

CHARACTERIZATION OF NITROCARBURIZED COATING BY PLASMA ELECTROLYTIC SATURATION

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Abstract

Plasma electrolytic saturation (PES) is an atmospheric pressure plasma deposition which is used for fabrication of nanostructural coatings. This process starts with the appearance of some sparks on the surface and finally by the formation of plasma envelope around the sample, particles and free radicals bombard the surface and diffusion takes place into the work-piece. In this paper, the effect of frequency (500, 1000 and 10000 Hz) as pulse parameters on properties of nitrocarburized layers deposited on AISI 1045 steel were investigated. The analytical characteristics of the coating were assessed using X-ray diffraction (XRD) and scanning electron microscopy (SEM) techniques. The corrosion behavior of coatings was analyzed by potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) in 3.5% sodium chloride solution. Moreover, the microhardness and wear resistance of coated samples were also studied. The results indicated that applying nitrocarburized layer in all cases, improved the corrosion resistance, microhardness and also wear resistance of the substrate. The coatings treated at the frequency of 10000 Hz, had corrosion resistance about 2.4 and 1.4 times higher than those of the samples prepared at the frequency of 500 Hz and 1000 Hz. The surface hardness of 10000 Hz treated sample was about 1040 Vickers, which was more than those of the two other ones. An increase in frequency also caused wear resistance to increase.

Keywords: PES, nitrocarburizing, frequency, corrosion, EIS, microhardness, wear

1 Introduction

AISI 1045 steel are from plain carbon steels family with good mechanical and metallurgical properties, have a relatively affordable price, which has been used in many applications like the cantilever, excel, connecting rod, crankshaft, small gears and also as a particular drilling application in the oil industry [1]. Because of high strength and toughness, good machinability and low cost, steels have been widely used in different industries. However, lower corrosion and wear resistance of steels in comparison with some materials like ceramics causes their usage to be limited. Therefore, different coating processes were used to overcome these problems [2]. Plasma electrolytic is a relatively new process which improves mechanical and chemical properties of metals and alloys. Based on the polarity of the electrode terminals, the process is divided into two branches of anodic [3] and cathodic [4]. In PES method, the sample is cathode and depending on the type of electrolyte, the surface can be subjected to different interstitial or

even substitutional diffusion. In comparison to common saturation methods (such as gas carburizing), the effective diffusion coefficient in PES method increases to 200–250% for non-metals and to 30–50% for metals. Therefore, the coating with favorable thickness may be applied on the different surface in very short time [5, 6].

Nitrocarburizing is a thermochemical process in which carbon and nitrogen free radicals diffuse into base metals at sub-critical temperatures [7]. Common diffusion coating methods cause an increase in temperature of sample and may affect the properties and structure of the base metal. Therefore, for fast modification of surface metals and alloys at very low temperatures, the plasma electrolytic process was used [8]. In a typical PEN/C process, an electrolyte containing carbon-rich and nitrogen-rich materials [9, 10] is used while an additive [11] is added to improve the electrical conductivity of the electrolyte. Since the voltage in this process is very high, quenching the samples in electrolyte cause nitrogen and carbon atoms /free radicals to diffuse into the surface. Therefore, the nitrogen and carbon atoms will not have enough time to precipitate at grain boundary [8]. Rapid quenching of phases formed at high temperatures along with small sparks in the electrolyte caused the average size of nanocrystallites to become less than 100 nm. Acceleration of high energy particles and atoms from electrolyte toward the substrate surface is the main cause of higher diffusion depth in this method compared to other methods. One of the most important features of this method for fabrication of nanostructure is a strong relationship between effective parameters and properties which are related to the nanometric. This process compared to other processes of producing nano structural coatings has a good potential to be in industrial lines. The control of effective factors in this process is easy, while the coating system is rather cheap and also have a potential to be used for complicated shape [12].

The main aim of the present investigation is to demonstrate the feasibility of PEN/C coatings on AISI 1045 substrate and study the effect of frequency on the microstructure, corrosion properties, hardness, and wear behavior of this coating.

