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Comparative study via nanoindentation of the mechanical properties of conversion corrosion protective layers on aluminum formed in Cr^{6+}-containing and Cr^{6+}-free solutions

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Abstract: The application of chemical conversion coatings (such as chromate, oxide, phosphate, etc.) on various metals and alloys is widely used technology that provides adequate corrosion protection and improves paint adhesion. Most common conversion protective layers are produced by chromating processes using hexavalent chromium containing electrolytes. Although the chromating process has many technological and economic benefits, due to the high toxicity and carcinogenic nature of the used hexavalent chromium the use of chromate conversion coatings is now restricted and it is necessary to find alternative coating materials with relevant properties.

The main purpose of this study is to compare the mechanical properties of traditional chromate conversion coatings with a suggested as their alternative chromate-free cerium-containing conversion coating. For this purpose two chromate-containing and one chromate-free coatings with different thicknesses were deposited on the same Al substrate. As a result of the nanoindentation tests the indentation hardness and modulus of the studied "film-substrate" systems were determined and their relevance to the mechanical properties of the coatings is discussed.

Keywords: conversion protective layers; nanoindentation; indentation hardness; indentation modulus

1. INTRODUCTION

It is known that the native oxide layer (with a thickness of only a few nanometers), formed on aluminum and its alloys provides a certain level of corrosion protection in neutral pH environment. Under aggressive conditions, such as acidic and alkaline environment however, this protection is insufficient which requires the formation of a much thicker surface oxide layer on the order of a few microns (in case of heavy exploitation conditions, including sea conditions – up to ~200 μm). Such layers could be obtained by anodic electrochemical treatment ("anodizing"), using relatively complex, expensive and energy consuming technologies. An alternative of this process are the chemical methods of applying protective and protective-decorative layers on aluminum and its alloys. The main advantages of such chemically "conversion" coatings are the fairly simple equipment design, practically negligible energy costs and significantly reduced complexity and labor intensity of the entire process. This type of coatings, obtained on aluminum and its alloys, are preferably used as an intermediate layer before applying the paint and other functional organic coatings, as their porous structure determines the required adhesion. The application of such protective system (Al/oxide layer/functional organic layer) fulfills one of the main requirements for protecting aluminum and its alloys – to suppress, as much as possible, the electrochemical activity of the highly electronegative basic metal.

The chemically deposited layer serves as an intermediate buffer layer which determines the bond strength between the organic coating and the aluminum substrate. Therefore, when thermal and mechanical stresses are applied to the system Al/functional layers, the mechanical properties of the chemically deposited intermediate oxide layer determines the bond strength between the top organic coating and the aluminum substrate.

Among the most commonly used conversion layers with proven properties are those obtained from hexavalent chromium-based electrolytes [1]. Due to their carcinogenic and toxic nature however [2], their usage has been forbidden by the European regulations [3]. During the past few years, extensive research to develop new, environmentally- and health-friendly compounds and technologies for deposition of functional oxide layers on Al and its alloys has been conducted.

The purpose of this study is to determine and compare mechanical properties of chemically deposited oxide layers on aluminum, considering

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the layer composition and processes technology. Three different coatings and technologies were used:

- "Alodine 1200" electrolyte and technology by the German brand Henkel (widely used current trade product);
- classical chromate electrolyte and technology (adopted as reference case) and
- thin cerium oxide layer free of toxic Cr^{6+} ions and simple electrochemical technology allowing cathodic deposition of these coatings that we developed (environment-friendly composition and technology).

2. THEORY OF NANOINDENTATION - BRIEF INTRODUCTION

Nanoindentation, also known as "depth sensing indentation" and "instrumented indentation" is a kind of mechanical test, which allows simultaneous registration of the applied load and indenter penetration depth. This method allows testing of small volumes, surface layers and very thin coatings against their mechanical response to the indenter penetration. As a result, an indentation curve that represents the relation between the applied load and the indenter penetration depth is obtained. Using analytical relationships and approximations, it is possible to derive mechanical characteristics such as indentation hardness (H_{IT}) and indentation modulus (E_{IT}) of the tested material from this curve.

