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Nanoindentation investigations of electrodeposited on steel substrate corrosion-protective zinc coating, additionally improved by Cr III conversion layer

S. Cherneva, D. Guergova, N. Boshkova, R. Iankov, D. Stoychev

***Abstract*— The protective Zn coatings on steel substrates are preferable because the zinc layers play a role of "sacrificial coatings" due to their more negative electrode potential compared to steel substrate. Besides, their protective ability strongly depends from aggressive nature of environment, which determines the need of additional efforts. Vastly improvement of the chemical stability and protective ability of the Zn coatings give the additional treatments aiming the formation of "finishing" conversion layer with desired chemical-resistant composition on the Zn surface influencing against corrosion attack. Having in mind the chemical nature of the conversion layers, it is possible to predict the improvement of the chemical and mechanical properties of the system "Conversion layer"/"Zinc coating"/"Steel substrate". The present study shows the results obtained concerning the indentation modulus and indentation hardness of the Cr III conversion layers and their dependence in the depth of indentation for the studied systems. The thickness of the steel substrate, protective Zn coating and finishing conversion layer are 820, 5 and 0,15 µm, respectively. It was established that the system "Conversion layer"/"Zinc coating"/"Steel substrate" is characterized with higher indentation hardness and modulus than the system "Zinc coating"/"Steel substrate", which improves their wear resistance and corrosion protection.**

***Keywords*—nanoindentation, mechanical properties, corrosion-protective zinc coatings, conversion layers**

I. Introduction

The electrodeposited zinc coatings find significant application for corrosion protection of low carbon steels. The protective zinc coatings are characterized with good corrosion-protective ability especially in the pH of the corrosion atmosphere in the range of 7 – 12. The protective Zn coatings on these steel substrates are preferable because the zinc layers play a role of "sacrificial coatings" due to their more negative electrode potential compared to low carbon steels.

Sabina Cherneva, Roumen Iankov
Institute of Mechanics, Bulgarian Academy of Sciences
Bulgaria

D. Guergova, N. Boshkova , D. Stoychev
Institute of Physical Chemistry, Bulgarian Academy of Sciences
Bulgaria

In the last decade there are series of investigations aimed to improve the protective properties of Zn coatings [1-8]. Simultaneously, it is known that vastly improvement of the chemical stability and protective ability of the zinc coating gives the additional treatment aiming the formation of conversion layer on the it surface. As a rule additionally formed conversion layers are consisting corrosion resistant chemical compositions influencing against corrosion attacks [9-12]. The overview of the specialized literature showed that while the investigations connected with the development of new electrolytes and regimes for deposition of zinc coatings (including the formation of additional conversion layers) with improved protective ability (the number on this matter papers, respectively) strongly increased, the investigations connected with definition of their mechanical properties are practically absent [13-18]. In this aspect, from adhesion, wear-resistant and corrosion-protective point of view, for these practically bi-layer ("Conversion layer"/"Zinc coating"/"Steel substrate") systems the data for their indentation modulus and indentation hardness are exceptionally important. The characterization of these parameters is important for the deposited separate layers ("Conversion layer"/"Zinc coating" and "Zinc coating"/"Steel substrate"), as well as for the whole system ("Conversion layer"/"Zinc coating"/"Steel substrate").

This characterization is very interesting and informative when two different indentation methods are applied during nanoindentation experiments: one cyclic method with control of the load on the indenter and another one - with control of the depth of indentation. Having in mind the necessity to replace the electrolytes, containing high toxicity and carcinogenicity Cr^{6+} ions with more acceptable Cr^{3+} ions, in this investigation we have investigated the system in which the conversion layers were deposited from solution containing only Cr^{3+} ions (complex salt of ammonia three(oxalate)-chromate) [18].

The aim of present work is to determine the changes (including in depth) of the indentation hardness (H_{IT}) and indentation modulus (E_{IT}) of the electrodeposited monolayer system "Zn coating/Steel substrate" and bi-layer system "Cr III conversion layer/Zn coating/ Steel substrate" and to estimate the surface peculiarities of the important from exploitation point of view mechanical properties of these systems, using indentation experiments.

