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Decorative protective coatings produced by atomic layer deposition and calculation of their spectral characteristics

V.V. Aksenova[1, 2✉], M.V. Mesh [3], D.S. Kolokolov[3],
T.Yu. Kartseva[3], N.A. Fedorov[4], A.S. Pavlyuchenko[2]

[1] Peter the Great St. Petersburg Polytechnic University, St. Petersburg, Russia;
[2] Ioffe Institute, St. Petersburg, Russia;
[3] JSC Koltsov's Design Bureau, St. Petersburg, Russia;
[4] ITMO University, St. Petersburg, Russia
✉ valeriyaakse@gmail.com

Abstract. In this paper, we consider the possibilities of using the atomic layer deposition process for producing decorative coatings based on aluminum oxide and titanium oxide on steel parts. The parameters of coatings based on aluminum oxide and titanium oxide of different colors were calculated. The calculations of the coating color and its optical characteristics are shown, and it is found that the developed software allows you to calculate the color of the coating. The properties of the resulting coatings have been studied and it has been experimentally established that these coatings can be used for chemical protection of surfaces.

Keywords: aluminium oxide, protective coating, atomic layer deposition, titanium oxide, decorative coating

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Декоративные защитные покрытия, наносимые методом атомно-слоевого осаждения, и расчет спектральных характеристик таких покрытий

В.В. Аксенова[1, 2 ✉], М.В. Меш[3], Д.С. Колоколов[3],
Т.Ю. Карцева[3], Н.А. Федоров[4], А.С. Павлюченко[2]

[1] Санкт-Петербургский политехнический университет Петра Великого, Санкт-Петербург, Россия;
[2] Физико-технический институт им. А.Ф. Иоффе РАН, Санкт-Петербург, Россия;
[3] АО «СКТБ Кольцова», Санкт-Петербург, Россия;
[4] Университет ИТМО, Санкт-Петербург, Россия
✉ valeriyaakse@gmail.com

Аннотация. В данной работе рассмотрены возможности применения процесса атомно-слоевого осаждения для нанесения декоративных покрытий на основе оксида алюминия и оксида титана на стальные детали. Были рассчитаны параметры покрытий на основе оксида алюминия и оксида титана разных цветов. Показаны результаты по разработке программного обеспечения для расчета цвета покрытия и его оптических характеристик и установлено, что разработанное программное обеспечение позволяет рассчитать цвет покрытия. Изучены свойства получаемых покрытий и экспериментально установлено, что эти покрытия можно использовать в качестве защитных.

Ключевые слова: атомно-слоевое осаждение, оксид титана, оксид алюминия, защитное покрытие, декоративное покрытие

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Introduction

One of the most common ways to protect a metal from corrosion is to isolate its surface from the external environment by depositing a protective coating. The use of atomic layer deposition to create anti-corrosion coatings is not yet widespread, but it is an up-to-date and promising method that has all the advantages necessary in this area, namely, the possibility of a wide range of materials deposition with atomic precision [1] to products of complex geometry with high uniformity of the obtained films.

This process can be used to create a protective and decorative coating on metals; this is especially important for processing products of complex shape, because the atomic layer deposition process will allow uniform coating of the entire surface of sample [2]. Due to the ability to precisely control the thickness, any color of the coating can be obtained by changing the thickness. Interference coatings used in the visible region of the range are characterized not only by optical parameters, but also by color [3]. Chromaticity coordinates are used to describe the color properties of interference coatings. They cover all colors visible to a standard observer and form the CIE chromaticity diagram.

The possibility of using atomic layer deposition as a method for creating anticorrosive and decorative coatings was approved in articles [4–6]. In [4], Al_2O_3 and TiO_2 coatings proved to be effective in protecting stainless steel substrates from corrosion and increasing the thickness of the coating increased its corrosion resistance. In [5] deposited layers of Al_2O_3 and TiO_2 were used to create ultra-thin protective coatings on copper to prevent water corrosion, and it turned out that the coating formed by a layer of titanium oxide on a layer of aluminum oxide was very resistant to water corrosion. TiO_2 layers 20 nm thick on Al_2O_3 layers 5 nm thick protected the copper substrate for 90 days in water at 90°C. Paper [6] systematically investigated the detailed processes for growing Al_2O_3 and TiO_2 thin films at a growth temperature of 80°C and their applicability for functional color coatings. Using the scheme TiO_2 (162 nm)/Al_2O_3 (48 nm)/TiO_2 (80 nm)/Al_2O_3 (60 nm), a pink coating was obtained on a stainless steel substrate with an intermediate layer of TiN, in addition, the colors were determined after finishing deposition of each of the layers.

