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RESEARCH ON CORROSION TESTING AND CHARACTERIZATION OF PROTECTIVE CHROMIUM COATINGS DEPOSITED ON Zy-4 SUBSTRATE

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***Abstract**: Present paper includes some results regarding the structural and morphological characterization of two chromium coatings, as well as results on corrosion behaviour. The coatings have been deposited by two PVD (Physical Vapor Deposition) methods namely: Electron Beam-Physical Vapor Deposition (EB-PVD) and Magnetron Sputtering (MS) on Zircaloy-4 substrate. The thickness, structure and morphology have been realized using SEM and XRD analysis. Adherent and compact coatings with columnar structure and a small number of fine cannelures were observed. Electrochemical measurements have been applied to evaluate the corrosion susceptibility of the chromium coatings. Smaller values of the corrosion rates were obtained for the coated samples. All methods used for coatings characterizing reveal a protective character of the chromium coatings.*

Keywords: chromium coated Zircaloy-4, SEM, XRD, electrochemical measurements

1. Introduction

Sustainable energy is a key for economic and technological development in all times and involves specific materials selection in order to get efficiency [1]. Nuclear energy being the single major low-carbon electricity source which represent 25% from total electricity generation of 2020 in Europe by fuel [2], older [2], [3] and newer [4], [5] materials and their performant coatings [6], [7] are worthy of investigation for new generation of nuclear reactors [8]. Safety exploitation of a nuclear power plant is a mandatory condition for successful use of nuclear energy. The materials from the reactor core are exposed to a very aggressive environment: high temperature, high mechanical loads, aggressive coolant chemistry, very high levels of radiation [9-11]. Fuel cladding is the outer layer of the fuel rods, standing between the reactor coolant and fuel pellets. So, the cladding material plays an important role since it is the most sensible structural component of a reactor, consisting of the second barrier to avoiding that fuel fission products can reach the primary coolant circuit [12].

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Improvement of nuclear fuel performance in normal and accident conditions make possible to reach the following goals: extending the service life of nuclear power plant (increasing economic competitiveness), increasing the fuel burnup (radioactive waste minimization), increasing nuclear reactor power, safe operation and reliability of power plants [9], [13]. Thereby have been developed three research directions: optimization of chemical composition and technology fabrication process of the zirconium alloys (resulting advanced materials, like: E635, ZIRLO, M5, MDA, HiFi, X5A, etc.); development of coatings on the current zirconium alloys and development of new advanced alloys [14-21]. The objective of these research is the development of a nuclear fuel system with higher performance in operation and accident conditions, known as ATF (Accident Tolerant Fuel) materials [22]. Certainly, it is not possible to improve all performance indicators for all potential scenarios, but the main advantages of using these materials should overcome other more vulnerable properties [23].

According to the specialized documentation have been proposed a lot of coating materials for zirconium alloys, with thickness in the range of 0.0215-250 µm [22], applied by various techniques [24-29]. Up to now have been proposed and applied the following types of coatings: metallic / nonmetallic / ceramic (oxide, nitride, carbide) / composite / multilayer to improve the corrosion resistance of the actual zirconium-based alloy used for fuel cladding [30]. Chromium based coatings have showed the best performance, both in normal and abnormal operation conditions of a nuclear reactor [9].

This study is focused on the improvement of corrosion performance of Zircaloy-4 (Zy-4) used like fuel cladding, through applying some chromium layers by two PVD (Physical Vapor Deposition), namely: Magnetron Sputtering (MS) and Electron Beam-Physical Vapor Deposition (EB-PVD) methods. The Cr coatings have been investigated and it was identified the coating elemental composition, coating thickness, uniformity and roughness, the eventually presence of cracks/pores and coating structural characteristics. Also, the assessment of corrosion behaviour of Cr coated Zy-4 alloys have been investigated by electrochemical methods, like: open circuit potential measurements, potentiodynamic polarization tests and electrochemical impedance spectroscopy. The present manuscript introduces a new advanced coating on Zy-4 elaboration and characterization having originality in comparison to our previous papers about coated and uncoated behavior of the same alloy [31], [32].

2. Experimental

2.1 Materials

The substrates used for coating deposition was Zy-4 samples, obtained from a Zy-4 tube, with an outer diameter of 13 mm and a wall thickness of 0.45 mm. The Zy-4 tube was cut into 20 mm sections and then halved lengthwise. In Table 1 is presented the chemical composition of the Zy-4 alloy. Before the coatings deposition, the substrates were ultrasonicated in isopropyl alcohol for 15 minutes, followed by nitrogen drying.

