CORROSION SUSCEPTIBILITY ASSESSMENT OF CrNx THIN FILMS DEPOSITED ON 310 H STAINLESS STEEL BY THERMIONIC VACUUM ARC METHOD

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Abstract

The paper's aim is to present results obtained after characterization of the chromium nitride thin layers applied on the surface of 310 H stainless steel (SS) using the thermionic vacuum arc (TVA) method. The surfaces of coated samples have been analysed using techniques as scanning electron microscopy (SEM), energy dispersive spectroscopy (EDX) and X-ray diffraction (XRD), respectively. In parallel, by using electrochemical methods (such as electrochemical impedance spectroscopy, EIS, and linear potentiodynamic polarization), the general corrosion susceptibility of coated samples and the protective character of the CrN_x layers, respectively, have been assessed. The EIS analysis with Bode and Nyquist plots, equivalent circuits and representative parameters, confirmed that the chromium nitride coated 310 H SS samples are more protective and provide better corrosion resistance. The same conclusion was also highlighted by the potentiodynamic method.

Keywords: *Corrosion resistance, Stainless steel, CrNx coating, TVA method*

Introduction

The supercritical water cooled reactor (SCWR) is one of the six innovative concepts selected by the Generation IV International Forum (GIF). This type of reactor operates above the thermodynamic critical point of water (374°C, 22.1 MPa). The severe environment existing in a SCWR reactor is unique and there are few data about the materials behaviour when exposed to such specific conditions. Although there are some studies on the effects induced by such extreme conditions in different alloys, a final decision has not yet been taken regarding the structural materials for SCWR. At present, depending on good corrosion resistance, the candidate materials are as follows: ferritic - martensitic alloys, austenitic steels and Ni based alloys, [1].

The austenitic stainless steels are considered a class of materials suitable for use in the SCWRs due to their high resistance to oxidation, creep and based on good radiation performance. Although these types of steels have a high oxidation resistance, they are susceptible to develop sigma phase when they are exposed for longer periods of time in water at supercritical temperature (550°C, 250 atm) [2]. Therefore, one way to improve these alloys performances is the application of thin ceramic layers on the surface by using various deposition techniques.

The paper objective was to characterize the chromium nitride thin layers applied on the surface of 310 H stainless steel (SS) using the thermionic vacuum arc (TVA) method.

The surfaces of coated samples have been analysed using different techniques as scanning electron microscopy (SEM), energy dispersive spectroscopy (EDX) and X-ray diffraction (XRD), respectively.

By using electrochemical methods (electrochemical impedance spectroscopy, EIS, and linear potentiodynamic polarization), the general corrosion susceptibility of coated samples and the protective character of the CrN_x layer, respectively, have been assessed as well.

Experimental set-up

To perform the proposed analyses, a 310 H SS sheet with a thickness of 2 mm was used. The chemical composition of the stainless steel [3] is given as follows: *310H SS alloy* - Fe (54.34%), Cr (24.13%), Ni (19.03%), Mn (1.61%), Si (0.71%), C (0.063%), N (0.04%), P (0.016%), S (0.001%).

From the 310H SS sheet, parallelepiped shape samples of 25 mm x 15 mm (length x width) were cut. Before coating, the samples were mechanical polished on abrasive paper until a 600 granulation was reached, then degreased in acetone, rinsed with distilled water and dried.

The depositions have been made in the Low Temperature Plasma Laboratory at the National Institute for Laser, Plasma and Radiation Physics using the thermionic vacuum arc (TVA) method. Thus, the CrN_x thin films were obtained by injecting N_2 gas into Cr plasma.

For coating, 1 - 3 mm Cr pellets (99.99% purity) purchased from NEYCO Company and N_2 gas (99.9999% purity) purchased from SIAD Company were used.

The surface morphology of the coating was investigated by scanning electron microscopy (SEM) using a Fei Quanta scanning electron microscope. The elemental composition of the samples was identified using an energy dispersive spectrum detector EDAX. To perform cross-section analyzes, small pieces were cut from the samples using a MECATOME T255/ 300/ 300 cutting machine and were hot embedded in conductive phenolic resin. By using a Vector Beta Grinder, samples sanding and polishing were done. To perform samples grinding, several granular carborundum discs (grit in the range 120 μm - 600 μm) were used, and the polishing was performed on a felt cloth soaked in a suspension of α-alumina in water.