II. EXPERIMENTAL

A. *Sample preparation*

The investigated samples are electrodeposited on a cut from low carbon sheet steel (High-Strength Low-Alloy steel - ISO 10322-1) substrates with sizes 20 x 10 x 0.82 mm. Zinc coatings are electrodeposited from electrolyte with a composition 150 g/l $ZnSO_4.7H_2O$, 30 g/l NH_4Cl, 30 g/l H_3BO_3, additives AZ-1 (wetting agent) - 50 ml/l and AZ-2 (brightener) - 10 ml/l, pH 4.5–5.0. Deposition conditions: cathode current density - 2 A/dm^2; room temperature – 22 °C; metallurgical zinc anodes. The coating thickness is approximately 5 µm. An additional immersion treatment of electrodeposited Zn coatings was applied for formation of transparent-colored conversion layer in solution, containing Cr III (ammonium tris (oxalato) chromate [III]) complex as it described in [18]. The conversion layer thickness is approximately 0.15 µm.

B. *Nanoindentation investigations*

The mechanical properties of the stainless steel substrate, as well as the systems “Conversion layer”/”Zinc coating”/”Steel substrate” and ”Zinc coating”/”Steel substrate” were investigated by means of nanoindentation experiments, using Nano Indenter G200 (Keysight Technologies, USA). The nanoindenter is equipped with a Berkovich three-sided diamond pyramid with centerline-to-face angle 65.3° and 20 nm radius at the tip of the indenter. We made series of 10 indentations on each sample. Two indentation methods were used-one cyclic method (10 loading-unloading cycles) with control of the load(maximum load 500mN) and another one with control of the depth of indentation(70nm depth limit). We had 10 s peak hold time at maximum load for both methods. The import data for both indentation methods are given in Table 1 and Table 2.

First indentation method was used for investigation of indentation hardness H_{IT} and indentation modulus E_{IT} *of* the substrate and the systems “Conversion layer”/”Zinc coating”/”Steel substrate” and ”Zinc coating”/”Steel substrate” and the second indentation method (with control of the depth of indentation)was used for investigation of the mechanical properties of the Cr III conversion layer only.

TABLE I. Input parameters for the indentation method with load control

Parameter	Unit	Values
Percent To Unload	[%]	90
Surface Approach Velocity	[nm/s]	10
Delta X For Finding Surface	[µm]	-50
Delta Y For Finding Surface	[µm]	-50
Maximum Load	[gf]	50
Load Rate Multiple For Unload Rate	[-]	1
Number Of Times To Load	[-]	10
Allowable Drift Rate	[nm/s]	0.05
Approach Distance To Store	[nm]	1000
Peak Hold Time	[s]	20
Time To Load	[s]	15
Surface Approach Distance	[nm]	5000
Surface Approach Sensitivity	[%]	40
Poisson Ratio	[-]	0.3

TABLE II. Input parameters for the indentation method with control of the depth of indentation

Parameter	Unit	Value
Percent To Unload	%	90
Surface Approach Velocity	nm/s	10
Depth Limit	nm	70
Delta X For Finding Surface	µm	-50
Delta Y For Finding Surface	µm	-50
Allowable Drift Rate	nm/s	0.05
Perform Drift Test Segment	[-]	1
Approach Distance To Store	nm	1000
Peak Hold Time	s	10
Surface Approach Distance	nm	5000
Surface Approach Sensitivity	%	40
Percent Unload In Stiffness Calculation	%	50
Poisson’s Ratio	[-]	0.3

III. Results and discussion

As a result of nanoindentation experiments we obtained the load–displacement curves (Fig.1,2,3) and calculated the indentation hardness (H_{IT}) and modulus (E_{IT}) of the substrate and investigated corrosion protective films by means of Oliver & Pharr approximation method.

The obtained results for indentation hardness and indentation modulus of the High-Strength Low-Carbon steel (ISO 10322-1) substrate are shown in Fig.4 and 5.