Materials and Methods

The process of atomic layer deposition was carried out on a PICOSUN P-300B ALD system. The Picosun-300B unit can operate in the temperature range from 20 to 500 °C. In this work, trimethylaluminum (TMA) + water vapor for Al_2O_3 and water vapor + titanium tetrachloride for TiO_2 were used from sources. The working pressure was 600 Pa.

For the calculation, a software package was developed that provides access to data on the refractive and absorption indices aggregated in the refractiveindex.info library [7] (for the studied coatings we used refractive indices spectra reported in the following papers: [8] for TiO_2, [9] for Al_2O_3, [10] for Mo; refractive index spectrum of the glass substrate was determined from our own experiments), based on which the transmission, reflection, and absorption spectra of layered thin films were calculated using the matrix method [11]. The resulting reflection spectrum is converted to color in the CIE XYZ system using analytical approximations of the addition functions of the three-color colorimetric system obtained in [12].

When calculating, the incidence of light was assumed to be normal, the spectrum of the incident light was taken to be the emission spectrum of a black body at a temperature of 5777 K, scattering, as well as surface irregularities, were not taken into account in the calculation.

The transmission and reflection spectra of the samples were studied on an Optronic Laboratories OL 770 spectroradiometer. The radiation was incident on the sample from the side of the film, normal to its surface.

Results and Discussion

A coating of aluminum oxide and titanium oxide in combination $Al_2O_3/TiO_2/Al_2O_3/TiO_2$ 60/60/60/60 nm with a total thickness of 240 nm was deposited by atomic layer deposition on a glass sample pre-coated with a 100 nm layer of molybdenum (Fig. 1). The reflection spectrum of the resulting coating is shown in Fig. 2. The transmission of a 100-nm-thick molybdenum layer is zero in the optical radiation range, which makes it possible to use such a coating as a test one.

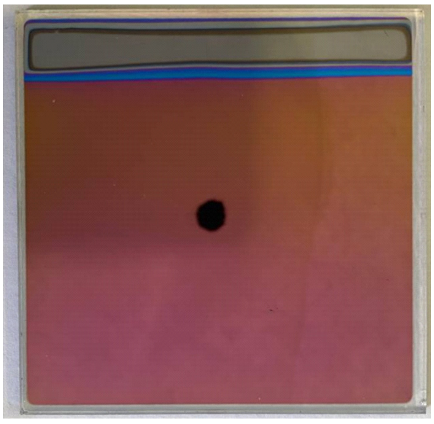

Fig. 1. Glass sample with a layer of molybdenum after atomic layer deposition

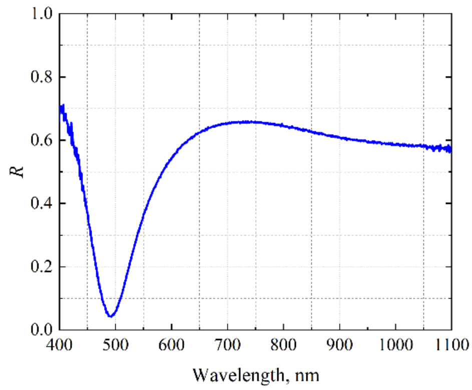

Fig. 2. Experimentally obtained reflection spectrum

In the case of comparing the experimentally obtained spectrum with the previously obtained calculated one, one can see a significant agreement (Fig. 3), which confirms the correctness of the used model for calculating the spectral characteristics of the coating. Visual inspection of the sample also confirms the correspondence of the calculated color characteristics to the color of the experimentally obtained coating (Fig. 4).

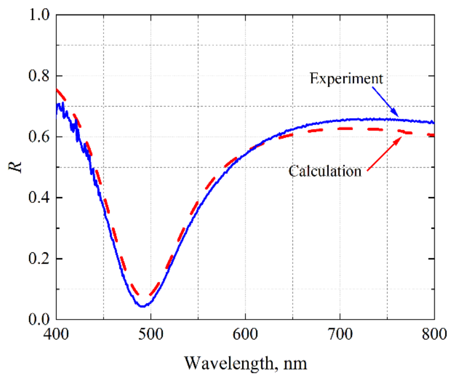

Fig. 3. Comparison of calculated and experimental reflection spectra

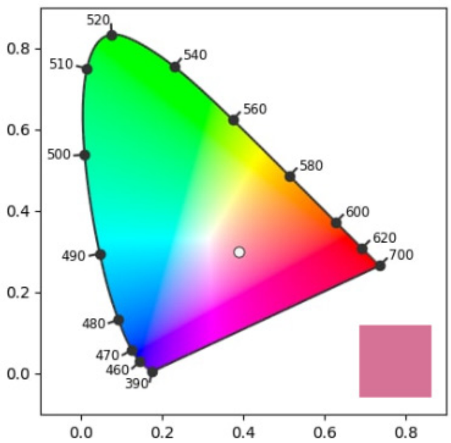

Fig. 4. Calculated color of the coating in normal light incidence

After that a similar coating was deposited on the surface of steel ring (Fig. 5). During the process, part of the sample was masked, which made it possible to obtain a two-color coating on the sample.