2 Experimental

Disk shape steel specimens ($\varnothing$ 30 mm $\times$ 5 mm) were prepared from as-extruded bars. The chemical composition of steel specified with OES analysis is shown in **Table 1**. Before deposition, in order to obtain a mirror surface, the samples were polished by silicon carbide abrasive papers (from 100 to 2000 grit). Then, the samples were immersed into 0.1 M HCl for 20 s and degreased in acetone for 5 min. The samples were biased negatively (as a cathode), while the spiral pipe rings from 316 L stainless steel were used to serve as an anode and also as cooling electrolyte as shown in **Fig. 1**. The coating process was carried out using a pulsed DC power supply at the constant voltage of 380 V, three different frequencies: 500 Hz, 1000 Hz and 10000 Hz and with a fixed duty cycle of 40% for 10 min.

Table 1 Chemical composition of AISI 1045 steel used in the present study

Elements	Fe	C	Si	Mn	P	S	Cr	Ni	Mo
wt%	Balance	0.47	0.21	0.57	0.023	0.028	0.11	0.05	0.01

In order to supply nitrogen and carbon in the envelope packet, an electrolyte was used to be composed of glycerol (3 g l⁻¹) and sodium nitrite (12 g l⁻¹). The electrical conductivity and pH of solution were 95 mS/cm² and 8.1, respectively.

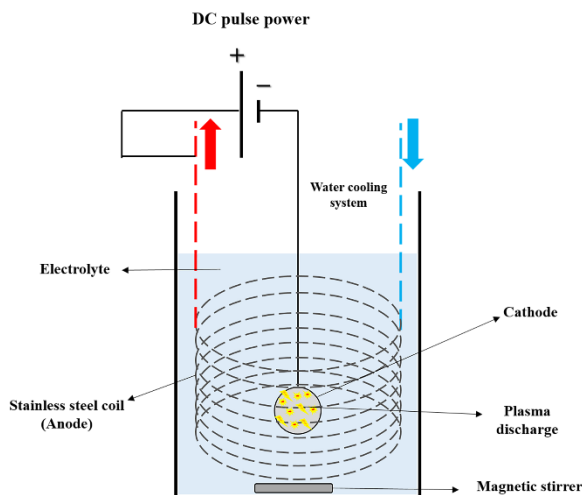


Fig. 1 Schematic diagram of the experimental set-up

The morphology and microstructure of the produced coatings were evaluated by a scanning electron microscope (SEM) model "Camson MV2300 Oxford model 7538" equipped with EDS device. The phase composition of PEN/C coatings were examined by means of a "Philips X'Pert Pro" X-ray diffractometer (XRD) using Cu $K\alpha$ ($\lambda=1.5406 \text{ \AA}$) radiation. Electrochemical measurements were carried out by a conventional three-electrode cell consisting of (i) saturated calomel electrode (SCE) as a reference electrode, (ii) the platinum foil as an auxiliary electrode and (iii) the coated samples as working electrodes. Potentiodynamic polarization studies were conducted from potential of -300 mV to 1000 mV vs. its open circuit potential (OCP) with a scan rate of 1 mV/s using "potentiostat EG & G Model 273". Electrochemical impedance spectroscopy (EIS) measurements were also done at open circuit potential with AC potential amplitude of ± 10 mV with frequency ranging from 100 kHz to 0.01 Hz by "Solarton SI-1260". The collected data for EIS tests were analyzed with an equivalent circuit using "Zview2" software. The microhardness of the untreated and modified-layer was measured using a Vickers microhardness tester (MH3 Coppa). The hardness was measured 5 times under a load of 25 g for 10 s. Dry wear tests were also conducted using Ball on disc instrument with a linear speed of 0.06 m/s, sliding distance of 100 m, with a normal load of 20 N. The wear tests were done against a 5 mm-diameter alumina ball with an initial hardness of 1400 Hv. After each 25 m, the samples were taken out from the device, and the weight loss was measured by a digital balance for an accuracy of 0.1 mg.

