OBTAINING ALUMINA COATINGS ON STEEL SUBSTRATES BY ELECTRODEPOSITION AND SOL-GEL METHODS

Izabela RUTKOWSKA, Magdalena GAWĘDA, Elżbieta DŁUGOŃ, Maciej SITARZ

AGH - University of Science and Technology, Cracow, Poland, EU,
rutkowskai95@gmail.com, mgaweda@agh.edu.pl, dlugon@agh.edu.pl, msitarz@agh.edu.pl

Abstract

The main subjects of this presentation are layers made of alumina obtained from organic and aqueous sols deposited on the steel substrates by the sol-gel and electrophoretic deposition (EPD) methods. Aluminum oxide has a very large specific surface area. As a result of the calcination process, in the burned aluminum layer acid-base active centers are created. It determines the use of aluminum oxide as a catalytic material. Due to its properties it is prospective as a carrier of catalysts. In the case of the sol-gel method, the sol was obtained by hydrolysis of the butoxy derivative of aluminum. Obtained sol was applied to the steel substrate by a dip-coating technique. Using the dip-coating technique, due to the ability to easily regulate the speed of immersion and ascent of the substrate from the sol, allows relatively easy control of the thickness of the obtained layers. In the case of EPD method, stable aqueous colloidal suspension of alumina was used. The main advantage of the EPD method is the ability to easily and quickly obtain homogeneous layers on conductive substrates (also on the profiled surfaces). The thickness of the layers can be easily controlled by changing the process conditions. Fresh layers obtained by both methods were heated for densification and better adhesion to the substrate. The structure (MIR) and microstructure (SEM with EDS) tests carried out showed that in both cases there were obtained tight layers of aluminum oxide on steel substrates. In order to determine the nature of the surface, the contact angle and surface free energy tests were also performed. The conducted research allowed to state that the coatings obtained by electrodeposition are characterized by better homogeneity and adhesion to the substrate. They also present a higher thickness than the sol-gel coatings. The contact angle tests show that both coatings are hydrophilic. The obtained layers are extremely promising materials due to their physicochemical and surface properties.

Keywords: Sol-gel, electrophoresis, Al_2O_3, SEM, EDS, MIR

1. INTRODUCTION

In recent years, intensive research related to surface engineering has been observed. One of the main methods of surface modification is coating application. The purpose of these activities is to give materials new features that affect their properties and at the same time the way they are used. There is a wide interest in protective ceramic coatings applied to metallic substrates, which are particularly exposed to corrosion. Due to this, thin layers of alumina applied by the sol-gel method using electrophoresis are increasingly used.

The sol-gel (sol-gel) method is widely used for the synthesis of crystalline and amorphous oxide materials. The method consists in preparing colloidal solutions (sols) as a result of hydrolysis and condensatiaon of used precursors. The advanced condensation process, most often combined with solvent evaporation, leads to gels from which ceramic coatings on substrates can be obtained after thermal treatment [1]. The sol-gel method allows covering thin, even surfaces with thin layers (coatings). The process of applying the coating is not accompanied by electrolysis of water, thanks to which there are no oxygen or hydrogen bubbles on the coating. The applied coatings are characterized by good adhesion to the substrate. Moreover, it is a relatively cheap method, which does not require expensive equipment to conduct synthesis [2,3,4]. There are also disadvantages of using the sol-gel method, which are mainly associated with cracking or delamination of ceramic coatings applied to metals that appear during the drying and thermal treatment of the layers.

Electrophoresis is the movement of electrically charged particles of material dispersed in suspension, which in the applied electric field move to an electrode having the opposite sign and under appropriate conditions deposit on its surface. The process of applying ceramic coatings depends on: the time of the electrophoresis process, the intensity of the current flowing, the grain size and the pH of the electrophoretic slurry. The electrophoretic method of applying the coatings gives the possibility of obtaining homogeneous layers on contoured surfaces in a relatively short time [5]. Due to the good adhesion, cohesive properties, consistency of the obtained coatings and their mechanical properties, the method is increasingly used to obtain anti-corrosion coatings from various types of sols [6].