The comparison between indentation hardness and indentation modulus of the electrodeposited monolayer system

"Zn coating/Steel substrate" and bi-layer system "Cr III conversion layer/Zn coating/Steel substrate" are shown in Fig.6 and Fig.7.

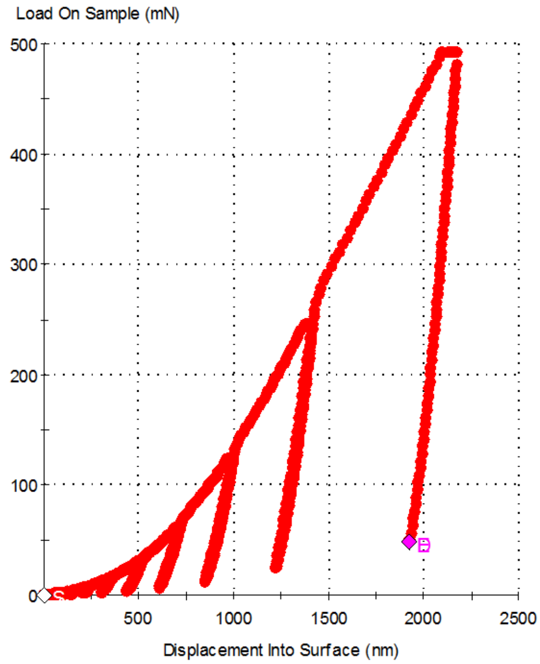

Fig.1 Average load-displacement curve for the substrate

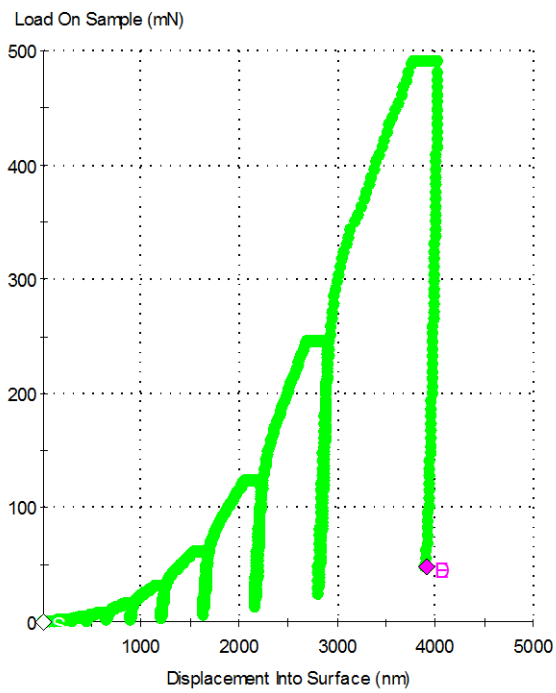

Fig.2 Average load-displacement curve for the system "Cr III conversion layer/Zn coating/Steel substrate"

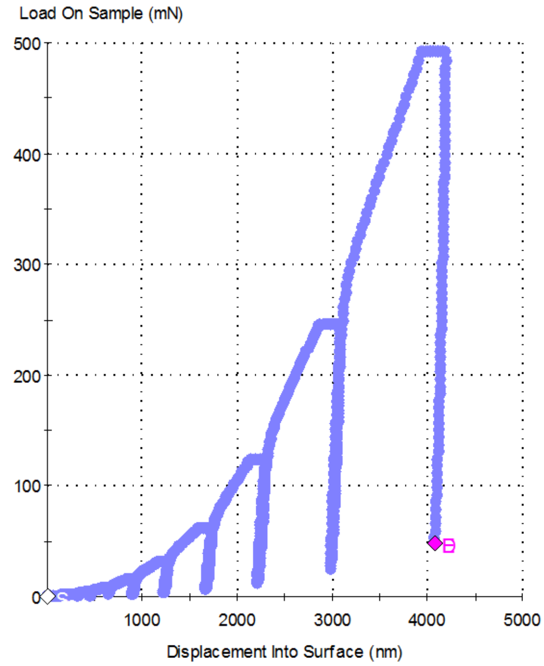

Fig.3 Average load-displacement curve for the system "Zn coating/Steel substrate"

