

## PROTECTIVE CERAMIC NANOCOATINGS

ABRASHOV Aleksey, GRIGORYAN Nelya, VAGRAMYAN Tigran, ZHILENKO Darya,  
MEN'SHIKOV Vladimir, KOLESNIKOV Artem

*MUCTR - D.Mendeleev University of Chemical Technology of Russia, Moscow, Russian Federation,*  
[abr-aleksey@yandex.ru](mailto:abr-aleksey@yandex.ru), [ngrig108@mail.ru](mailto:ngrig108@mail.ru), [vagramyan@muctr.ru](mailto:vagramyan@muctr.ru), [daryazhilenko@mail.ru](mailto:daryazhilenko@mail.ru),  
[vm\\_uti@muctr.ru](mailto:vm_uti@muctr.ru), [artkoles@list.ru](mailto:artkoles@list.ru)

### Abstract

Recently, as an alternative to the adhesive phosphate layers deposited on steel nanoscale adhesive coatings obtained from solutions hexafluorotitanic and hexafluorozirconic acids found their application worldwide. This paper is devoted to the development of technology of these coatings.

A process of applying titanium oxide and zirconium oxide nano-coating on a steel base, which satisfy the requirements of the adhesive layers under the paintwork. The solution contains: 1.2 g / l  $H_2TiF_6$ ; 0.02-0.16 g / l  $Ni^{2+}$ , 1-3 g/l  $(NH_4)_2MoO_4$ . It is found that the allowable value of the solution pH in the range 4.5-5.5 units. By means of X-ray photoelectron spectroscopy (XPS) the chemical composition of coatings was defined and we assume that the protective film includes  $TiO_2$  ( $ZrO_2$ ), FeO and  $Fe_2O_3$  mainly.

The effect of temperature of the solution to the properties of coatings showed that its heating up to 40° C does not affect the appearance and the protective ability of the coating.

It is stated that the thickness of the coating increases during the first three minutes, and stabilized at values of 50-60 nm for titanium oxide coatings and 60-70 nm for zirconium oxide coatings.

The morphology of coatings was examined by atomic force microscopy (AFM). It was found that the crystallite size is up to 300 nm, and the surface is quite homogeneous.

Corrosion tests have shown that obtained ceramic nanocoatings have protective ability which corresponds the requirements for the adhesive layers under the paint coatings. These coatings have protective characteristics which are highly competitive with silicone and amorphous phosphate coatings and are similar to the protective characteristics of crystalline phosphate coatings.

**Keywords:** Corrosion protection, conversion coatings, zirconium-oxide coatings, titanium-oxide coatings, surface treatment

### 1. INTRODUCTION

Currently in technologies of the painting of metal surfaces phosphate coatings with small specific density are widely used as adhesive layers under painting. Known technologies of crystalline phosphate application have such disadvantages as high energy consumption due to high operating temperature processes - 70-90 °C, the use of sophisticated equipment at a sufficiently strict control of coating formation and others. [1-5].

Currently in technologies of painting of metal surfaces as an alternative to the adhesive phosphate layers on the steel in the world have become increasingly used nanoscale adhesive coatings obtained from solutions hexafluorotitanic and hexafluorozirconic acids [6-10]. The advantages of these new technologies are their lower energy consumption and technological effectiveness comparing with phosphating processes. Solutions for application of these coatings do not require heating, strict control of process, easy to apply and give less toxic sludge.

The aim of this work was to develop a process applying the adhesive ceramic titanium-oxide and zirconium-oxide nanoscale coatings under the paint layer.

## 2. EXPERIMENTAL MATERIALS

Ceramic nanocoating were applied to a cold rolled steel plate A622 which is widely used in the automotive and other industries. Solutions for the deposition of coatings prepared from reagent grade "A.C.S." and distilled water.

pH control of solutions was carried out using a portable pH-410 pH-meter.

Rapid evaluation of protective coatings was performed with Akimov reagent - a solution containing  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  82 g / l; NaCl 33 g / l; 13 ml / l of 0.1 N HCl. According to the Akimov method protective coating ability (PAC) is estimated as the time in seconds when the color changes from gray to reddish-brown in the control plot solution drop.

The thickness of protective layers was determined by ellipsometry using an ellipsometer Gartner on the solid-state laser LSM-S-111 with a green colour-filter.

The surface morphology was studied using an atomic force microscope INTEGRA Prima (NT-MDT, Russia). Scan Mode - semicontact, cantilever - HA\_NC Etalon (NT-MDT, Russia).