This paper compares the efficiency of obtaining aluminum layers, on a metal substrate, using a dip-coating method (sol-gel) and electrophoretic deposition. The surfaces of the samples made of chromium-nickel steel were compared, to which coatings from aluminum sols were applied using the aforementioned methods.

2. MATERIALS AND METHODS

Two types of soles were used in the work. An organic aluminum sol was used to carry out the process of applying the sol-gel coatings. Following reagents has been used fror the preparation: Al aluminum butoxide $(OC_4H_9)_3$ - 97%, C_5H_9OH acetyl acetone - 97%, Butanol-2 C_4H_9OH - 99%, Hydrochloric acid HCl - 36%. A mixture of butanol-2 and a butoxy aluminum derivative was formed. Acetyl acetone and concentrated hydrochloric acid were then added dropwise, thoroughly stirring using an ultrasonic stirrer for 30 minutes. After this time, a clear milky-white sol was obtained. The obtained sol was poured into a plastic, sealed container and stored at a reduced temperature.

For the electrophoresis process, the aluminum hydroxide sol was obtained as a result of the aluminum chloride hydrolysis [7]. It is a water sol, prepared according to the recipe contained in unpublished data M. Bursy. It contains pseudobemite particles with a diameter of a dozen or so Å, which as a result of thermal treatment processes, pass into a ceramic coating at a temperature of about 500°C in the Al_2O_3 gamma. The prepared sol has the following parameters: pH 4.45 and a conductivity K = 2.56 mS. The electrophoresis process was carried out as a cataphoresis - the coated surface was a negative electrode.

Samples in the form of metal sheets measuring 1.5cm x 2.5cm, made of chromium-nickel steel, were mechanically cleaned with sandpaper. Then chemical cleaning was carried out by: - Ultrasonic degreasing: The plates were placed in a beaker filled with acetone and placed in an ultrasonic bath for 15 minutes. - Digestion: The plates were digested by immersing them in a 5% HF solution for 30 seconds. - Affixing: Each plate was individually immersed in royal water for 30 seconds. After each of the above-mentioned activities, the plates were rinsed thoroughly with distilled water and dried.

Aluminum coatings were applied on such prepared substrates using dip-coating technique (sol-gel) and electrophoresis to the plates by a special apparatus located in the Coating Lablatory, the Department of Silice Chemistry and High-Molecular Compounds, the Faculty of Materials Science and Ceramics (WIMiC), AGH University of Science and Technology. For the first batch of samples, the sol was applied with a dip-coating technique at a constant speed of 20 cm/min.

The electrophoresis was carried out in a rectangular glass organic dish, 6x4x7cm. Coatings were applied on both sides of the plaques. The process used was an aluminum hydroxide (aqueous) sol with an acid reaction. The coated plate was a negative electrode. The positive electrode was a plate of the same dimensions, made of 1H18N10 stainless steel. The voltage source was a power supply, with the possibility of regulating the output voltage. The process of applying electrophoresis coatings was carried out on three samples. Parameters of the electrophoresis process: - time of applying the coating - 10 seconds, - voltage - 10 V, - current intensity - 3.96 mA.

In order to cure the obtained layers deposited using the electrophoresis process and the sol-gel method and to conduct coating tests, the samples were subjected to a drying process and then placed in an electric furnace and fired at 600°C with the rate 10□C/min for 30 minutes.

The microstructure analysis of the obtained layers was carried out using the NOVA NANO SEM 200 scanning electron microscope combined with the EDS X-ray dispersion microanalysis microanalyzer. Structural investigations of the aluminum precursor and precursor after firing at 600oC for 30 minutes were also carried out. The tests were carried out using infrared absorption spectroscopy on a VERTEX 70v spectrometer. The wetting angle test for calcined aluminum coatings was carried out using a sitting drop technique. A goniometer from the Krüss DSA25E brand was used for the tests.