The selection of chromium as coating material was based on several advantages that chromium coatings provides: low neutron cross-section, high thermal conductivity, high-temperature oxidation resistance, very high Cr-Zr eutectic temperature, higher wettability compared to zirconium

The selection of coating material was based on the neutron cross-section, thermal conductivity, thermal expansion, melting point, phase transformation behaviour, and high-temperature oxidation resistance.

Table 1

Composition of Zircaloy-4 alloy (%)

Alloying Elements, [wt.%]				
Sn	Fe	Cr	O	Zr
1.32	0.29	0.14	0.12	Balance

Cr coatings studied in this paper have been deposited using two physical techniques, Thermionic Vacuum Arc and Electron Beam-Physical Vapor Deposition.

2.2 Characterization methods

XRD analysis was carried out using a Rigaku Ultima IV diffractometer in Bragg-Brentano (θ-θ) geometry with Cu $K_{\alpha1,\ \alpha2}$ radiation (1.5418 Å, 45 KV, 40 mA) and a D/teX Ultra high-speed one-dimensional detector. A graphite monochromator was placed in the diffracted beam to suppress background intensity. The slit configuration was as follows: DS=1 mm, SS-open, RS-open, DHL=1 mm and Soller slit 5° in the incident and in the diffracted beam. The XRD patterns were scanned in 2θ range of 25° - 105° / 30° - 90° with 0.05° / 0.01° step size and 1°/min scan speed.

For the morphological characterization scanning electron microscopy (SEM, Hitachi SU 8230 scanning electron microscope) at a pressure of 4 Pa at 20 kV were used. To identify the elemental composition of the samples an energy dispersive spectra detector (EDS) was used.

2D roughness profile was measured by Mitutoyo SURFTEST SJ-210 profilometer, with a measuring range up to 360 µm.

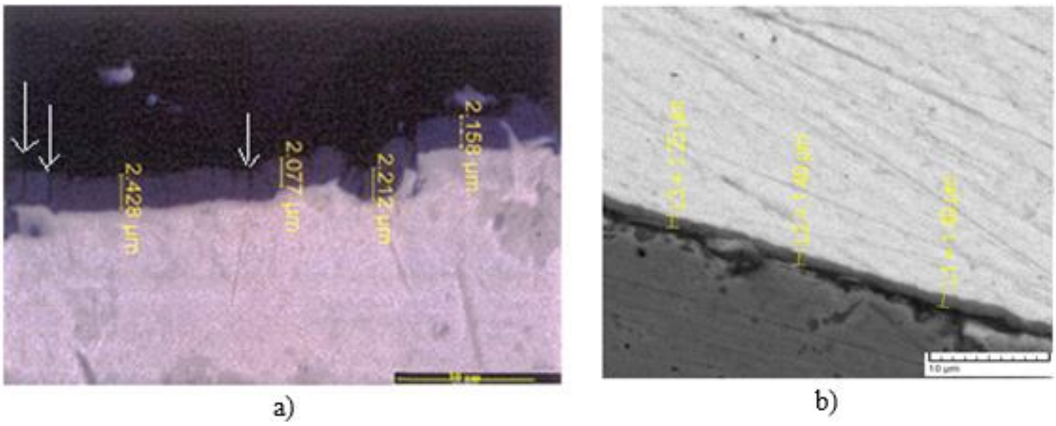
Electrochemical measurements were performed using a PARSTAT 2273 (Princeton Applied Research, AMETEK, OakRidge, TN, USA) equipment. The system consists of a three-electrode electrochemical cell with three-electrode: a saturated calomel reference electrode (SCE) and two auxiliary electrodes (graphite rods). The tests were carried out at room temperature (22 ± 2 °C). The following methods were used: open circuit potential variation, electrochemical impedance spectroscopy and potentiodynamic measurements. Open circuit potential measurements were performed in a specific primary circuit solution, LiOH with pH = 10.5. Potentiodynamic tests were also made in LiOH solution, with a scan rate of 0.5 $mV \cdot s^{-1}$ and a potential range from -250 to 1000 mV relative to OCP (open circuit potential). Electrochemical impedance spectroscopy measurements were realised in a chemically inert solution (0.05 M boric acid and 0.001 M borax solution) with a pH = 7.3 and with an amplitude of 10 mV in the frequency range from 100 mHz to 100 kHz after OCP stabilization.