The coating composition and structure was investigated by Grazing Incidence X-ray Diffraction (GIXRD) method using a X'Pert PRO MPD Diffractometer in a θ–2θ geometry with CuK_α radiation (l = 1.5406 Å). The GIXRD patterns were made at a grazing angle of 5º. In order to set the experimental analysis conditions, the X'Pert Data Collector program was used.

Corrosion susceptibility assessment was performed by two electrochemical methods, namely: electrochemical impedance spectroscopy (EIS) and linear potentiodynamic polarization. The experiments were performed using an electrochemical system PARSTAT 2273 potentiostat/ galvanostat, with an electrochemical cell which contains: a working electrode (the uncoated and coated 310 H stainless steel sample), a saturated calomel reference electrode (SCE) and auxiliary electrode (graphite rod).

The electrochemical tests were carried out at the room temperature (22 ± 2°C) in a chemically inert solution (0.05 M boric acid with 0.001 M borax) with pH = 7.7÷7.8.

The impedance spectra [4] were obtained at open circuit potential, with a scan frequency range 100 kHz - 100 mHz and an *ac* amplitude of 10 mV. To obtain quantitative data, experimental EIS results were simulated with equivalent electrical circuits as appropriate models, by means of the potentiostat ″ZSimpWin″ software.

Potentiodynamic measurements were made with a scan rate of 0.5 mV/ s, in a potential range between –0.250 V vs. OCP up to +1.0 V.

Results and discussion

Scanning electron microscopy (SEM)

In order to obtain information on the morphologies of uncoated and CrN_x coated 310H SS samples, SEM analysis was applied. SEM surface morphologies for uncoated and coated samples are shown in Fig. 1.

In the case of the CrN_x coated 310 H SS sample it can be seen a relatively uniform CrN_x coating layer (Fig. 1b), which presents small exfoliated or uncoated areas along the sanding traces.

In both cases, due to the fact that the samples were polished on abrasive paper up to a 600 granulation, the sanding traces can be observed.

Fig. 2 presents the surface EDX analysis for the CrN_x coated sample.

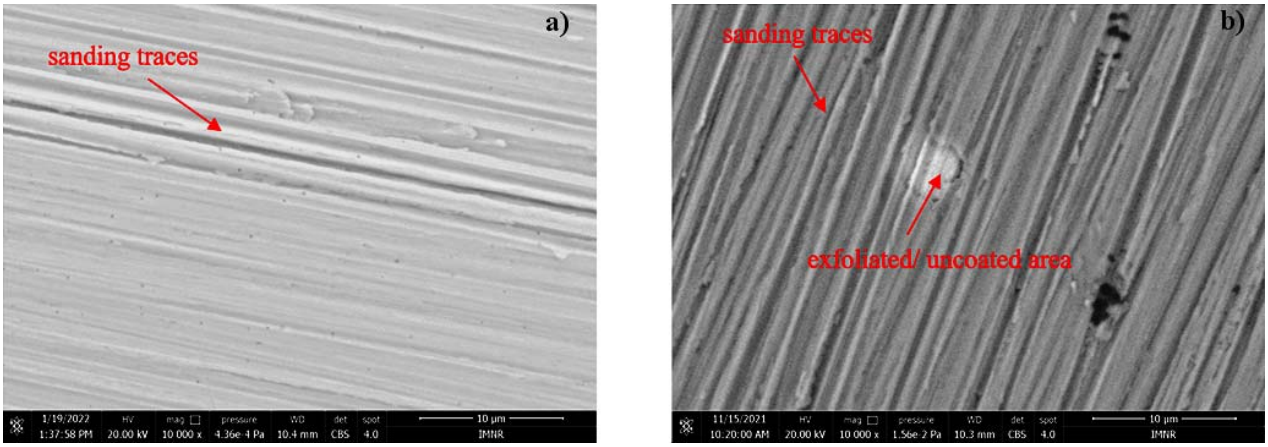


Fig.1 The surface morphologies of uncoated sample (a) and CrN_x coated 310 H SS sample (b) at a magnification of (x10000)