3 Results and discussion

3.1 Current-voltage characteristics

The current-voltage diagram of the cell is presented in **Fig. 2**. The current was increased linearly by rising voltage until the voltage of 160 ± 5 V was reached (region I). In this region, the current-voltage behavior of system varied according to Ohm's law ($V=IR$). An increase in voltage up to 270 ± 5 V leads to a rise in current and the peak of current occurs at 12 ± 0.5 A (region II). In region III, the current was dropped dramatically to 4 ± 0.5 A, and the discharge inception happened. Thereafter, increasing voltage did not have any significant effect on current, and only

the surface temperature was raised (region IV), this was in good agreement with literature reports [13].

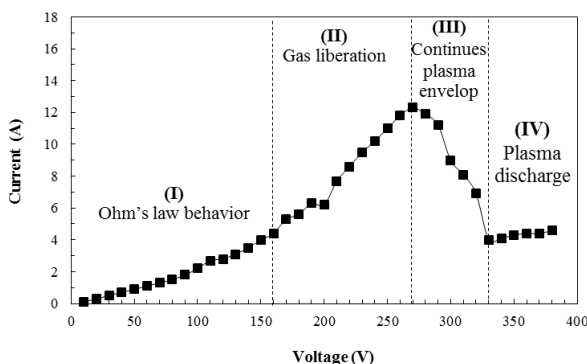


Fig. 2 Typical current-voltage diagram of the sample coated at a frequency of 500 Hz

3.2 Phase analysis

Fig. 3 shows XRD patterns for PEN/C treated samples. The XRD pattern for the PEN/C layer indicated the formation of Fe_3C , $\epsilon\text{-Fe}_{2.3}\text{N}$, $\gamma\text{'-Fe}_4\text{N}$, and $\text{Fe}[\text{Fe}(\text{CN})_6]_3$ phases on the surface layer. The major peak in all the curves belongs to $\epsilon\text{-Fe}_{2.3}\text{N}$, which is one of the most important target phases in the nitrocarburizing process.

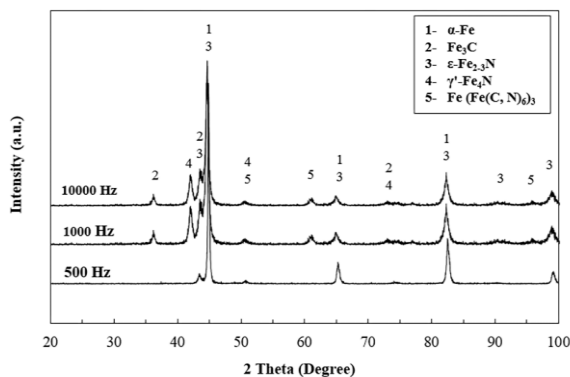


Fig. 3 X-ray diffraction patterns of PEN/C surface layer

Frequency changes only affect the width and intensity of the peaks, as reported in the literature [14]. However, by increasing frequency, the peaks gradually broadened which was an indication of grain refinement. This contributed to the life time of a single arc in the process. At high frequencies (for example 10000 Hz), the pulse width is nearby to the arc's life time, so one or two arcs were formed in each pulse and produced a discontinuous glow discharge. Therefore, the electrolyte had a chance to crystallize the nucleus [15]. Nevertheless, the coated sample at a frequency of 10000 Hz formed smaller grain sizes than that of the others.

The full width at half maximum (FWHM) is commonly used to show the refinement of grain. Grain size determined by Scherrer's equation [16] is also shown in **Table 2**. Formation of the smaller nanocrystalline coating was obtained on the surface by increasing frequency.

Table 2 Grain size determined by Scherrer's method (for major peak)

Frequency (Hz)	FWHM (°)	Crystallite size (nm)
500	0.11	77
1000	0.16	53
10000	0.21	42

3.3 Microstructure of PEN/C coating

Surface morphology images of nitrocarburized layers are shown in **Fig. 4**. Porous morphology with crater-like pores was a feature of the coating produced by this method. It is obvious that an increase in frequency from 500 Hz to 10000 Hz leads to a reduction in the size of pores while the number of pores will rise considerably. This phenomenon attributes to the reduction of input power in each pulse and also lower surface melting. On the other hand, some studies found that in the case of pulse regime, unlike DC regime, the dielectric layer which was formed by glow discharge during the process, was destroyed consecutively [14].