3. RESULTS and DISCUSSION

3.1. Microscopic SEM examination with X-ray microanalysis

3.1.1. Examination of the morphology and chemical composition of the coatings applied by dip-coating technique (sol-gel)

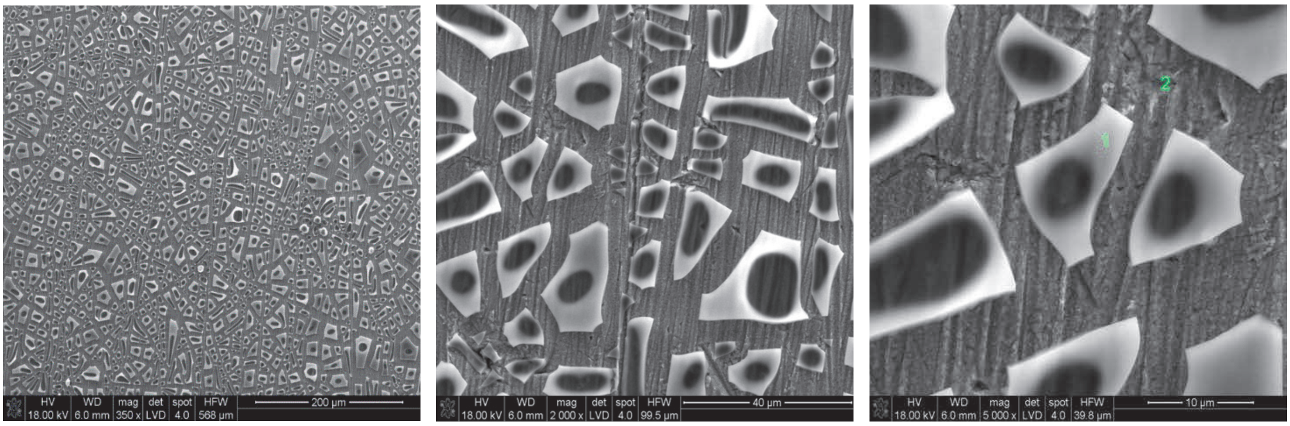

Figure 1 SEM photo of chrome-nickel steel covered with organic sol (dip-coating) at 350x, 2000x, 5000x magnification

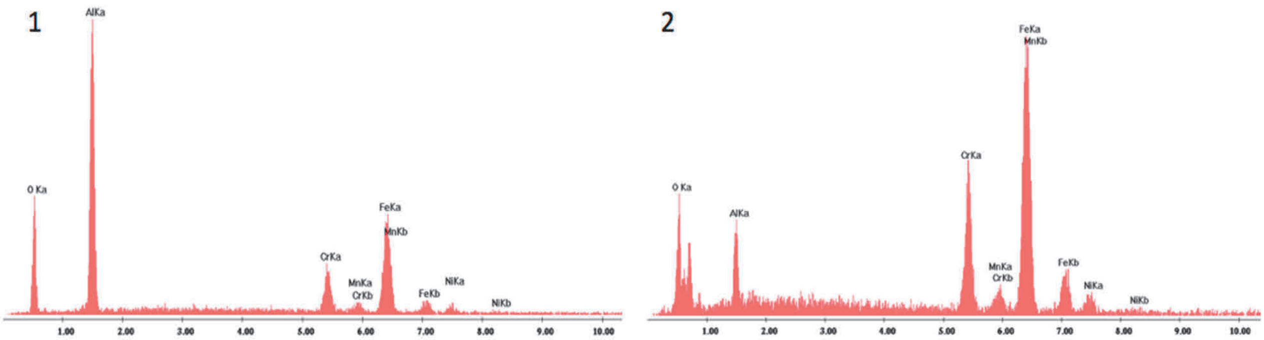

Figure 2 Point microanalysis of EDS, points marked at Figure1C

Figure 1 show the obtained SEM photos of stainless steel coated with an organic aluminum sol using dip-coating technique, successively made at the following magnifications: 350x, 2000x and 5000x. A homogeneous network of cracks is visible. There are gaps between individual fragments of the obtained coating. The resulting cracks are most likely a consequence of the thermal treatment of the coating. Despite the presence of airtightness, the coating maintains continuity and is good adhesion to the substrate. This conclusion can be formulated by analyzing the results of EDS tests (**Figures 2**:1,2).