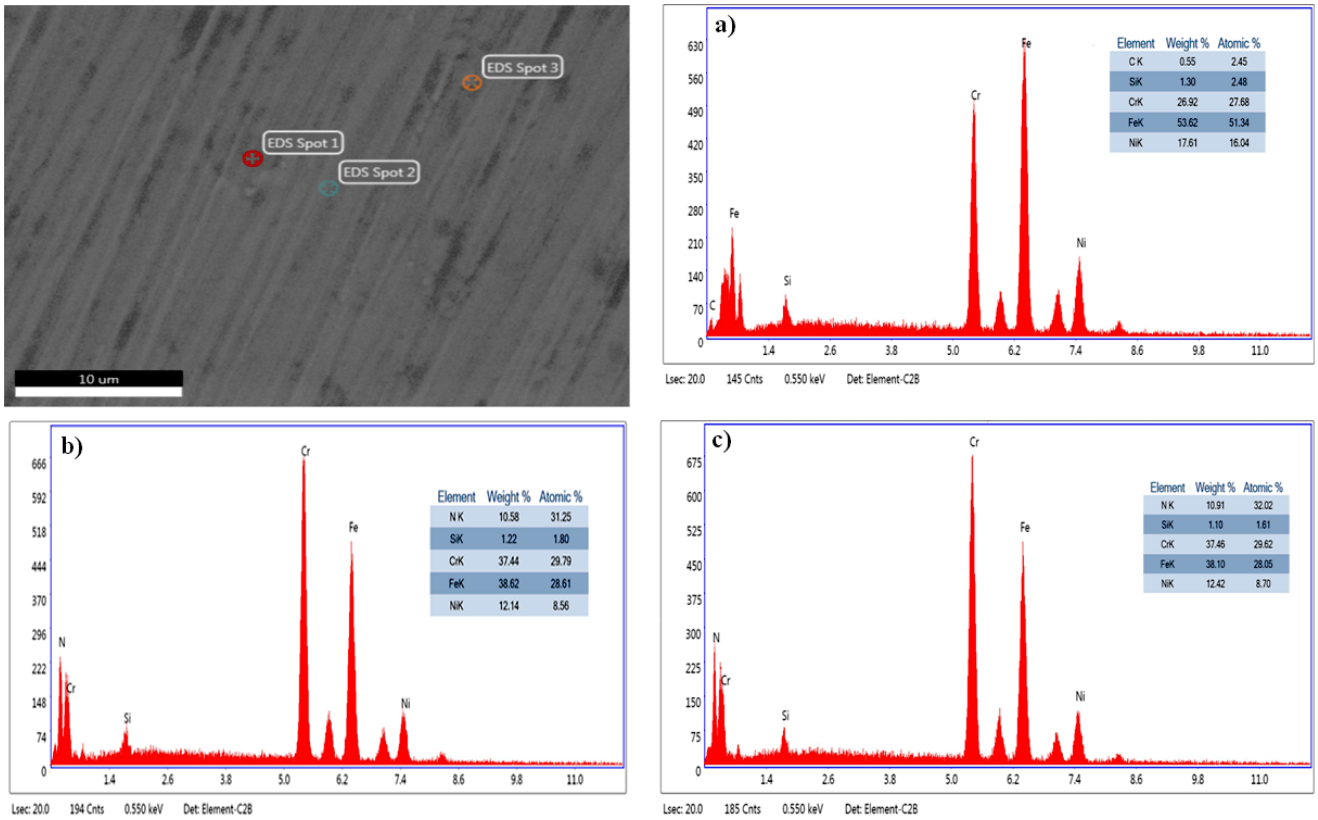


Fig. 2. EDS analysis on surface for CrN_x coated 310H SS samples
(a) EDS spot 1; (b) EDS spot 2; (c) EDS spot 3

The surface EDX analysis on the CrN_x coated sample shows that in exfoliated or uncoated area, the elements corresponding to the substrate (Cr, Fe and Ni) are present (Spot 1). An increase in Cr and N contents (up to 37.5% and 11%, respectively) and a decrease in Fe and Ni contents (up to 38% and 12.5%, respectively) can be observed on the coated area (spots 2 and 3).