The modern nanoindentation instruments allow registering of very small loads and displacements with very high accuracy and precision. Figure 1 schematically presents the nanoindentation experiment as well as depicts the main parameters, derived from the "load-displacement" curve.

There are three main parameters that can be derived from the curve shown in Figure 1: 1) maximal load P_{max}; 2) maximal displacement (penetration depth) h_{max} and 3) the elastic stiffness at unloading [5]. The elastic stiffness, or contact stiffness is determined as the slope of the tangent at the upper part of the unload curve during the initial stage of unloading and is equal to $S = dP/dh$. The first portion of the unloading curve can be described by a simple power law relationship $P=K(h-h_f)^m$, with K and m being fitting parameters [6]. The deformation during unloading is assumed to be linear elastic and the indentation modulus of the tested material can be described by the contact theory of elasticity [6]. Following the Oliver and Pharr's theory [6], the contact compliance in case of axisymmetric indenter penetrating elastic isotropic half-space is described via the equations:

$$C_s = \frac{1}{S} = \frac{dh}{dP} = \frac{\sqrt{\pi}}{2} \cdot \frac{1}{\sqrt{A}} \cdot \frac{1}{E_r}, \quad (1)$$

$$\frac{1}{E_r} = \frac{\left(1-\nu_s^2\right)}{E_{IT}} + \frac{\left(1-\nu_i^2\right)}{E_i}, \quad (2)$$

where A is the projected contact surface area, C_s is the ductility of the specimen and P – the applied force. In these formulas E_r is the elastic reduced modulus explaining the elastic deformation of both the indenter and the specimen. E_{IT}, E_i; ν_s and ν_i are the modules of elasticity and the Poisson ratios of the specimen and the indenter, respectively. The following relation is used to determine the reduced modulus employing the information provided by the measured load-displacement curve $P(h)$:

$$E_r = \left.\frac{dP}{dh}\right|_{h=h_{max}} \frac{\sqrt{\pi}}{2\beta\sqrt{A(h_c)}}, \quad (3)$$

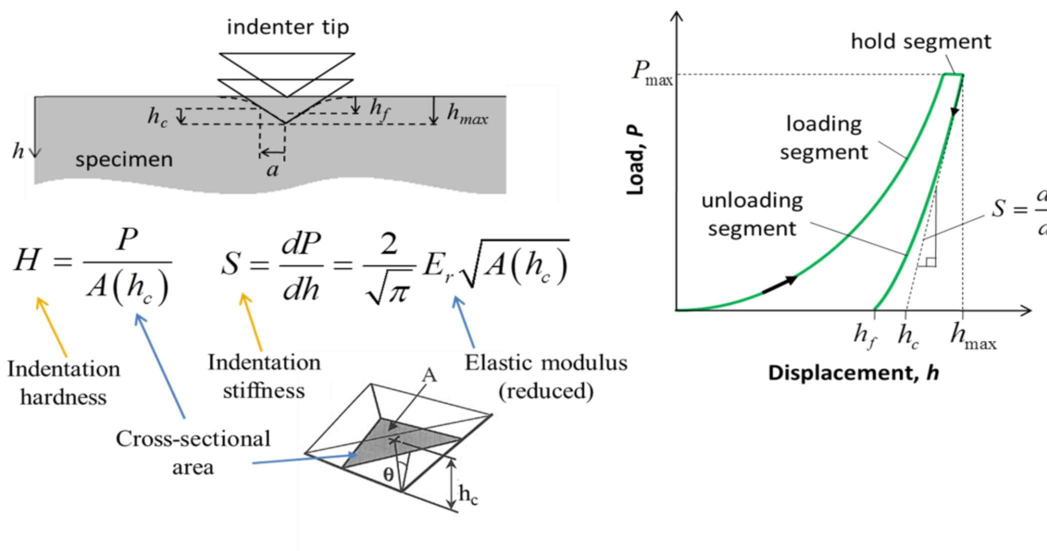


Figure 1. Scheme of the nanoindentation experiment, "load-displacement" curve and main analytical relationships [4].

