskevich A.S., Danilenko I.A., Konstantinova T.E., Danilov F.I., Electrodeposition of Fe and composite Fe/ZrO<sub>2</sub> coatings from a methanesulfonate bath, *Surf. Eng. Appl. Electrochem.*, 51, 65-75, (2015).
- [6] Danilov F.I., Tsurkan A.V., Vasil'eva E.A., Protsenko V.S., Electrocatalytic activity of composite Fe/TiO<sub>2</sub> electrodeposits for hydrogen evolution reaction in alkaline solutions, *Int. J. Hydrogen Energy*, in press, doi: 10.1016/j.ijhydene.2016.02.112.
- [7] Gernon M.D., Wu M., Buszta T., Janney P., Environmental benefits of methanesulfonic acid: comparative properties and advantages, *Green Chem.*, 1, 127-140, (1999).
- [8] Guglielmi N., Kinetics of the deposition of inert particles from electrolytic baths, *J. Electrochem. Soc.*, 119, 1009-1012, (1972).
- [9] Sonawane R.S., Kale B.B., Dongare M.K., Preparation and photocatalytic activity of Fe–TiO<sub>2</sub> thin films prepared by sol–gel dip coatings, *Mater. Chem. Phys.*, 85, 52-57, (2004).