On the 310H SS surface a thin layer of CrN_x has been deposited.

Fig. 3 presents the SEM on cross-sections of the samples before (a) and after coating (b). From the SEM image shown in Fig. 3b, relatively uniform and adherent deposition layers on the substrate can be seen. The coating thickness measured by SEM was around 303.55 nm.

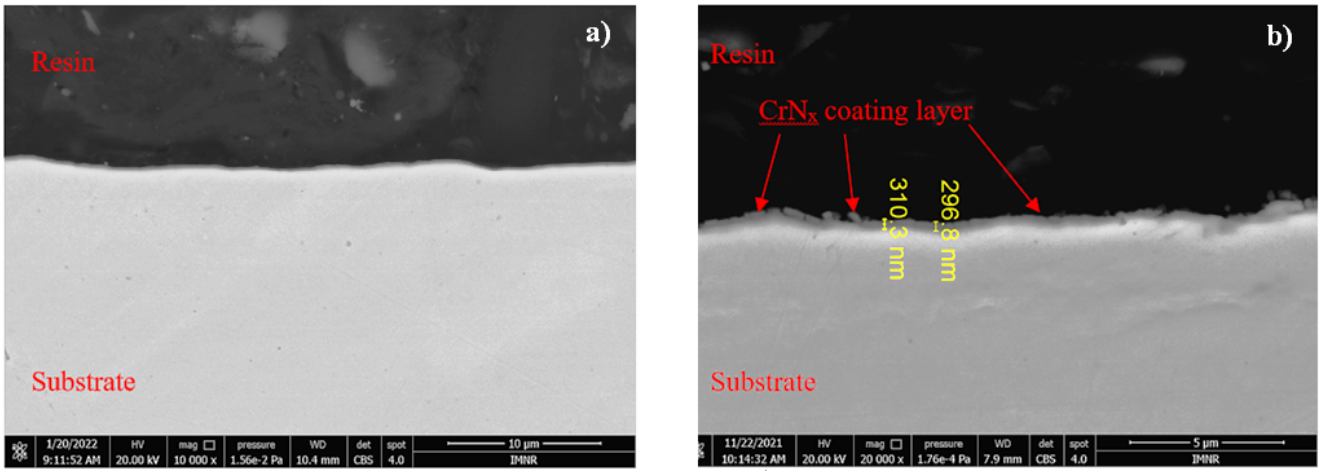


Fig. 3. SEM on cross-sections of the samples before (a) and after coating (b)

Grazing Incidence X -Ray Diffraction (GIXRD)

The chemical composition and the structure of the CrN_x coating layer were assessed using Grazing Incidence X-ray Diffraction (GIXRD) method. Fig. 4 illustrates the GIXRD patterns of the CrN_x coating.