XPS spectra were obtained using a special CLAM100 camera mounted on the Auger microscope HB100 (Vacuum Generators, GB).

Corrosion tests of adhesion ceramic nanoscale coatings with polyester paint powder were carried out in salt fog chamber Ascott S120iP in accordance with the international ASTM B117 standard adopted in the automotive industry, and in accordance with GOST 9.401-91.

The adhesion of the coatings was measured using Elcometer adhesion tester 107 by transverse incisions, in accordance with international standard ASTM D3359.

## 3. EXPERIMENTAL WORK

Taking into account the information given in related publications, solutions were prepared basically of hexafluorotitanic ( $\text{H}_2\text{TiF}_6$ ) or hexafluorozirconic ( $\text{H}_2\text{ZrF}_6$ ) acid and nickel ions that were chosen after preliminary experiments with a number of heavy metal ions, because namely nickel ions provide good coating quality.

The effect of  $\text{H}_2\text{TiF}_6$  ( $\text{H}_2\text{ZrF}_6$ ) and metal ions concentration on the appearance and protective ability of coatings was investigated. It was found that in the absence of ions  $\text{Ni}^{2+}$  the coating is discontinuous and the traces of corrosion of the metal base are observed. Uniform coatings with good appearance are formed in the concentration range of 1-2.5 g / l acid and 20 to 60 mg / l  $\text{Ni}^{2+}$ . Protective ability (PAC) of these coatings was determined by Akimov express method, it is about 15 s, which is slightly lower than that of the phosphate coatings.

These experiments allowed to determine the range of concentrations of the solution components that promotes to deposit good quality coatings with high protective ability. The protective capability of the coating measured by Akimov express method is about 12-15 s, which is slightly lower than that of the phosphate coatings.

### 3.1. Determination of process parameters

Studies have shown that the allowable pH of the solution is in the range of 4.5-5.5 units. At pH less than 4.5 the coating does not form, and at pH higher than 5.5 the coating becomes inhomogeneous and discontinuous. Thus, the interval of pH = 4.5-5.5 is optimal, that also corresponds with the coating formation mechanism described in the literature. It is known that in this pH range or hexafluorozirconic or hexafluorotitanic acid is hydrolyzed forming titanium oxide ( $\text{TiO}_2$ ) or zirconium oxide ( $\text{ZrO}_2$ ), that adsorb on initially contact plated nickel. Further, the coating expands to form a continuous film.

In this study the protective ability was determined, depending on the duration of the process. It was found that the protective ability of coating increases at the first 3-5 minutes of the process. Then stabilizes and reaches the value of 15 s by Akimov method.

It was found that heating of solution up to 40 °C does not affect significant changes in the appearance and protective ability of coatings. Heating over 40 °C causes protective ability change for the worse. The temperature range was set as 18-25 °C, and it was noted that heating the solution up to 40 °C (e.g. in the summertime) is allowed.

The influence of some additives was investigated (ones recommended for phosphating solutions) on the protective ability of ceramic nanocoatings. Among them, nitrogen-containing compounds such as sodium metanitrobenzosulfonate (m-NBS), hydroxylamine sulfate, sodium molybdate. It was found that addition of Na<sub>2</sub>MoO<sub>4</sub> in an amount of 1-3 g / l significantly improves the ability of the protective coating. The positive effect of other additives in solution was not observed, moreover, in some cases decreased protective ability and appearance worsen [6].

Thus, in the solution sodium molybdate Na<sub>2</sub>MoO<sub>4</sub> was included in an amount of 1-3 g / l.

The effect of drying temperature to protective ability increases: the highest value is observed (30 s.) for layers being dried at a temperature of 130-200 °C.

It is found that the degreasing of metal surfaces prior to coating deposition should be performed using inorganic chemicals than organic solvents or Vienna lime, for inorganic chemicals the coating has a slightly higher protective ability.

Stirring of working solution also affects the protective properties of the coatings produced: mechanical or ultrasonic agitation of the working solution can increase protective ability 1.5 times.

### 3.2. Investigation of the chemical composition of coatings

To investigate the chemical composition of the coatings X-ray photoelectron spectroscopy (XPS) method was used. XPS survey spectra of the coatings revealed the presence of titanium (zirconium) compounds, iron, molybdenum, fluorine and oxygen [6].