For Berkovich indenter tips the coefficient $\beta = 1.034$. The projected area of the contact between the indenter and the specimen as a function of the contact depth h_c is introduced by the following approximation [6]:

$$A(h_c) \approx \approx C_0 h_c^2 + C_1 h_c + C_2 h_c^{1/2} + C_3 h_c^{1/4} + C_4 h_c^{1/8} + C_5 h_c^{1/16} \quad (4)$$

The coefficients in equation (4) are determined by a calibration procedure that consists of a nanoindentation experiment on standardized quartz sample (fused silica) with known elastic modulus and hardness, independent of the indentation depth. Finally, the indentation modulus and hardness are calculated using the following equations [6]:

$$H_{IT} = \frac{P_{\max}}{A(h_c)}, S = Km(h_{\max} - h_f)^{m-1} \quad (5)$$

$$E_{IT} = (1-\nu_s^2)\left[\frac{2\beta}{S}\sqrt{\frac{A(h_c)}{\pi}} - \frac{1-\nu_i^2}{E_i}\right]^{-1}. \quad (6)$$

3. EXPERIMENTAL

A series of nanoindentation tests on samples coated by three different conversion protective layers were performed. The purpose was to determine the basic mechanical characteristics of the thin layers – indentation hardness and indentation modulus – in order to compare chemical compounds and used technologies. The device used for the purpose is Nano Indenter Agilent G200 (Keysight Technologies) with a standard XP indenter head, which provide depth accuracy of <0.01nm and applied load accuracy of 50 nN. The tip of the head is sharp tree-sided Berkovich pyramid. The performed calibration of the indenter tip according to equation (4) gave C_0=24.5, C_1=191.949, C_2=9.1145, C_3=2.9682, C_4=1.9721, C_5=1.6836.

The three thin coatings that are studied obey different thickness and chemical composition – the details are given in Table 1. The samples were prepared in the following way. First, specimens with dimensions 2x1x0.1cm, were cut from sheets of the conventional structure material – “technically pure aluminum AD-3”. The specimens were decreased in advance in organic solvent, etched after that for 1 minute in aqueous solution of NaOH (60g/L), then heated to 60^{o}C and “enlightened” and finally put in aqueous solution of HNO_3 (50%). After they were washed with distilled water they were processed in the solutions and under the conditions given in Table 1. On the surface of the sample piece with Cr^{6+}-free coating it was observed a spot and in order to have representative data we performed indentation test in the spot area (Spot) and outside it (No Spot). It is expected to have difference in the quality and properties of the film in the colored (Spot) area. More detailed information about preparation conditions, structure and anti-corrosion behavior of these systems is given in [8].

We used two methods for indentation testing and these methods were applied to each of the three coating-substrate systems.

XP\G-Series Basic Hardness, Modulus at a Depth: allows indentation test program consisting in one single load – unloading cycle under displacement control. The indenter tip approaches the sample surface starting from prescribed *Surface Approach Distance* with a velocity defined as *Surface Approach Velocity*. After the indenter tip touches the sample surface, according to the criterion given by the *Surface Approach Sensitivity*, it starts to penetrate the material following a loading program with a *Strain Rate Target* until *Depth Limit* is reached. The *Depth Limit* defines the maximum applied load for the particular test and this load is kept constant for defined by the user *Peak Hold Time*. When the *Peak Hold Time* is exceeded the unloading starts up to a prescribed percentage (*Percent to Unload*) from the maximum achieved load followed by *Drift Test Segment* before the indenter to be completely withdrawn.

Table 1. Characteristics of the coatings and their processing parameters.