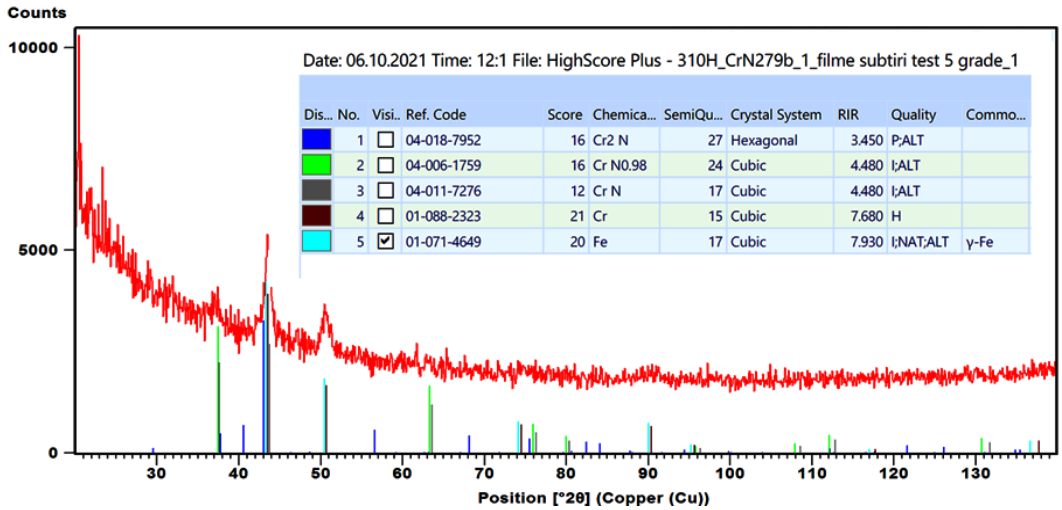


Fig. 4. GIXRD patterns of the CrN_x coated 310H SS sample

GIXRD analysis highlighted the presence in the coating layer of Cr (15%), CrN (17%), $CrN_{0.98}$ (24%) and Cr_2N (27%), respectively, compounds. The coating layer being very thin (approximately 300 nm), the metal substrate was also identified (which is explained by the appearance of γ-Fe forms, 17%).

The Cr, CrN, $CrN_{0.98}$ and γ-Fe compounds have a cubic crystallization form, while the Cr_2N compound has a hexagonal crystalline structure.

Electrochemical Impedance Spectroscopy

The characterization of the CrN_x coating layers has been performed by an EIS method. This method does not accelerate the electrochemical reactions at a metal/ solution interface [5]. Impedance spectra obtained for uncoated and CrN_x coated 310 H SS samples are presented in Fig. 5. The spectra were measured at open circuit potential.

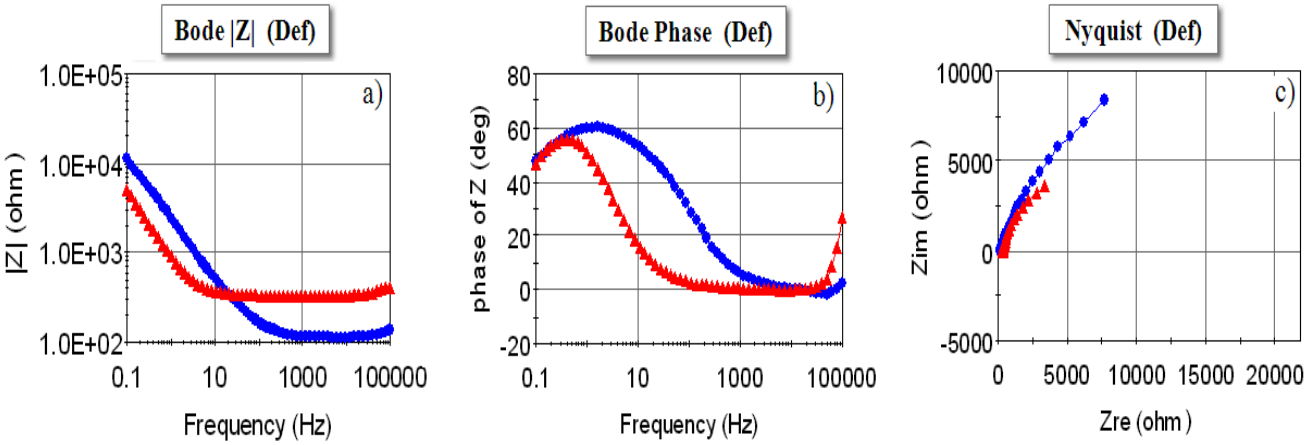


Fig. 5. Impedance Bode plots (a), phase angle plots (b) and Nyquist diagrams (c) obtained for uncoated and CrN_x coated 310 H SS sample (red color - uncoated 310 H SS sample, blue color - CrN_x coated 310 H SS sample)

From Fig. 5a can be seen that Bode plots show higher values for electrical resistivity in case of CrN_x coated 310H SS sample. Generally, a higher electrical resistivity (impedance) at a low frequency (< 10 Hz) means a higher protectiveness of the coating. Impedance magnitude, |Z|, is proportionally in line with coating resistance and in an inverse ratio to coating capacity; as such, a higher impedance value indicates good corrosion resistance. Fig. 5a shows a high value of impedance modulus for coated samples (about 10^4 Ω), and between 10^3 Ω ÷ 10^4 Ω for uncoated samples. Comparing the impedance magnitude order, CrN_x coated 310H SS sample has better corrosion resistance than the uncoated sample. It is also observed that impedance decreases with frequency increasing, which shows that the coating layers had capacitive components.