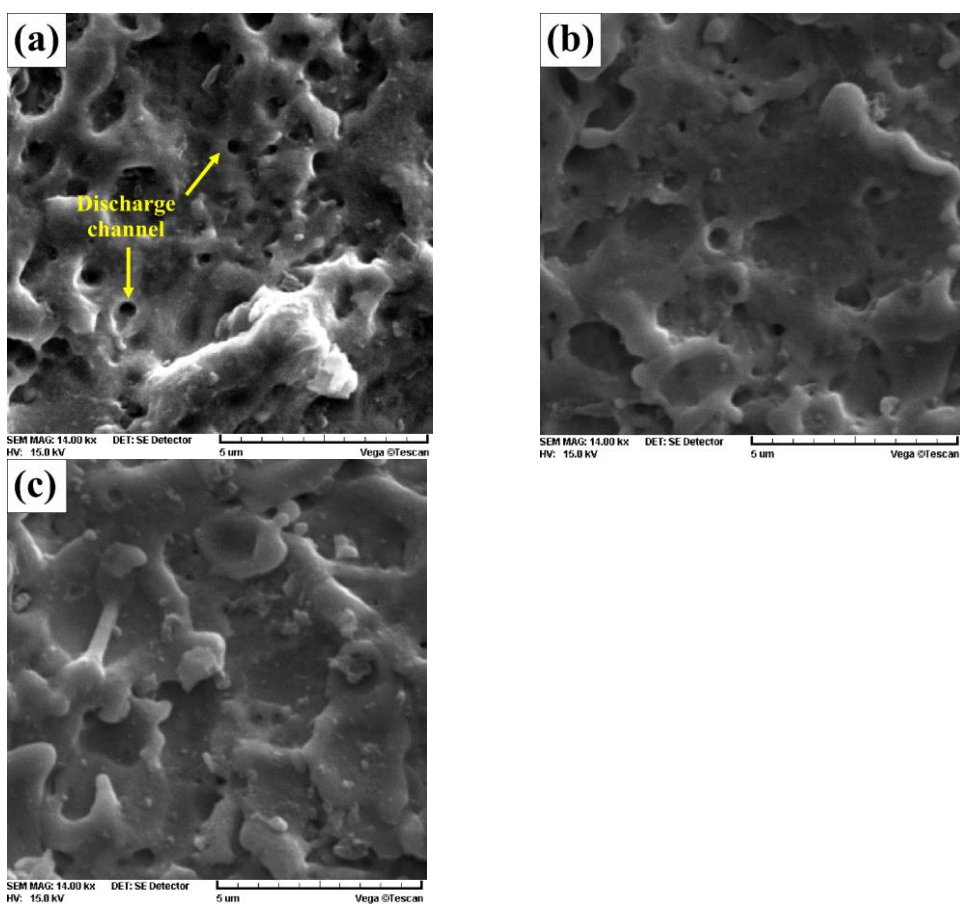


Fig. 4 Surface morphology of the PEN/C coating prepared at different frequencies: (a) 500 Hz, (b) 1000 Hz and (c) 10000 Hz

Fig. 5 shows the cross section images of nitrocarburized layers on AISI 1045 substrate. An increase in frequency caused a lower thickness of the formed layer on the surface. An increase in frequency leads to an increase in the number of pulses per second (or pulse width reduction) and the time for growth for nitrocarburized crystallite was limited. Therefore, there was a short time for diffusion to occur and the thickness of the layer was increased. However, the formation of a more compact layer is related to the existence of very small nanocrystalline grain on the surface. The thickness measurements were done by cross section images. The average thickness of the nitrocarburized layer was approximately 43, 21 and 18 μm , as shown in (**Fig. 5 a, b & c**). In addition, some large pores were observed at coating/substrate interface at a lower frequency (500 and 1000 Hz), whereas large pores were not seen at 10000 Hz. This could be due to more compact layer.