No.	Electrolytes	Concentration	Time of formation, min	T,^{o}C	Colour	Thickness, µm
1	Al in air media	-	> 1	Room temperature	Colourless	$3x10^{-3}$ [7]
2	Alodine 1200	9 ml/l A 8 g/l B	1	25	Light yellow	1.1
3	CrO_3 $(NH_4)HF_2$ $K_3[Fe(CN)_6]$	8 g/l 2 g/l 1.5 g/l	1,5	25	Golden brown	1
4	$CeCl_3.7H_2O$ $CuCl_2$ C_2H_5OH	66 g/l $1x10^{-3}$ g/l dissolving agent	60 (CD=1mA/cm^2)	12	Pale yellow	0.78

XP\G-Series Basic Hardness, Modulus, Tip Cal, Load Control. This method allows within one indentation test to perform loading-unloading cycles up to prescribed maximum load and number of cycles. The indenter approaches the sample surface with *Surface Approach Velocity* starting from the predefined *Surface Approach Distance*. The cyclic load algorithm starts when the criterion *Surface Approach Sensitivity* is satisfied. The maximum load for the i-th cycle of the loading program is defined as:

(*Maximum Load/Time to Load*)*(2^*i* /2^*Number of Times to Load*)

The loading stage of each cycle ends when *Load on Sample* reaches the values *Maximum Load* *(2^*i* /2^*Number of Times to Load*). At the maximum load for each of the cycles the *Load on Sample* is kept constant for time equal to the *Peak Hold Time*. After that the indenter is withdrawn with a rate defined as *Load Rate Multiple for Unload*Loading Rate*, until *Load on Sample* reaches *Percent to Unload*Load Limit*. This process of loading and unloading is repeated until reaching the specified number of cycles (*Number of Times to Load*).

Besides the mechanical characteristics of the coatings, the characteristics of the substrate are determined too. A single method was used for conducting the experiment following the program with 10 cycles to maximum indenter load (method - XP\G-Series Basic Hardness, Modulus, Tip Cal, Load Control).

3.1. Indentation testing program A

The method applied in testing program A is XP\G-Series Basic Hardness, Modulus at a Depth. Each testing procedure consists of 25 indentation tests per sample with 70 µm distance between the centres of the imprints and prescribed maximum penetration depth approximately quarter of the film thickness – 250 nm for Alodine 1200 and Cr^{6+}-containing film and for 200 nm for the Ce-containing film (the chosen indentation depths are ~25% of films thicknesses). The peak hold time at maximum reached load is 20 s.

3.2. Indentation testing program B

The testing program B employs the method XP\G-Series Basic Hardness, Modulus, Tip Cal, Load Control with 4 loading cycles with maximal loading of 0.95 mN providing this way experimental data at indentation depth close to that prescribed in testing program A. The distance between imprints is 50 µm and the total number of indentations is 25. The aim of this type of nanoindentation testing program is to investigate the influence of the cyclic loading on the results when penetrating the coatings under low force.

3.3. Indentation testing program C

The testing program C employs the same method as B testing program with prescribed parameters for the method given in Table 3. The distance between the centers of the imprints is again 150 µm and the number of the indentation tests per sample is kept 25 for checking the repeatability.

Figure 2 presents the comparison between the results obtained within A and B testing programs. We compare the results when cyclic and no-cyclic load is applied to the specimens. The maximum indentation depth - h_{max} for each specimen in both cases (A and B programs) is ~25% of film thickness. Figure 3 presents the results from Indentation testing program C.