A two-point X-ray analysis carried out at points located in two different places in visible areas with different morphology (**Figure 1C**) allows to state that the layer of aluminum oxide is present on the whole surface of the sample under test.

The analysis made in point 1 showed an intense line from Al. However, in point 2 the strongest line comes from Fe and Mn. A line with a lower intensity coming from aluminum is also visible. There were also small lines showing the presence of elements originating from the substrate: Ni and Cr. Thus, the aluminum concentration is much lower at point 2 than at 1. This shows the continuity of the coating but its different thickness at the points tested. Undoubtedly, it can have a negative impact on the protective properties of the obtained coating.

3.1.2. Examination of morphology and chemical composition of coatings applied by EPD method

Figure 3 shows pictures of samples with coatings applied by means of an electrophoresis process, made with scanning electron microscope at the following magnification: 350x, 2000x, 5000x. It is easy to notice that the obtained coating is homogeneous, compact, does not leave the substrate. No cracks have been observed, thus the coating is very tight.

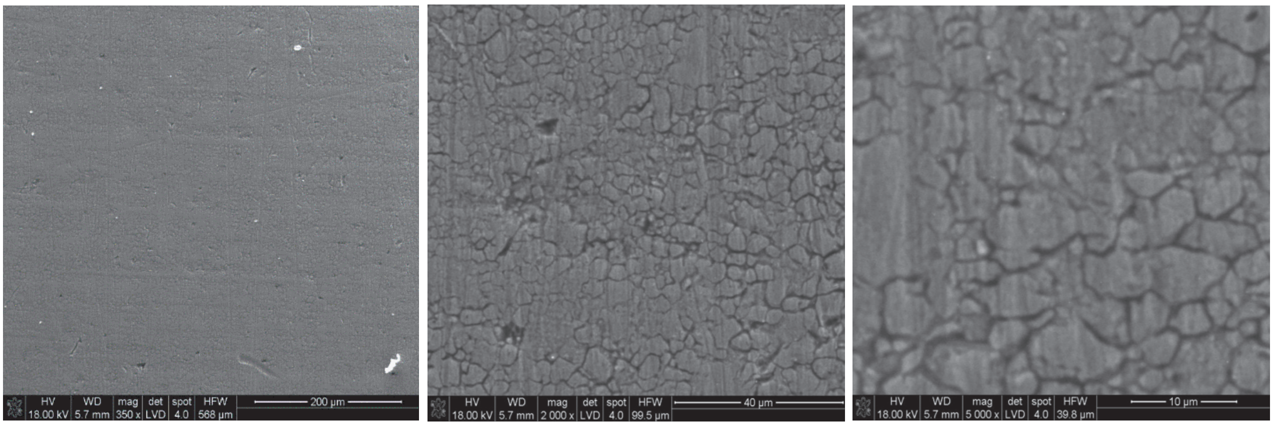

Figure 3 SEM photo of chrome-nickel steel covered by using electrophoretic deposition at 350x, 5000x, 2000x magnification