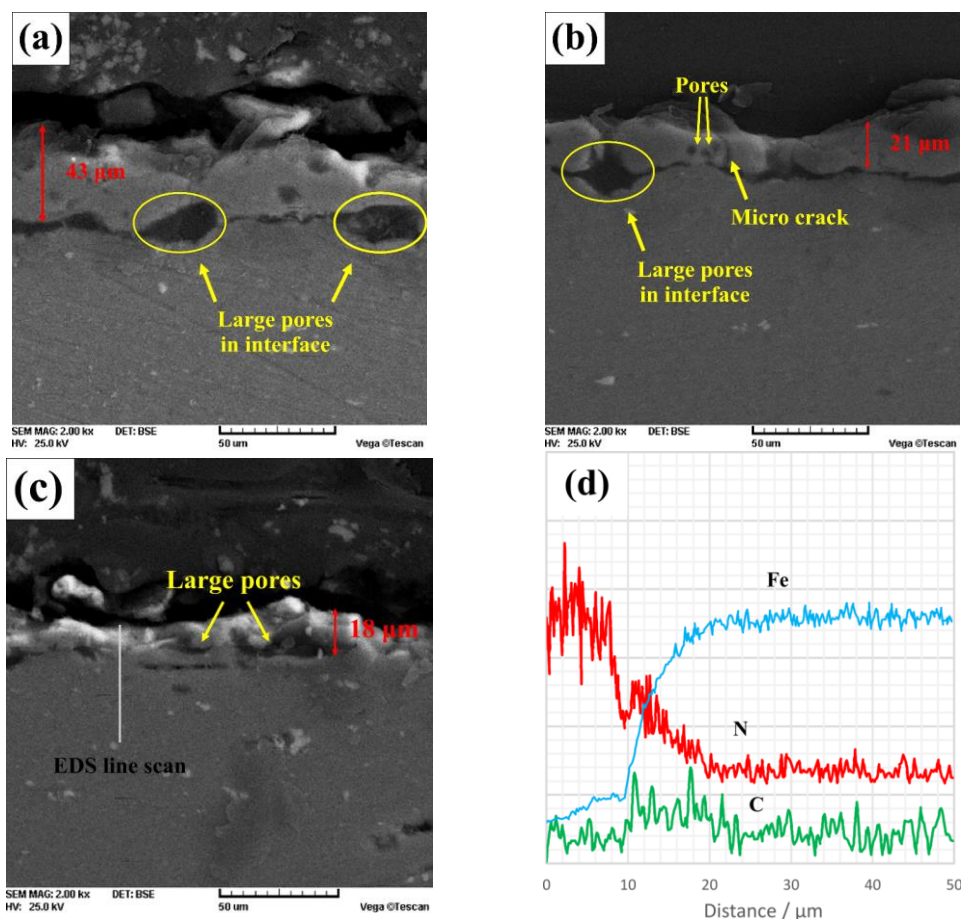


Fig. 5 Cross section of the PEN/C layer prepared at different frequencies: (a) 500 Hz, (b) 1000 Hz, (c) 10000 Hz and (d) EDS line scan for the sample prepared at a frequency of 10000 Hz

3.4 Corrosion behaviour

The potentiodynamic polarization curves of treated and untreated samples are shown in **Fig. 6**. **Table 3** also shows the values of corrosion potential, current density, Tafel slopes (β_a / β_c) and

R_p for all samples which were extracted from the polarization curves. Based on the approximate linear polarization behavior near OCP, the polarization resistance was determined from Stern-Geary equation [17]:

$$R_p = \frac{\beta_a \beta_c}{2.303 i_{\text{corr}} (\beta_a + \beta_c)} \quad (1.)$$