The results about mechanical properties of investigated films and the substrate on figures 4-7 were obtained using the cyclic indentation method with load control. Figure 6 and 7 show that the double layer system "Cr III conversion layer/Zn coating/Steel substrate" has higher indentation hardness and modulus than the system "Zinc coating"/"Steel substrate", which means that the Cr III conversion layer improves the mechanical properties of the Zn/Steel substrate system, which leads to better wear resistance and corrosion protection ability of this system.

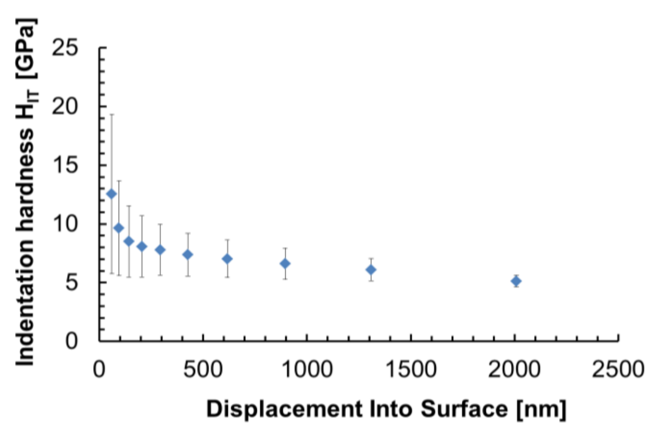

Figure 4. Indentation hardness of the substrate

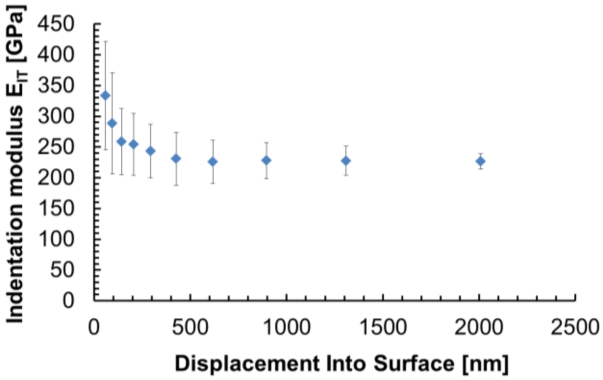

Figure 5. Indentation modulus of the substrate

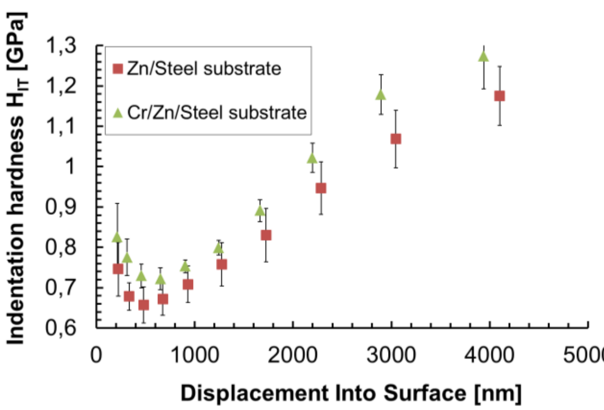

Figure 6. Comparison of indentation hardness of the films

With increasing the depth of indentation, the indentation hardness and indentation modulus of the Cr III/Zn/Steel substrate system first decrease, because of the influence of the softer Zn sublayer and then start to increase, because of the influence of the harder steel substrate. Both Cr/Zn/Steel substrate and Zn/Steel substrate systems has smaller indentation hardness and modulus than the High-Strength Low-Carbon steel (ISO 10322-1) substrate.