Table 2. Input parameters for indentation testing program B

Input parameters for indentation testing program B	Units	Value
Percent to Unload	%	90
Surface Approach Velocity	nm/s	10
Maximum Load	gf	0.095
Number of Times to Load	integer	4
Peak Hold Time	s	20
Surface Approach Distance	nm	5000
Poisson's Ratio	[-]	0.3

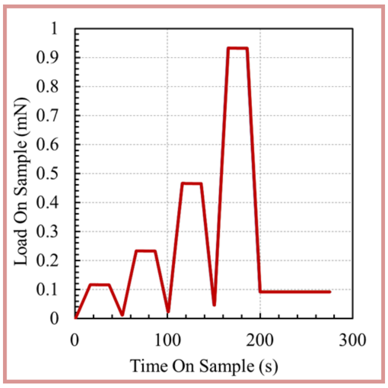
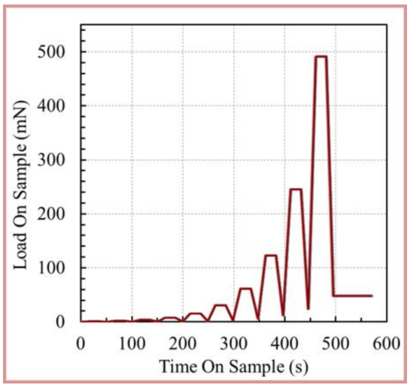
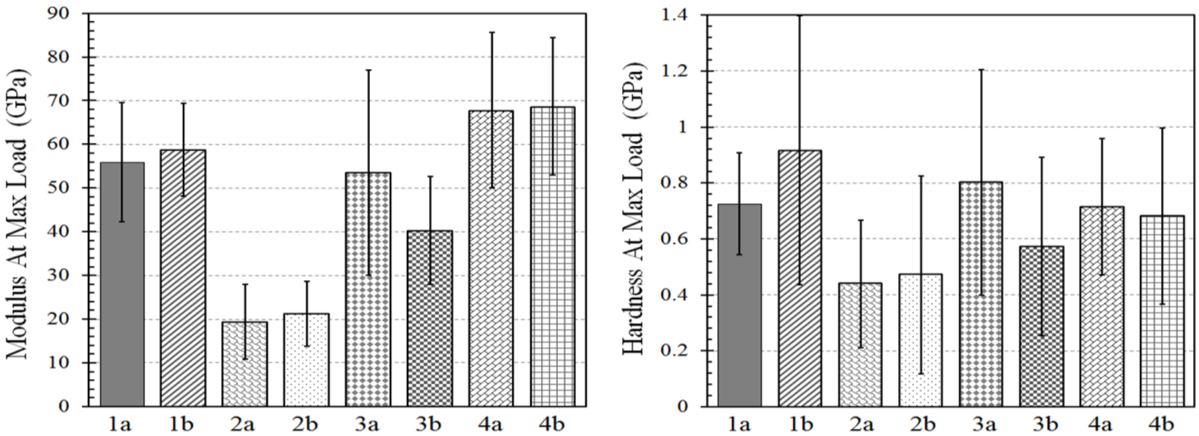


Table 3. Input parameters for indentation testing program C.

Input parameters for indentation testing program C	units	values
Percent to Unload	%	90
Surface Approach Velocity	nm/s	10
Maximum Load	gf	50
Number of Times to Load	integer	10
Peak Hold Time	s	20
Surface Approach Distance	nm	5000
Poisson's Ratio	[-]	0.3





Sample		Modulus at Max Load GPa	Hardness at Max Load GPa	Disp at Max Load nm	Max Load mN
1a	Alodine1200 (Cr^{6+}-containing) / AD-3 h_{max} 250 nm	55.888	0.725	259.7	1.136
1b	Alodine1200 (Cr^{6+}-containing) / AD-3 4 cycles up to 0.095gf (0.95 mN)	58.717	0.917	220.6	0.918
2a	Cr^{6+}-containing film / AD-3 h_{max} 250 nm	19.419	0.44	267.4	0.687
2b	Cr^{6+}-containing film / AD-3 4 cycles up to 0.095gf (0.95 mN)	21.228	0.472	347.4	0.913
3a	(Cr^{6+}-free) Ce-film NoSpot / AD-3 h_{max} 200 nm	53.542	0.802	214.1	0.826
3b	(Cr^{6+}-free) Ce-film NoSpot / AD-3 4 cycles up to 0.095gf (0.95 mN)	40.261	0.573	288.8	0.915
4a	(Cr^{6+}-free) Ce-film Spot / AD-3 h_{max} 200 nm	67.815	0.714	211.1	0.755
4b	(Cr^{6+}-free) Ce-film Spot / AD-3 4 cycles up to 0.095gf (0.95 mN)	68.643	0.682	256.9	0.915

Figure 2. Indentation modulus and hardness at max load for all samples – test programs A and B

Table 4 presents the comparison between the determined indentation hardness and modulus for all samples and for the substrate at maximum load 500 mN (results obtained from experimental program C).