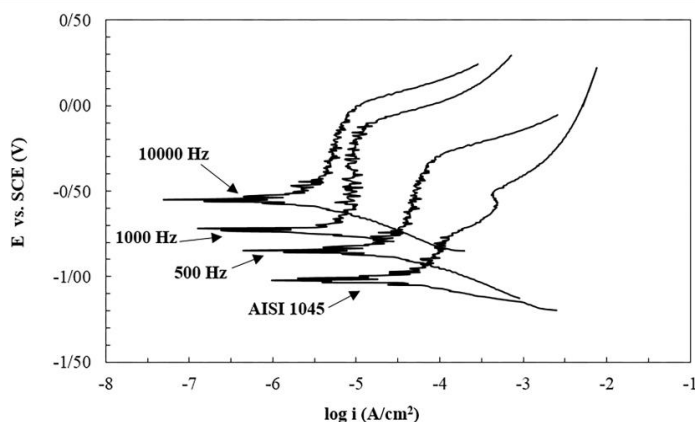


Fig. 6 Polarization curves for untreated and PEN/C samples at different frequencies

The results showed that formation of nitrocarburized films on AISI 1045 steel surface caused a decrease in corrosion current densities and made samples highly corrosion resistant. The cathodic Tafel slopes were almost equal for all samples, but anodic Tafel slopes were changed based on the conditions. The lowest corrosion current density was obtained at the highest frequency (10000 Hz), which was attributed to the presence of more compact layer on the surface. In more porous coated samples, more active areas were exposed to the corrosive solution. This led to an intensification of corrosion for the coated samples was decreased. The samples prepared at the highest frequency (10000 Hz) despite to lower thickness, had the highest corrosion resistance. The main reason for this could be the existence of smaller nanocrystallite and a more compact layer.

Table 3 Corrosion parameters obtained from potentiodynamic polarization tests

Frequency (Hz)	E_{corr} (V)	i_{corr} (A/cm ²)	β_c (V/dec)	β_a (V/dec)
AISI 1045	-1.03	2.12 e-05	0.063	0.218
500	-0.86	8.03 e-06	0.058	0.199
1000	-0.63	1.77 e-06	0.059	0.140
10000	-0.55	1.2 e-06	0.061	0.264

EIS test was also employed to analyze the corrosion characteristics of coated samples. **Fig. 7** shows EIS plots for untreated and PEN/C samples under different frequencies in 3.5 wt% NaCl solution. In order to simulate and analyze the collected EIS spectra, an equivalent electrical circuit was selected to have the best fit on EIS data (**Fig. 8**). **Table 4** also shows the kinetic parameters obtained from EIS plots.

The constant phase element (CPE) was used instead of the ideal capacitive element due to deviations from ideal dielectric behavior which is related to the surface inhomogeneities. The impedance for CPE is expressed by the following equation:

$$Z_{\text{CPE}} = \frac{1}{[A(j\omega)]^n} \quad (2.)$$

where Z_{CPE} is the impedance of CPE [$\Omega \cdot \text{cm}^2$], j is the square root of -1 and ω is the angular frequency ($\omega=2\pi f$). The parameters of n and A , are related to CPE-P and CPE-T, which is the exponent and the admittance for CPE, respectively. The equivalent circuit includes the solution resistance (R_s), the R_p and CPE_p were correspond to the porous layer, whereas the elements R_b and CPE_b are attributed to the barrier layer of the coating [18].

Nyquist plot (**Fig. 7a**) indicated that the corrosion resistance of substrate was increased evidently up to 42 times after PEC/N treatment. In addition, the sample prepared at the highest frequency (10000 Hz) had the highest value for corrosion resistance among all samples. All the coated samples had high values of corrosion resistance (R_b) which was in the range of 16403-39353 Ωcm^2 . This implies that an excellent corrosion resistance was obtained for the metals after surface modification. As it was stated before, the existence of more compact layer at a higher frequency and the less porous structure was the main reason for high corrosion resistance. Moreover, increasing the frequency from 500 Hz to 10000 Hz caused an increase in the value of $\text{CPE}_p\text{-T}$ (as seen in **Table 4**).