3. Results and discussions

3.1 Scanning electron microscopy and Energy-dispersive X-ray analysis

SEM and EDS analysis were used to measure the thickness and elemental composition of deposited coatings. The structure and the presence of eventual defects in the coatings have also been investigated.

From the SEM cross section micrographs illustrated in the Fig. 1 it was measured the coating thickness with an average value of 2.3 µm for EB-PVD coating and 1.4 µm for MS coating. Also, it was identified a columnar structure of the chromium coatings with some cannelures indicated by white arrows.



a) b)

Fig. 1 SEM cross section micrographs of as-deposited Cr coating by: a) EB-PVD and b) MS

The chromium coating surface morphologies and the element distribution on the coating surface are illustrated in Fig. 2. It can be noted the presence of chromium with the highest concentration and small concentrations of zirconium and oxygen.

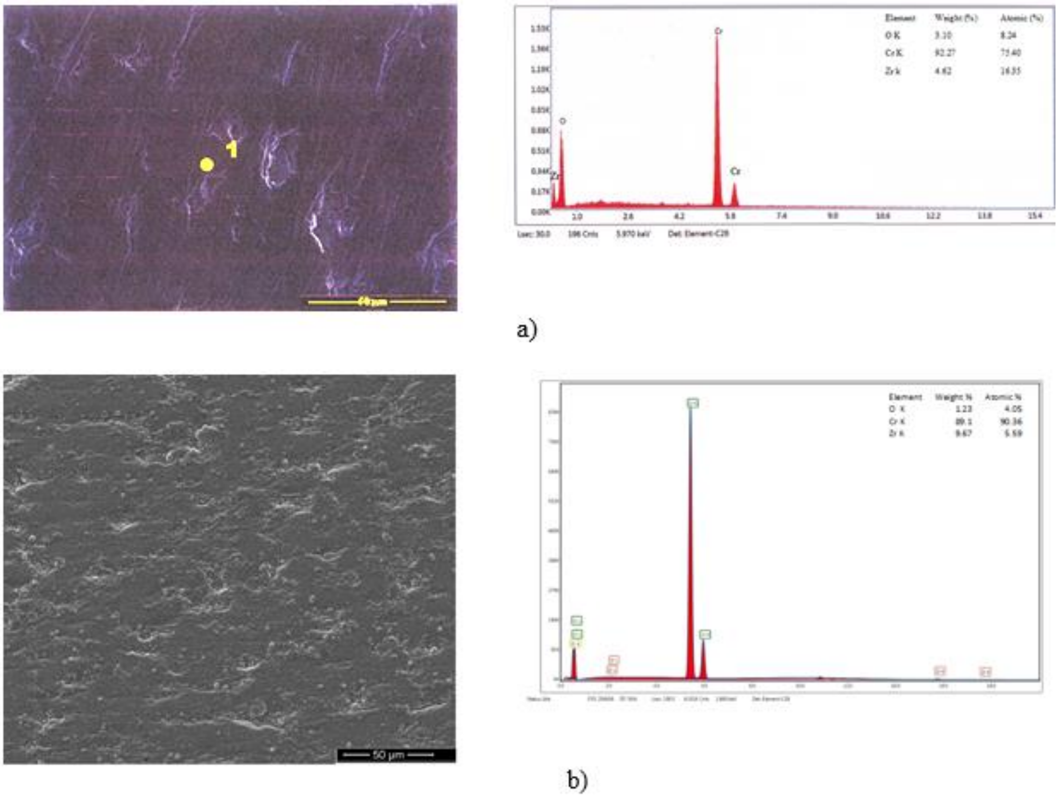


Fig. 2 SEM surface morphology and EDS spectra surface area scan for Cr coated Zy-4 by: a) EB-PVD and b) MS

3.2 XRD Measurements

The phase structures of the deposited coatings by EB-PVD and MS, respectively have been analysed by XRD.

In Fig. 3 are presented the results from qualitative and quantitative phase analysis of the Cr coated Zy-4 X-ray diffraction patterns. Qualitative phase analysis was realised with Integred X-ray Powder Diffraction Software PDXL 2.4 program, using the ICDD PDF4+ 2021 database.