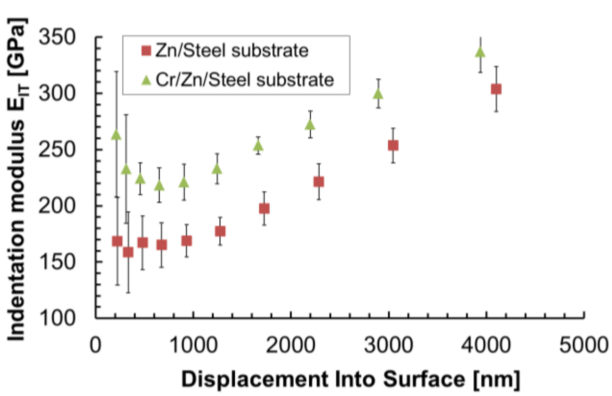

Figure 7. Comparison of indentation modulus of the films

In order to obtain mechanical properties of the Cr III conversion layer only, we realized additional nanoindentation measurements with the indentation method with control of the depth of indentation. The results show that indentation hardness of the Cr III layer, using this method is 0.843 GPa and its indentation modulus is 103.331 GPa. These values are smaller than the values of indentation hardness and modulus of the whole system Cr/Zn/Steel substrate, obtained by means of the cyclic method with load control (H_{IT}=1.229 GPa, E_{IT}=330.6 GPa).

These relative low values of the indentation hardness and indentation modulus of the formed on the Zn surface chromate conversion layer can be attributed to its chemical composition, the chemical state of the Cr ion, respectively. The ammonium tris (oxalate) chromate crystals grown on the Zn coating are thin elongated prisms and have a monoclinic structure in which three oxalate groups of the complex ion are planar, while the three inner oxygen atoms form octahedral surrounding with a central Cr ion [18]. The valent state of this ion is Cr[III] in comparison with the conversion layers, obtained in solutions containing six-valent chromium ions, which are characterized with highest thickness, protective ability and wear-resistance, connected with the presence of mobile oxidized Cr^{6+} ion [19].

At the same time the results for indentation hardness and indentation modulus of the Zn layer, which we obtained, are in good agreement with these, obtained from other authors [20, 21]. Unfortunately publications about investigation of mechanical properties of Cr III conversion layers are practically absent. We found only one [22], but authors of this publication made plasma source ion implantation (PSII) of nitrogen ions in order to improve the mechanical properties of electrodeposited trivalent chromium layers, moreover in their case they didn't have Zn sublayer, that's why it is not possible to compare our results about indentation hardness and modulus with their.

IV. Conclusion

The use of the aforementioned advance approach for characterization in a local area allows evaluating the influence of the different layers on the mechanical characteristics of the whole system (substrate-multilayer). In our previous works [23, 24] we started with investigations of single layers and then continued to develop this approach investigating different multilayer systems [25].

In present work zinc coatings with thickness 5 µm were electrochemically deposited on High-Strength Low-Carbon sheet steel (ISO 10322-1, ASTM A1008) substrate with thickness 820 µm. Their protective ability strongly depends from aggressive nature of environment, which determines the need of additional efforts to improve its protective properties, that's why our zinc coatings were additionally protected by means of chromium conversion layers with thickness 150 nm. Cr III conversion layers were used, because they are less toxic than the layers, obtained from electrolytes, containing Cr^{6+} ions. The mechanical properties of the electrodeposited monolayer system "Zn coating/Steel substrate" and bi-layer system "Cr III conversion layer/Zn coating/Steel substrate" were investigated by means of nanoindentation experiments. Dependence of indentation modulus and indentation hardness on the depth of indentation, as well as their surface peculiarities were investigated and discussed. It was obtained that the system, containing Cr III conversion layer has not only better corrosion protection ability, but also better mechanical properties(the results for the substrate-multilayer system containing Cr III conversion layer indicate that the indentation hardness is 7.6% higher and the indentation modulus is 11.8% higher) than the zinc plated steel substrate without chromium conversion layer on the top, which means that adding of Cr III conversion layer leads also to higher wear resistance and adhesion of the obtained system, which is very important from practical point of view.

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