4. DISCUSSION

The main feature of the obtained data is that at small displacements of the indenter (up to about 25% of the thickness of the tested coatings), there is relatively large scatter of the experimental data. This can be seen in Figure 2 where the error bars are given. The main reasons for this scatter in the mechanical characteristics are most probably related to:

- non-uniform or non-homogeneous coating;
- severe roughness of the substrate surface, which determines severe roughness of the coatings as well;
- difference in the particular thickness of the tested coatings or/and varied coating thickness along the particular sample piece.

Increasing the depth of the penetration, when the indenter reaches the substrate and penetrates it,

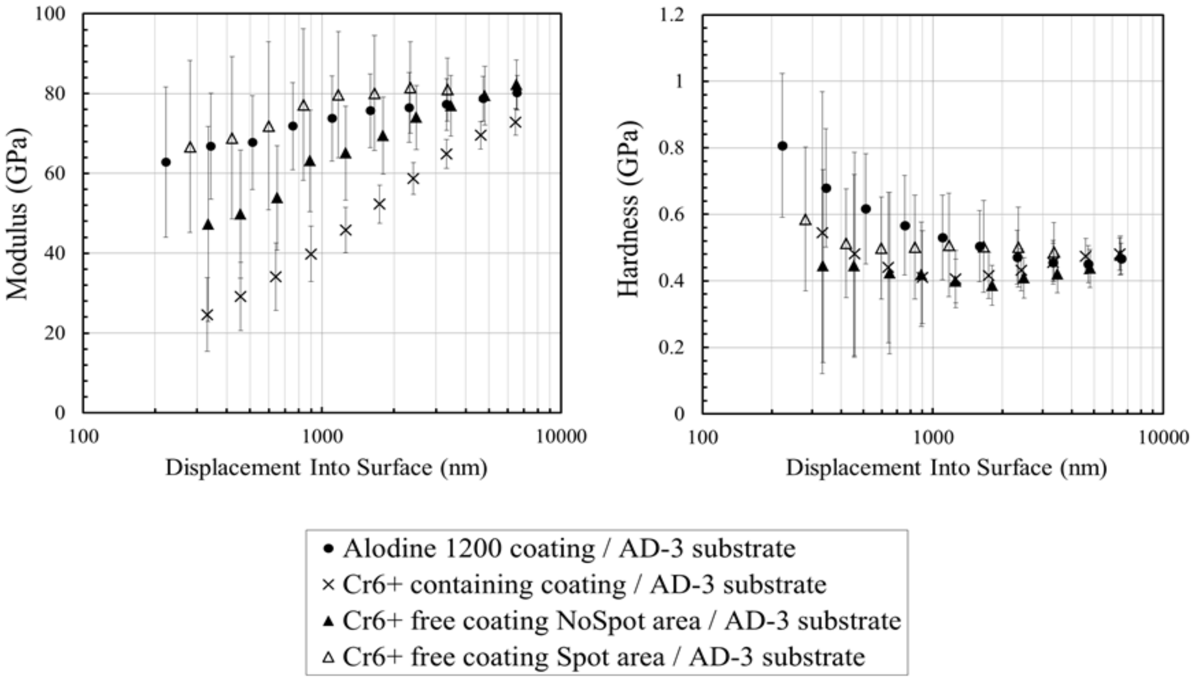


Figure 3. Indentation modulus and hardness for all samples – test program C.