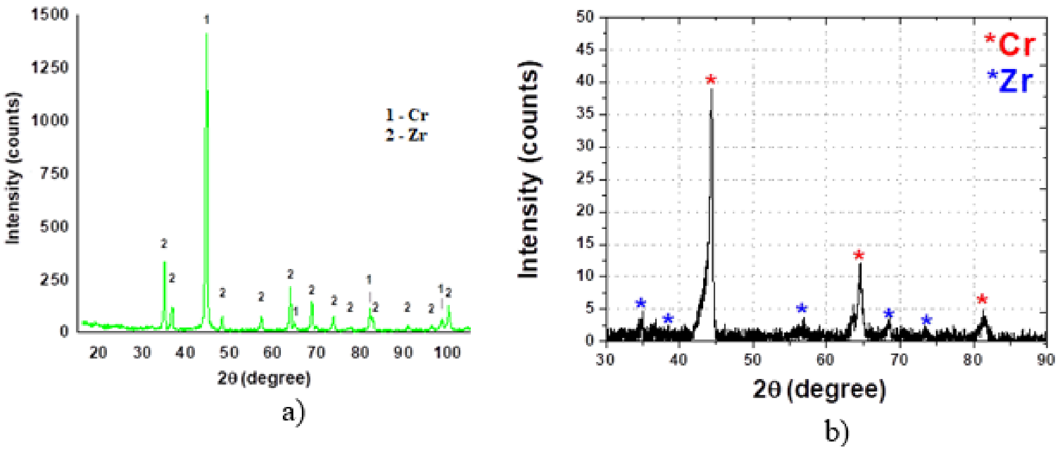


Fig. 3. X-ray diffraction patterns of Cr coatings deposited on Zy-4 substrate: a) by EB-PVD; b) by MS

In the above figure, the presence of two textured polycrystalline phases can be observed, highlighted by the presence of multiple diffraction peaks.

The crystalline phase corresponding to metallic chromium appears to be the main phase, space group Im-3m, with a volume centered cubic arrangement of atoms in the unit cell. This phase is identified by the presence of the ordered growth of crystallites on the orientations (110), (200), (211) respectively with preferential growth on the (110) orientation. Compared to the crystal symmetry of chromium coating obtained in the specialized literature, in the present case the chromium nanocrystallites show a more pronounced growth on the (200) orientation, compared to (211). This characteristic is determined by the plasma parameters selected to develop the coatings.

In additions to the crystalline phase of chromium specific to the deposited coatings, a weak crystalline phase specific to the Zr substrate with an arrangement of face-centered cubic atoms was identified. No crystalline phases of any oxides are observed.

3.3 Roughness measurements

Roughness measurements were made on uncoated and coated Zy-4 alloy. The average values of the roughness parameters are summarized in Table 2.

Table 2

Roughness values for uncoated and coated Zy-4 alloy

Sample	Side	Ra (μm)	Rmax (μm)	Rz (μm)
Zy-4	inner	0.487	5.27	4.31
	outer	0.476	3.87	3.27
Coated Zy-4 MS	inner	0.413	5.77	4.24
	outer	0.268	4.03	3.27
Coated Zy-4 EB-PVD	inner	0.416	5.35	4.11
	outer	0.458	3.38	3.2

R_a: average roughness;R_{max}: the largest single roughness depth within the evaluation length
R_z: difference between the tallest “peak” and the deepest “valley in the surface”

The parameter usually used for roughness evaluation is R_a, average roughness. So, from Tabel 2 we can observe a slight decrease of average roughness for the coated samples by magnetron sputtering, but also by electron beam physical vapor deposition. Because of the sample geometry we could not applied metallographic preparation, only a pickling surface treatment. So, we consider that chromium coating filled the eventual small lacks on the surface resulting a homogenous surface and therefore the decrease of the average roughness.

3.4 Electrochemical characterization

3.4.1 Open circuit potential measurements

The generalized corrosion behaviour prediction of uncoated Zy-4 alloy and coated Zy-4 alloy was studied by applying open circuit potential measurements. The tests have been carried out at room temperature in simulating primary chemistry solution of CANDU reactor (LiOH, pH = 10.5).

In Fig. 4 are presented the superimposed curves obtained after testing.