The protective character of the coating layer is also provided by the higher values of maximum phase angle (approx. -60.17° for the coated sample and -55.92° for the uncoated samples). Fig. 5b shows that the Bode plots present a maximum phase angle smaller than 90°, indicating that the coating layers have a capacitive behaviour. Generally, a phase angle closer to 90° on a wider range of frequency (10^{-1} Hz < f > 10 Hz) indicates capacitive properties and a higher protectiveness of the coating [6].

Using the ZSimpWin software of the potentiostat, an equivalent circuit has been selected to model the experimental impedance data.

The models obtained are shown in Fig. 6, and Table 2 presents the obtained values of equivalent electrical circuit elements. In all cases, a good correlation between experimental data and simulated data was noticed.

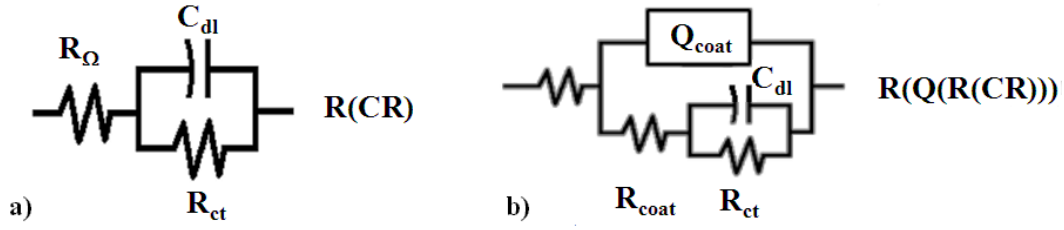


Fig. 6. Model for the equivalent electrical circuits proposed for fitting the experimental impedance spectra (a) uncoated 310H SS sample; (b) CrN_x coated 310H SS sample

Table 2. Values of equivalent electrical circuit elements for uncoated and CrN_x coated 310H SS samples

Element circuit		***Uncoated 310 H SS***	***CrN_x coated 310 H SS***
R_Ω, [$\Omega \times cm^2$]		1398	463.7
DE_{coat}	Q_{coat} [$S\ sec^n / cm^2$]	-	2.57×10^{-5}
	n	-	0.6847
R_{coat}, [$\Omega \times cm^2$]		-	3.616
C_{dl}, [F/ cm^2]		5.204×10^{-5}	1.455×10^{-6}
R_{ct}, [$\Omega \times cm^2$]		2.276×10^{4}	1.597×10^{5}
Chi-square (χ^2)		1.7×10^{-3}	1.850×10^{-3}

where: R_Ω - ohmic resistance of the solution; DE_{coat}, Q_{coat}, R_{coat}, n - distributive element, constant phase element, resistance of the coating layer, and exponential factor; C_{dl}, R_{ct}. - capacity of double layer, and charge transfer resistance.

The higher polarization resistance value with an order of magnitude (1.331×10^5 $k\Omega \times cm^2$) obtained from extrapolation of Nyquist diagrams (see Fig. 5c) indicates a good corrosion resistance of the CrN_x coating layer. In Table 3, the R_p values obtained from the Nyquist diagram extrapolation are presented.

Tabel 3. Rp values obtained by Nyquist diagram extrapolation

Sample type	***Polarization Resistance from the Extrapolation of Nyquist Diagrams ($\Omega \times cm^2$)***
Uncoated 310 H SS	2.301×10^4
CrN_x coated 310 H SS	1.331×10^5

Potentiodynamic Polarization Tests

In order to see the CrN_x coated 310 H alloy behaviour, the potentiodynamic polarization plots of the sample before and after coating were recorded and are shown in Fig. 7.