Table 4. Indentation hardness and modulus for all samples and the substrate at maximum indentation load 500 mN (data obtained from indentation testing program C).

Sample	Modulus at Max Load, GPa	Hardness at Max Load, GPa	Displacement at Max Load, nm	Max Load, mN
Alodine 1200 (Cr^{6+}-containing) /AD-3 10 cycles up to 50 gf (500 mN)	80.211	0.467	6642.3	483.578
Cr^{6+}-containing film / AD-3 10 cycles up to 50 gf (500 mN)	72.901	0.481	6557.2	483.266
(Cr^{6+}-free) Ce-film NoSpot / AD-3 10 cycles up to 50 gf (500 mN)	82.288	0.477	6589.2	484.937
(Cr^{6+}-free) Ce-film Spot / AD-3 10 cycles up to 50 gf (500 mN)	80.940	0.488	6512.5	484.045
Al: AD-3 10 cycles up to 50 gf (500 mN)	85.722	0.481	6543.3	483.384

the scatter in the data gradually decreases. In this case, the obtained mechanical characteristics of the system are determined by the characteristics of the aluminum substrate, Figure 3.

5. CONCLUSIONS

In this study the mechanical properties of environment-friendly thin oxide layers of CeO_2 on aluminum substrate are determined via nano-indentation testing. The importance of the obtained results is related to the fact that the CeO_2 coatings may be considered as a long-term alternative to toxic and carcinogenic chromate conversion films, currently used to protect Al and its alloys. The comparison of the mechanical properties of the chromate and the newly proposed chromate free coatings determined by nanoindentation shows that the properties of the cerium oxide layer are not inferior to those of Alodine 1200 and, moreover, are better than the mechanical characteristics of chemically applied classic chromate layers. The next outcome is that the results show that instrumented indentation is a promising experimental technique giving the opportunity to determine mechanical properties of these coatings, which is an important addition to the complete characterization of the chemical and mechanical behavior of metal-functional layer systems.

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СРАВНИТЕЛНО ИЗСЛЕДВАНЕ ЧРЕЗ НАНОИНДЕНТАЦИЯ НА МЕХАНИЧНИТЕ СВОЙСТВА НА КОНВЕРСИОННИ ЗАЩИТНИ СЛОЕВЕ ВЪРХУ АЛУМИНИЙ, ОТЛОЖЕНИ ОТ СЪДЪРЖАЩИ И НЕСЪДЪРЖАЩИ Cr^{6+}РАЗТВОРИ

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(Резюме)

Нанасянето на химични конверсионни покрития (хроматни, оксидни, фосфатни и др.) върху различни метали и сплави е широко използвана технология, осигуряваща корозионна защита и подобряване на адхезията при нанасянето върху тях на лаково-бояджийски и други покрития. Най-често използвани в практиката са Cr^{6+}-съдържащите (т.нар. хроматни) конверсионни покрития, които се характеризират с много добри корозионно-защитни свойства. Въпреки известните технологични и икономически предимства обаче, използването им, към настоящия момент, е прекратено поради тяхната висока токсичност и канцерогенност. Необходимо е да се намерят достатъчно добри алтернативи на тези покрития, чиито свойства в максимална степен да се доближават до тези на хроматните. В настоящото изследване, чрез експеримент на наноиндентация, са определени механичните характеристики на три системи от типа „покритие - подложка". В две от тези системи, върху отделни подложки от технически чист алуминий АД 3 с дебелина 1мм, са нанесени две конверсионни покрития с различни дебелини. В третата система, върху подложка със същите характеристики, е нанесено несъдържащо Cr^{6+} цериевооксидно покритие, което е пример за ново екологично конверсионно покритие. Целта на изследването е да бъдат сравнени механичните характеристики на две различни по състав хроматни покрития с предложеното ново, несъдържащо хром цериевооксидно покритие. В резултат от проведените експерименти са определени и сравнени две от основните механични характеристики на разглежданите системи – твърдост при индентация (H_{IT}) и индентационният модул (E_{IT}).