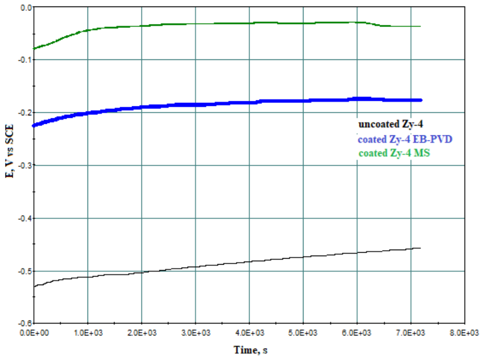


Fig. 4. Open circuit potential variation for uncoated and coated Zy-4 alloy

The curve trends offer qualitative information about the surface of the samples. Thus, we can see a relatively constant corrosion potential evolution with time, without high variations, indicated a continuous and stable coating. The most electronegative corrosion potential value was noticed for uncoated Zy-4 (-0.53 V), and the corrosion potential values recorded for the Zy-4 coated by EB-PVD and Zy-4 coated by MS were (-0.23 V) and (-0.09 V), respectively.

3.4.2 Potentiodynamic polarization tests

The corrosion behaviour in CANDU reactor primary conditions was also evaluated by potentiodynamic polarization tests. In Fig. 5 are illustrated the potentiodynamic curves for uncoated and coated Zy-4. The curve trends show a pronounced thermodynamic tendency of corrosion for the uncoated Zy-4 (more electronegative value of Ecorr and higher corrosion current). Also, it can be seen a better corrosion behaviour for coated Zy-4 by MS.

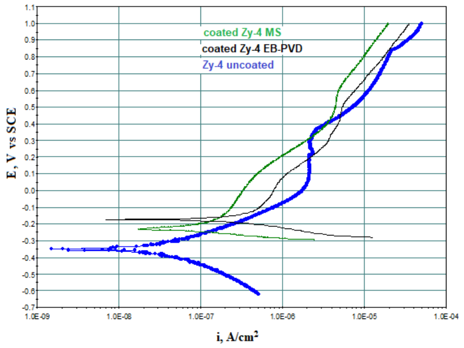


Fig. 5 Polarization curves for uncoated and Cr coated Zy-4 alloy

The Tafel extrapolation method was applied on the polarization curves to obtain the kinetic parameters, which are shown in Table 3.

Table 3

Polarization parameters of uncoated and coated Zy-4 alloy

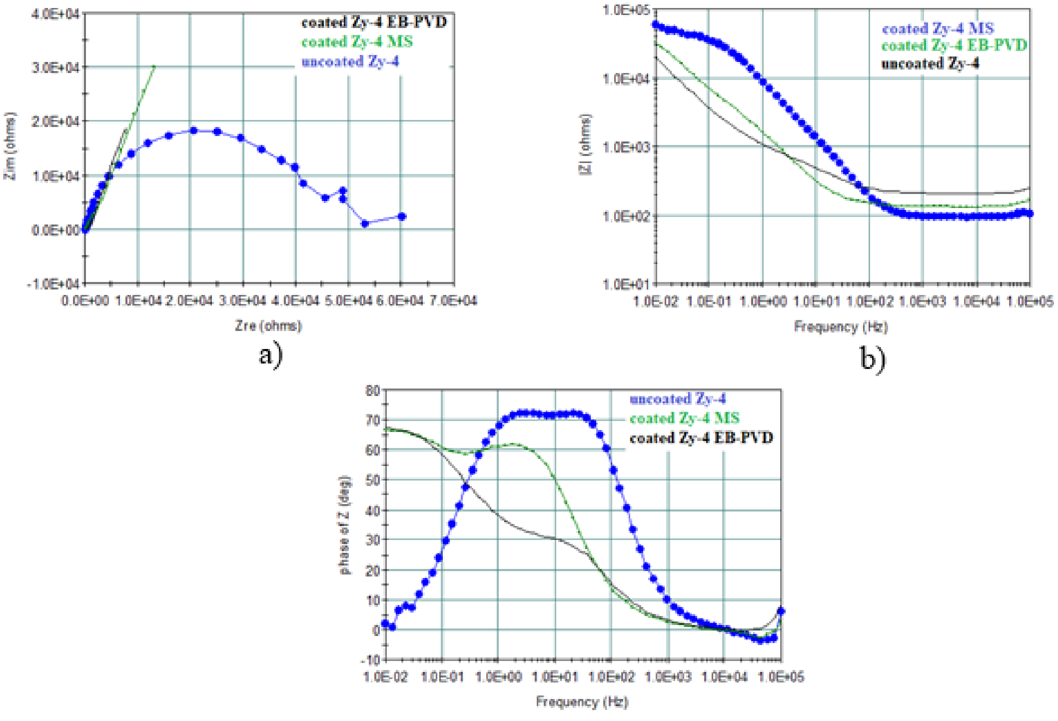
Sample	E_{corr}, mV	i_{corr}, μ/cm^2	V_{corr}, mm/year	R_p, ℧·cm^2
uncoated Zy-4	-350	2.47	$5.89\cdot10^{-3}$	$1.3\cdot10^{4}$
Coated Zy-4 MS	-229	0.23	$5.21\cdot10^{-4}$	$2.1\cdot10^{5}$
Coated Zy-4 EB-PVD	-173	0.67	$1.53\cdot10^{-3}$	$1.7\cdot10^{4}$