Fig. 5. Steel ring after atomic layer deposition

After that, SEM images of two parts of the sample of different colors were obtained (Fig. 6). The surface of the ring, on which the decorative coating was deposited, has a significant roughness obtained during metalworking operation. Although the atomic layer deposition method allows coatings on uneven surfaces, the layer thickness may vary depending on the nature of the roughness. In addition, the resulting color of the coating varies due to the reflection of light at different angles.

a) *b*)

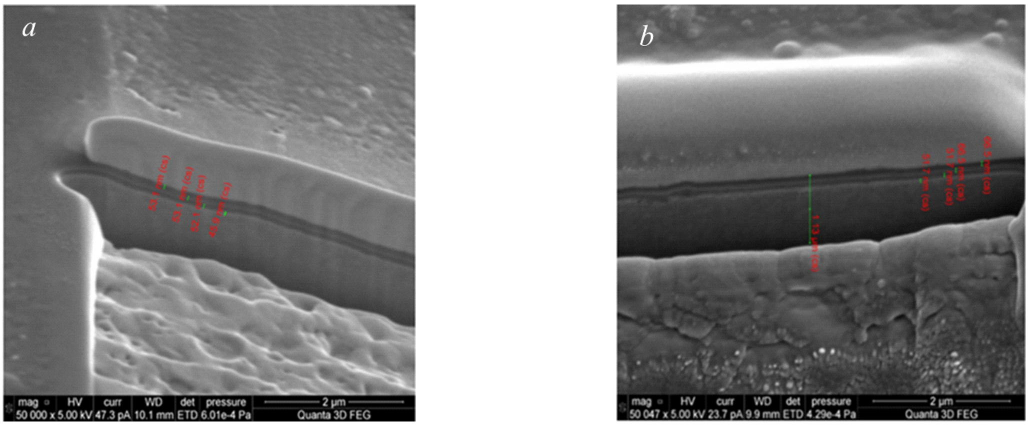

Fig. 6. SEM-image of the blue (*a*) and violet (*b*) parts of sample 1

A steel plate was also coated, which was then sent for a moisture test in a moisture chamber to check their corrosion properties along with a similar uncoated plate. They were exposed to high humidity in the moisture chamber. The test consisted of 9 cycles, each of them was carried out in two stages: 12 hours at a temperature of 55 °C and a humidity of 93 %, then 12 hours at a temperature of 25 °C and a humidity of 95 %.

After the test, no corrosion was found on inspection on the coated sample (Fig. 7, *b*), in contrast to the uncoated sample (Fig. 7,*a*). Tests in a climatic chamber showed that the resulting decorative coating based on aluminum and titanium oxides is corrosion resistant. This makes it possible to further use this type of coating in the field of protection of steel products from corrosion.

a) *b*)

Fig. 7. Photos of uncoated (*a*) and coated (*b*) samples after testing in a climatic chamber

Conclusion

In this work, decorative protective coatings obtained by the ALD method on metal surfaces were developed. It was experimentally established that the developed coatings have protective properties that are not inferior to traditional protective films.

The use of atomic layer deposition to create decorative coatings is just beginning in industry and research. And this work proposes to use interference coatings with a periodic structure to give decorativeness to metal structural elements. The possibility of obtaining uniform coatings with controlled thickness and the developed method for calculating color will expand the possibilities of using color coatings in optical systems and the electronics industry.

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THE AUTHORS

AKSENOVA Valeriya V.
valeriyaakse@gmail.com
ORCID: 0000-0002-9202-6165

KOLOKOLOV Daniil S.
k.d@koltsov-kb.ru
ORCID: 0000-0002-9624-6579

PAVLYUCHENKO Alexey S.
alexey.pavluchenko@gmail.com
ORCID: 0000-0001-5390-276X

MESH Maxim V.
mesh@koltsov-kb.ru

FEDOROV Nikifor A.
nfedorov@niuitmo.ru

KARTSEVA Tatyana Yu.
karceva.t@koltsov-kb.ru

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