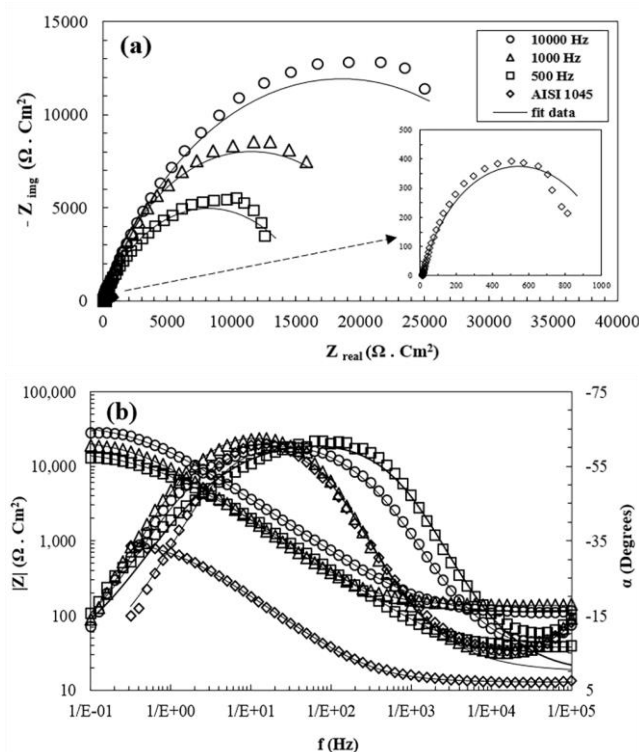


Fig. 7 EIS plots for untreated and treated samples at different frequencies: (a) Nyquist, (b) bode and phase angle diagram

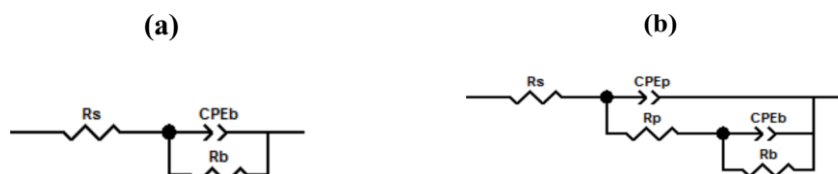


Fig. 8 Equivalent electrical circuit for (a) untreated and (b) coated samples

During the EIS test, porous nitrocarburized layer became denser by passivation, which was reflected in a larger value of CPE_p -P. This response and the high values for R_b obtained from the Nyquist plot indicated the presence of a barrier layer formed on metal after the surface treatment.

Table 4 AC impedance parameters for nitrocarburized samples

Frequency (Hz)	R_s	Porous layer		R_p	barrier layer		R_b
		CPE_p -T	CPE_p -P		CPE_b -T	CPE_b -P	
AISI 1045	10.9	-	-	-	1.9×10^{-3}	0.59	925.3
500	9.4	2.56×10^{-7}	0.88	118	2.74×10^{-5}	0.68	16403
1000	9.6	7.46×10^{-10}	0.98	135	2.07×10^{-5}	0.78	27384
10000	9.6	3.17×10^{-10}	0.98	105	1.34×10^{-5}	0.73	39353

Nevertheless, the electrochemical properties of layers depend strongly on the nanocrystallite size and thickness of layers which was varied with frequency. A Higher value of CPE_p -T for sample produced at lower frequencies showed the presence of porous layer on the surface.

3.5 Microhardness

Increase in surface hardening is one of the most important aims of nitrocarburizing process [19]. Vickers microhardness profiles of untreated and PEN/C samples under different frequencies are measured and illustrated in **Fig. 9**. The surface hardness of coated samples was increased up to 5 times in comparison with that of AISI 1045 substrate. The highest value of hardness was obtained exactly on the top of surface (in the compound layer) due to the formation of carbide/nitride phases which were detected in X-ray diffraction pattern in **Fig. 3**.

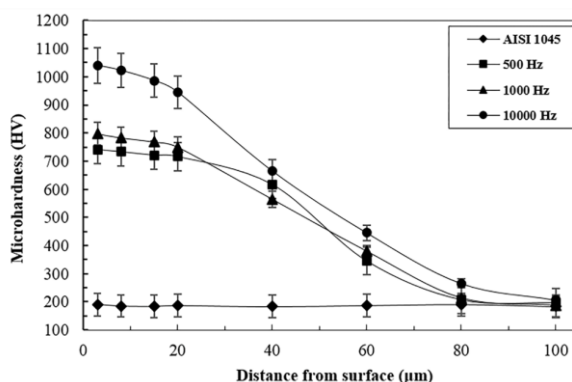


Fig. 9 Microhardness profiles of untreated and nitrocarburized samples at different frequencies