The main parameters are the corrosion potential (Ecorr), corrosion rate (V_{corr}), corrosion current density (i_{corr}) and polarization resistance (Rp). As is showed in the table, the higher corrosion density and corrosion potential values have been obtained for the uncoated Zy4, while the coated Zy-4 MS has the smaller values. Also, it was recorded the lowest corrosion rate and the highest value of the polarization resistance for the coated Zy-4 MS sample.

3.4.3 Electrochemical impedance spectroscopy

The chromium coatings were also characterized by EIS in primary circuit conditions.

The Nyquist and Bode diagrams (Fig. 6) were recorded at open circuit potential for the Cr coated Zy-4 by MS and EB-PVD, respectively, after 10 minutes of immersion in LiOH solution. The data obtain from these diagrams allows a qualitative characterization of the coatings.



a)

b)

c)

Fig. 6 Nyquist (a), Bode |Z| (b) and Bode Phase (c) diagrams for uncoated and Cr coated Zy-4 alloy by MS and EB-PVD

From Bode |Z| diagram (Fig. 6(b)) we can notice higher values of impedance for Cr coated Zy-4 samples, which denote that the coatings provide better anticorrosive properties than the uncoated sample and these data are in accordance with the smaller corrosion rate obtained for the coated samples by linear polarization.

The values of the phase angles (Fig. 6 (c)) are higher for the uncoated sample, but we can observe that at lower frequency this tends to zero, while in the case of coated samples, after the curve reaches a maximum the trend is to rise further. Both uncoated and coated samples show phase angle values less than 90° meaning that the coatings are not totally capacitive. From Nyquist diagram (Fig. 6 (a)) it can be observed that for the coating deposited by magnetron sputtering it was recorded a higher value of the capacitive semicircle diameter, which means a higher polarization resistance, so better corrosion protection. Also, we can see regular Nyquist semicircles which indicates smooth and uniform coatings.

4. Conclusions

In summary, in the present study it has been characterized two coatings deposited by magnetron sputtering and electron beam–physical vapor deposition methods on Zy-4 substrate. The coatings have been characterized using SEM/EDS, XRD analysis, roughness measurements and electrochemical tests.

The results of structural and morphological characterization show strong preferential orientation of coatings, typical columnar microstructure of the PVD coatings, uniform coatings with a thickness about 2.3 µm and 1.4 µm, respectively. For the chromium coating deposited by EB-PVD was noticed the presence of some cannelures, without any other defects.

Roughness results show a slight decrease for the coated samples, so the coatings induce a surface smoothing effect.

The corrosion testing results indicate a better corrosion behaviour of the coated samples. The open circuit corrosion potential recorded for the coated samples present values shifted to more anodic domain compared to uncoated sample and it was also seen a constant trend of Ecorr with time, which means a continuous and stable chromium coating and there are not reactions to the solution-coating interface. The same corrosion behaviour it is also confirmed by potentiodynamic tests: a pronounced thermodynamic tendency of corrosion for the uncoated Zy-4 (more electronegative value of Ecorr and higher corrosion current). Also, it was seen a better corrosion behaviour for chromium coated Zy-4 by MS.

A qualitative characterization of the coatings was done by EIS. A good corrosion resistance of the coated sample was suggested by the higher values of impedance and of the capacitive semicircle diameter, which means a higher polarization resistance, so better corrosion protection. Also, there was seen regular Nyquist semicircles which indicates smooth and uniform coatings.

Further work will study the corrosion behaviour of chromium coated Zy-4 at high temperature and pressure in LiOH solution (primary circuit conditions).

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