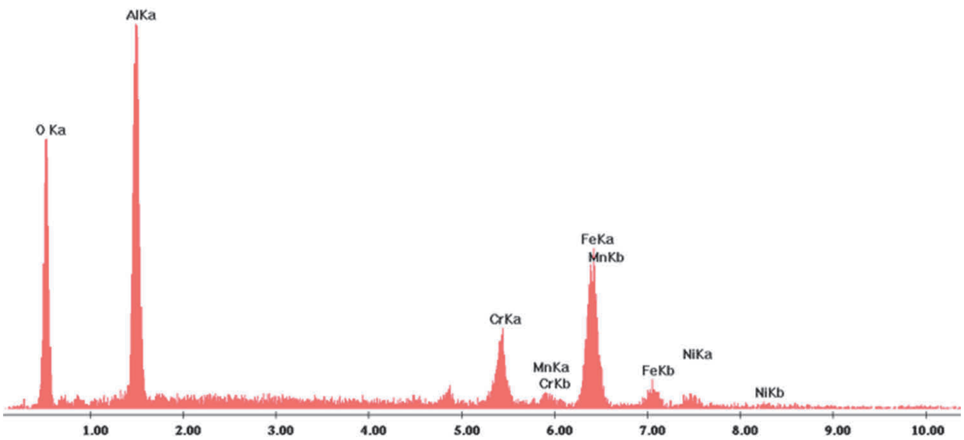

Figure 4 Average microanalysis of EDS

The EDS microanalysis (**Figure 4**) did not show different concentrations of ingredients at individual points. The obtained spectrum shows lines from aluminum and iron. Thus, it can be concluded that the obtained coating has a similar thickness on the whole surface.

3.2. Infrared absorption spectroscopy

Figure 5 shows spectra in the mid-infrared range (MIR) of the aluminum precursor sample (precursor) and the precursor burn-out at 600°C (after heating). For both obtained spectra, one can distinguish characteristic bands coming from stretching vibrations O-H around 3400-3600 cm^{-1} and bands originating from bending vibrations H-O-H at about 1600 cm^{-1}. These bands are characteristic of water molecules.

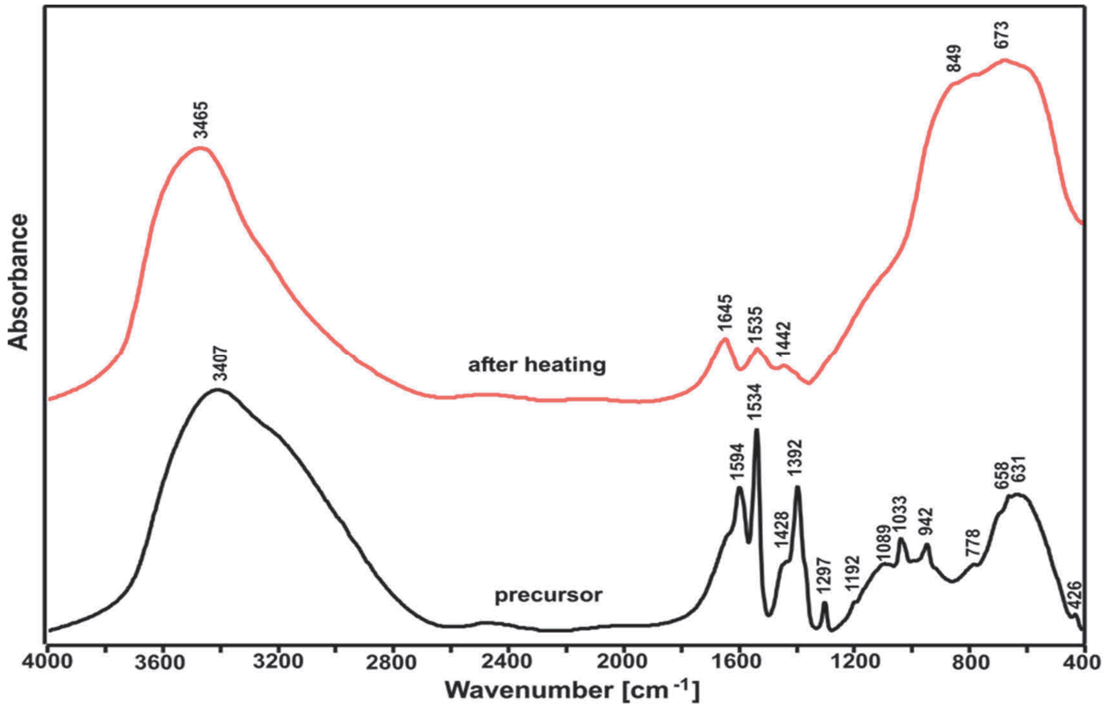

Figure 5 Infrared spectra of an aluminium coating after heating in 600°C and a precursor

In the range of 500-765 cm^{-1} there are bands characteristic for stretching vibrations of Al-O bonds for aluminum in octahedral coordination, while in the range of 765-910 cm^{-1} there are bands corresponding to vibrations of aluminum-oxygen connections for Al^{3+} in tetrahedral configuration.