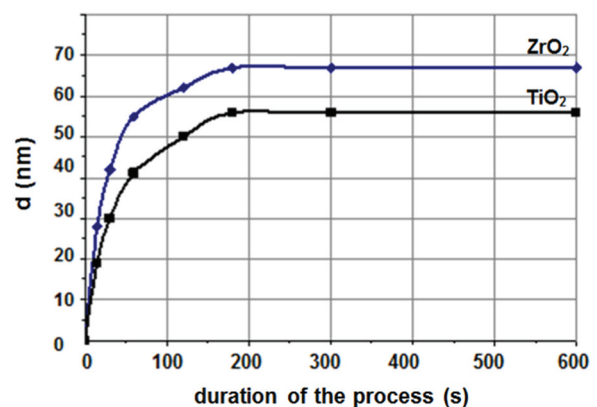
Analysis of spectra allows to determine which compounds of these elements are included in the coating. Wide oxygen peak can be interpreted as a mixture of oxides of iron, titanium, and molybdenum. Iron presents as a mixed oxide FeO-Fe<sub>2</sub>O<sub>3</sub>. The energy of Ti2p (Zr2p) peaks denotes these elements to be in oxidized form TiO<sub>2</sub> (ZrO<sub>2</sub>).

Furthermore, it has been found that nickel is generally present only in the first coating layer, which is consistent with the above described coating forming mechanism.

### 3.3. The thickness of the obtained coatings

The coating thickness was determined by ellipsometric method. Thickness growth in time is shown in **Figure 1**.

It is stated that the thickness of coatings increases during first three minutes, and is stabilized at values of 50-60 nm for titanium-oxide coatings and 60-70 nm for zirconium-oxide coatings.



**Figure 1** The dependence of the coating thickness on the duration of the process  
ZrO<sub>2</sub> - zirconium oxide coatings; TiO<sub>2</sub> - titanium oxide coatings

### 3.4. Surface morphology

Atomic force microscopy (AFM) allowed us to estimate grain size and the degree of development of the surface (Figure 2). It is found that the crystallite size is about 300 nm.

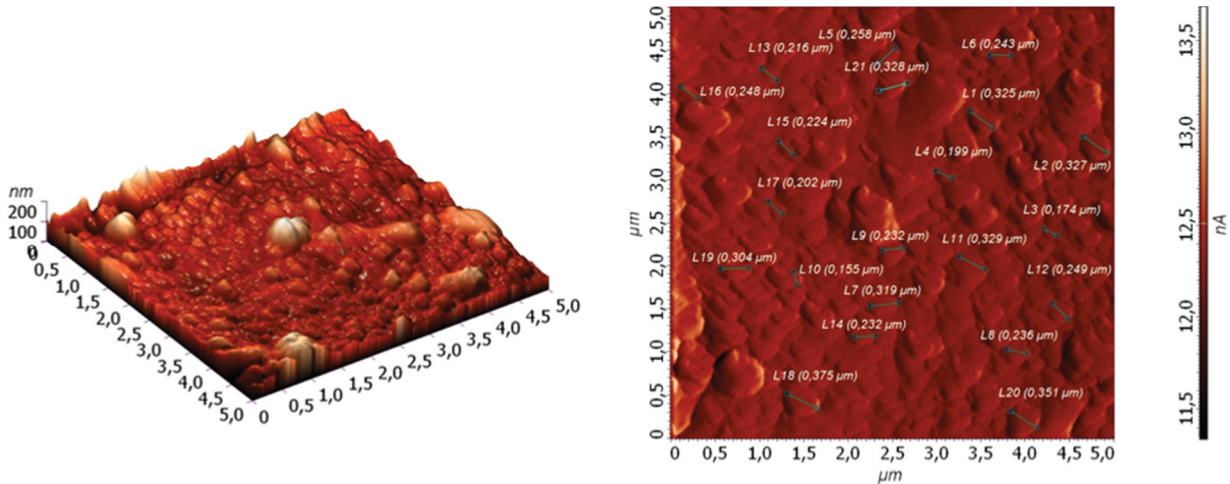


Figure 2 Surface morphology

Analysis of 3D micrographs of titanium oxide coatings leads to the conclusion that the structure of the layer is amorphous, because no clear globular shape is observed and the surface is very homogeneous.

### 3.5. Corrosion tests

Cyclic corrosion tests (ASTM B117) of steel samples with the adhesive zirconium oxide coating and titanium oxide coating, painted by dry polyester powder were carried out and then compared with other adhesive coatings. The thickness and specific density are shown in Figure 3. It should be pointed out that ceramic nanocoatings have lowest thickness and specific density in comparison with other coatings.