The results show that by moving away from the surface to inside, the value of hardness decreases. The reduction in microhardness confirms that the process is under diffusion control. In addition to the thickness of the layer, another factor which influenced on surface hardness was the formation of nanocrystallite on the surface. According to Hall-Petch equation ($H = H_0 + K_h / \sqrt{d}$), the value of hardness (and also strength) increased according to the pile-up mechanism of dislocations at grain boundaries. Based on this equation, reduction in crystalline size at higher frequency caused an increase in hardness value. Achievement of a moderate hardness profile caused an improvement in wear behavior of nitrocarburized coatings.

3.6 Wear behaviour

Fig. 10 illustrates the weight loss of worn sample vs. sliding distance. The untreated AISI 145 sample showed severe weight loss even at first 25 m of sliding distance which is an indication of low wear resistance. Moreover, the weight loss of this sample after 100 m sliding distance was about 6-10 orders of magnitude higher than that of nitrocarburized samples. Based on Holms-Echard equation [20], the wear resistance directly related to the surface hardness. The wear resistance of coated sample at a higher frequency (10000 Hz) was higher than that of two other lower frequency samples due to the higher hardness and existence of smaller nanocrystallite on the surface.

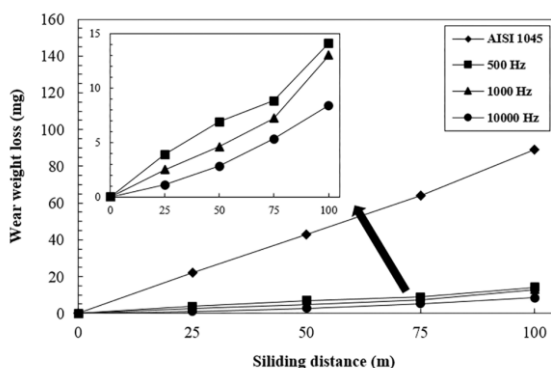


Fig. 10 Weight loss of untreated and nitrocarburized samples as a function of sliding distance at different frequencies

4 Conclusion

The results derived from the present study can be summarized as follows:

1. Nitrocarburized coating prepared at different frequencies was successfully deposited on the steel by pulsed plasma electrolytic saturation technique.
2. The formed layers were mainly composed of nitride, carbide and nitrocarbide phases, such as Fe_3C , $\epsilon\text{-Fe}_{2-3}\text{N}$, $\gamma'\text{-Fe}_4\text{N}$, and $\text{Fe}[\text{Fe}(\text{CN})_6]_3$.
3. Both electrochemical techniques (polarization and EIS) indicated excellent corrosion resistance for nitrocarburized coated steel in 3.5% sodium chloride solution. In EIS test, the corrosion resistance of coated samples was increased up to 43 times rather than an untreated sample. Also, for potentiodynamic polarization tests, the corrosion current density for coated samples reached to the value of $1.2 \times 10^{-6} \text{ A/cm}^2$ in comparison with that of untreated sample ($2.12 \times 10^{-5} \text{ A/cm}^2$).

4. An increase in frequency from 500 Hz to 10000 Hz, not only reduced the size of nanocrystallite to about half its value (from 77 nm to 42 nm) but also improved the corrosion resistance of the substrate (from 16403 $\Omega \cdot \text{cm}^2$ to 39353 $\Omega \cdot \text{cm}^2$). So that the samples prepared at a frequency of 10000 Hz had the highest corrosion resistance.
5. The surface hardness of coated samples was considerably 5.5 times higher than that substrate (190 Hv), and by increasing frequency from 500 Hz to 10000 Hz, this value increased from 741 Hv to 1040 Hv.
6. The weight loss values of coated samples were extremely lower than that of the substrate (decreased to 0.1 of its value) which means to a better wear resistance of those. Moreover, employing higher frequency caused the lower value of weight loss (8.1 mg for 10000 Hz).

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