It was observed that for the fired precursor the intensity of bands characteristic for vibrations stretching Al-O joints for aluminum in tetrahedral coordination is much higher. This is related to polymorphic transition of alumina with increasing temperature. The much wider half-width of the bands on the precursor spectrum after firing is also characteristic, which indicates the increasing amorphousness.

3.3. The contact angle test of a coatings applied by dip coating technique (sol-gel) and electrophoretic deposition

The obtained value of the contact angle is less than 90 ° (**Figure 6**). The tested coating thus has hydrophilic properties, i.e. it has a good surface wettability. The obtained value of the contact angle is much smaller than 90°. The tested coating thus has hydrophilic properties, i.e. it has a very good wettability of the surface.

Differences in the wettability of the obtained coatings should be related to their different morphology determined on the basis of microscopic examination (SEM).

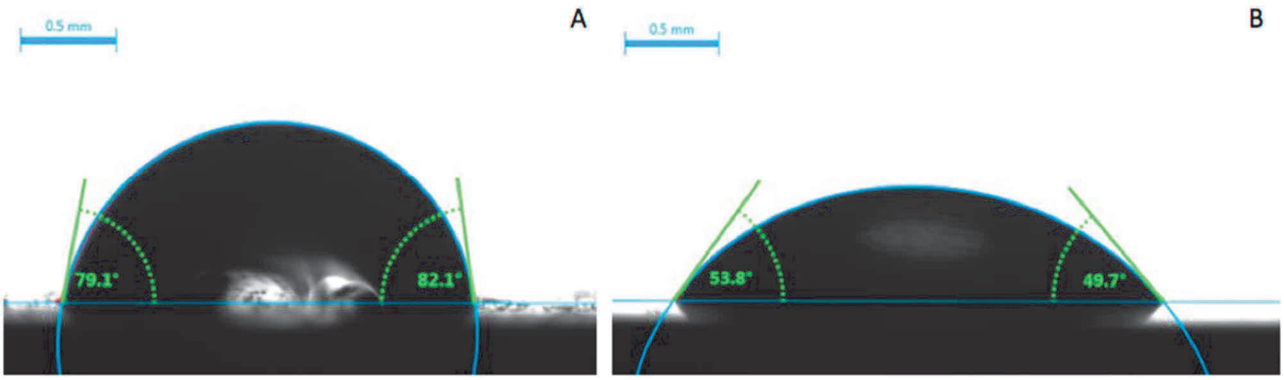

Figure 6 Contact angle test,: A. Layer applied using sol-gel method, B. Layer applied using EPD method

4. CONCLUSION

1) The obtained coatings applied by dip-coating technique (sol-gel) and by electrophoresis after heat treatment show very good cohesion and adhesion to the selected metal sheet.
2) Coatings applied by means of electrophoresis have a dense packing of very fine grains, they conceal the metal surface well and are well connected to the substrate. After the EDS analysis, it was found that the obtained coating has practically the same thickness on the surface covered.
3) Coatings obtained using dip-coating technique (sol-gel) are characterized by different thickness of the layer, which may have a negative effect on the protective properties due to the peeling of the coating or the appearance of cracks in places of thinner layer thickness during material exploitation
4) The results of spectroscopic studies in the mid-infrared range showed the presence of bands derived from Al-O bonds for aluminum in octahedral and tetrahedral configuration.
5) For the spent precursor, the intensity of the bands characteristic of the stretching vibrations of the Al-O joints for tetrahedral aluminum is much higher, which is related to the polymorphic transition of alumina with the increasing temperature.
6) The contact angle tests of the obtained coatings applied with both methods allowed to state that the surfaces are hydrophilic in nature. Moreover, the method of obtaining the coating for its wettability has been significantly influenced

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