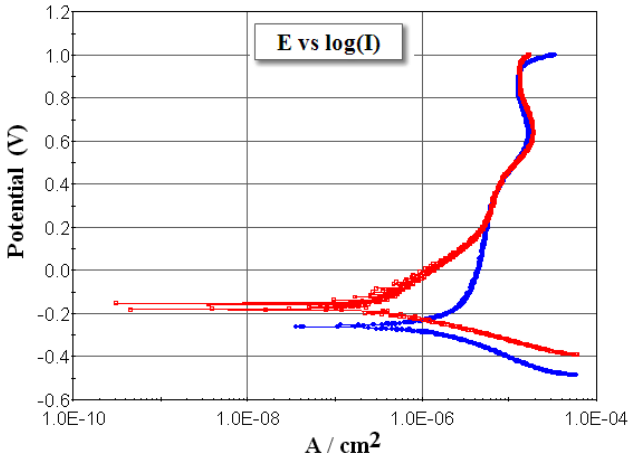


Fig. 7. Potentiodynamic polarization plots for uncoated (blue color) and CrN_x coated (red color) 310 H SS samples, at a scan rate of 0.5 mV/s

Applying the Tafel slope extrapolation method for Fig. 7 polarization plots, the electrochemical parameters shown in Table 4 were obtained. The main parameters are the corrosion potential (E_{corr}), corrosion rate (V_{corr}), current density (i_{corr}) and polarization resistance (R_p).

Table 4. Electrochemical parameters from Tafel slopes and polarization resistance

Sample type	*Electrochemical parameters from Tafel slopes*			*Electrochemical parameters from polarization resistance R_p values*			
	E_{corr} [mV]	i_{corr} [$\mu A/cm^2$]	V_{corr} [mm/ year]	E_{corr} [mV]	R_p [$k\Omega \times cm^2$]	i_{corr} [$\mu A/ cm^2$]	V_{corr} [mm/ year]
Uncoated 310 H SS sample	-261.16	1.29	3.225×10^{-3}	-258.23	26.57	0.99	4.04×10^{-3}
CrN_x coated 310 H SS sample	-165.70	2.22×10^{-1}	5.55×10^{-4}	-164.97	115.68	2.06×10^{-1}	5.14×10^{-4}

Analyzing the electrochemical parameters, it can be seen that the CrN_x coated samples are more protective and provide better corrosion resistance. This is indicated by lower values of passivation current densities, more electropositive values of corrosion potentials and lower values of corrosion rate.

The EIS analysis with Bode and Nyquist plots, equivalent circuits and representative parameters, confirmed that the chromium nitride coated 310 H SS samples are more protective and provide better corrosion resistance, aspect highlighted by the potentiodynamic method as well.

Conclusions

The aim of this paper was to characterize the chromium nitride thin layers applied on the surface of 310 H stainless steel using the thermionic vacuum arc method.

After deposition, the surfaces of coated samples were analysed using SEM, EDX and XRD techniques. The general corrosion susceptibility of coated samples and the protective character of the ceramic layers were assessed using linear potentiodynamic polarization and EIS methods.

The SEM analysis highlighted the presence of a relatively uniform CrN_x coating layer; the coating layer presents small exfoliated or uncoated areas along the sanding traces.

The surface EDX analysis on the CrN_x coated sample showed that in exfoliated or uncoated area, the elements corresponding to the substrate (Cr, Fe and Ni) are present. An increase in Cr and N contents (up to 37.5% and 11%, respectively) and a decrease in Fe and Ni contents (up to 38% and 12.5%, respectively) was observed on the coated area. This means that on the 310 H stainless steel surface a thin layer of CrN_x has been deposited.

The coating thickness measured by SEM in cross-section was around 303.55 nm.

From GIXRD analysis, the presence in the coating layer of Cr (15%), CrN (17%), $CrN_{0.98}$ (24%) and Cr_2N (27%) compounds was noticed; the coating layer being very thin (about 300 nm), the metal substrate was also identified (which is explained by the appearance of γ-Fe form, 17%).

EIS analysis with Bode and Nyquist plots, equivalent circuits and representative parameters, confirmed that the CrN_x coated 310 H SS samples are more protective and provide better corrosion resistance. The same conclusion was obtained using the potentiodynamic method.

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