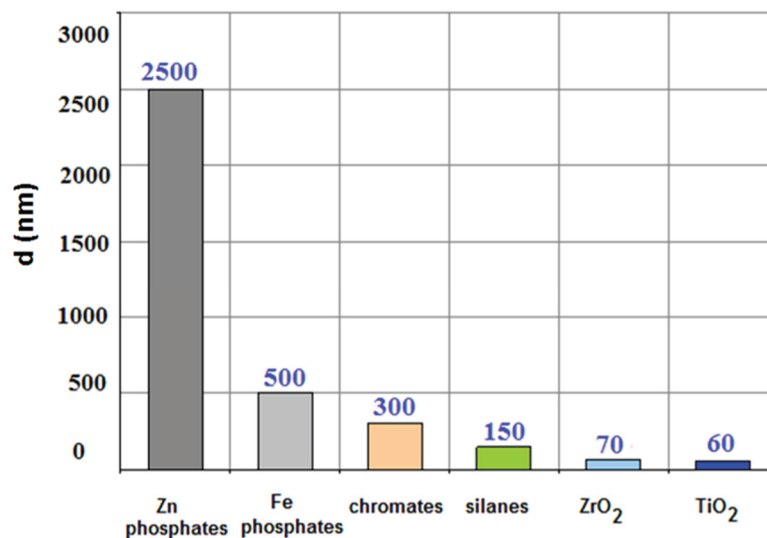
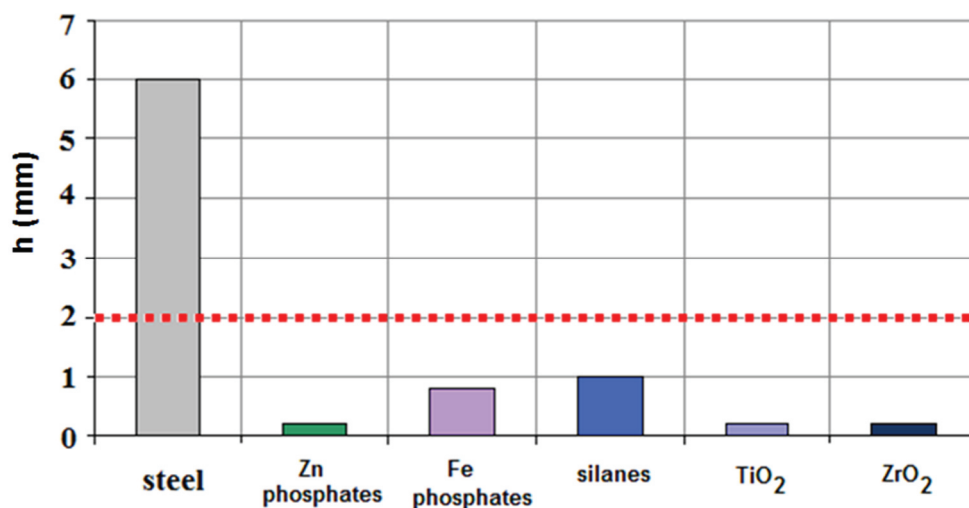


Figure 3 The maximum thickness of conversion coatings under the paint layer, nm

Zn phosphates - crystalline phosphate coatings; Fe phosphates - amorphous phosphate coatings; chromates - chromate coatings; silanes - organo-silicon coatings; ZrO<sub>2</sub> - zirconium oxide coatings; TiO<sub>2</sub> - titanium oxide coatings

Corrosion tests shown that the ceramic protective nanocoating satisfies the requirements for the adhesive layers under the paint layer, because the width of penetration of the corrosion on the notch groove in these cases does not exceed 2.0 mm, after 240 hours of testing (**Figure 4**).



**Figure 4** Results of corrosion tests (ASTM B117)

steel - uncoated steel; Zn phosphates - crystalline phosphate coatings; Fe phosphates - amorphous phosphate coatings; silanes - organo-silicon coatings; ZrO<sub>2</sub> - zirconium oxide coatings; TiO<sub>2</sub> - titanium oxide coatings

These coatings have protective characteristics which are not inferior to silicone and amorphous phosphate coatings and approaching to the protective characteristics of crystalline phosphate coatings.

Adhesion test of coatings with the developed adhesive sublayer was performed by transverse incisions using adhesion tester. It was found that the coatings revealed very good adhesion - grade 0 according to ASTM D3359 standard, which is not worsened even after corrosion tests.

#### 4. CONCLUSION

During this work the process of applying the adhesive ceramic titanium-oxide and zirconium-oxide nanoscale coatings under the paint layer was developed.

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