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CORROSION RESISTANCE OF NITROGEN-DOPED DLC COATINGS PRODUCED IN GLOW DISCHARGE CONDITIONS ON NITRIDED AUSTENITIC STEEL

Nitrogen-doped DLC (diamond-like carbon) coatings were produced on 316L nitrided austenitic steel in direct current and pulsed glow discharge conditions. The chemical composition, surface topography, hardness and corrosion resistance of the obtained carbon coatings were examined. The coatings varied in surface morphology, roughness and hardness. Direct current glow discharge made it possible to produce a coating characterized by lower hardness, greater thickness and higher nitrogen content. The coating featured improved corrosion resistance and adhesion compared to coatings produced in the pulsed process.

Keywords: DLC coating, nitrided layer, DC, pulsed glow discharge, corrosion, adhesion

1. Introduction

Methods for obtaining and structurally modifying DLC (Diamond-Like Carbon) coatings are a rapidly developing field in surface engineering. These coatings are usually produced using two basic methods: Physical Vapour Deposition (PVD) and Chemical Vapour Deposition (CVD) [1]. In PVD methods, graphite is most commonly used as a target [2,3]. In turn, CVD methods utilize hydrocarbon gases, such as methane or acetylene, resulting in hydrogen also being present in the coatings alongside carbon [4-6]. With these methods it is possible to produce coatings on metallic substrates [2,3,6-9], polymers [5,10,11], ceramics [12] and sinters [13]. They differ in properties depending on the ratio of sp^3 diamond bonds to sp^2 graphite bonds. Other components are often added to coatings to modify their structure and properties such as adhesion to the substrate, hardness, elastic modulus or biocompatibility. For this purpose, the following elements are often used: Si [10], Ti [12], Nb [14], W [15], Ag [16], Ge [17]. Nitrogen is also used to modify DLC coatings. An increasing number of studies deals with the use of nitrogen thanks to its ability to improve a coating's mechanical properties and adhesion to the substrate at the same time [18]. Moreover, nitrogen doping reduces a DLC coating's brittleness by increasing the number of sp^2 C=N bonds and reducing the mismatch between the mechanical properties of the coating and of the substrate [19,20]. Introduction of nitrogen into the coating leads to the replacement of hydrogen atoms with nitrogen atoms, which reduces the number of C-H bonds and accelerates the transformation of sp^3 into sp^2. The reason why this transformation takes place is because C-H bonds play an important role in stabilizing the sp^3 structure [21]. Therefore, introduction of nitrogen into the DLC coating results in an increase in graphitization, which on one hand reduces residual stress and hardness, while on the other improves adhesion to the substrate [18,22]. Biological properties can also be improved by introducing nitrogen into DLC coatings [23,24]. The technology developed by the author of this work enables the production of carbon-based coatings under direct current (DC) and pulsed glow discharge conditions. Glow discharge treatment is typically used to produce diffusion layers, such as nitrided [25], nitrocarburized [26] or oxidized [6] layers. One of the key advantages of the system is that it combines two separate processes in a single operation. The first process involves the formation of hard diffusive layers, while in the second one, DLC coatings are deposited on pre-treated material. This is a major advantage as it improves economics. The use of diffusion layers, e.g. a hard nitrided layer, is very important to ensure good adhesion of DLC coatings to the substrate. As a result of their high stress levels, the coatings do not exhibit good adhesion to relatively soft substrates such as steel. Therefore, increasing the hardness of the substrate often results in improved adhesion [13,20]. The corrosion resistance of austenitic steels and modified surfaces is a very important parameter,

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which very often determines whether a given material will be used as a biomaterial. Currently, studies are being conducted on the tribocorrosive properties of DLC coatings applied on 316L steel [27], as well as on the influence of silicon [28] or silver [29] in DLC coatings on their corrosion resistance. Another work [9] deals with the corrosion resistance of DLC coatings exposed to phosphate buffered solution (PBS). Yet another one [30] investigates the potentials and current densities of thick (37 µm) and soft DLC coating produced on nitrided layers. It is noted that the available literature contains only a few reports concerning the testing of nitrogen doped DLC coatings and, in particular, the corrosion testing of such coatings. There is also no comparison provided of the corrosion resistance of coatings produced under DC and pulsed glow discharge conditions on austenitic steels. The current study is intended fill this gap. The aim of the study was to investigate the influence of DC and pulsed glow discharge treatment on the corrosion resistance and the adhesion of N-DLC coatings produced on nitrided 316L austenitic steel.

2. Experimental

The investigations were carried out on 25×4 mm samples made of 316L steel, whose flat surfaces were ground using SiC sandpaper from 240 up to 800 grit. The samples were then cleaned in an ultrasonic bath using acetone. The hardness of 316L steel was 264±3 HV0.05 (corresponding to 2,6 GPa) as measured using a Zwick hardness tester under a load of 490 mN. The coatings were produced in 20 minutes at 350°C in a CH_4:N_2 atmosphere at a working gas ratio of 9:1 and a working chamber pressure of 4.5 hPa. A current of 0.34 A and voltage of 400 V was applied in the direct current (DC) process, while the pulsed discharge process employed a current of 0.44 A and a voltage of 840 V at a frequency of 160 kHz. The coatings were deposited on a previously glow-discharge nitrided layer, which was produced over a period of 6 hours at a temperature of 440°C in an atmosphere consisting of N_2:H_2 at a 1:3 ratio and a pressure of 1 hPa. The nitrided layer had a hardness of 1218±24 HV0.05 (11,9 GPa), as measured using a Zwick hardness tester. The temperature of the process guaranteed the formation of an S-phase layer (expanded austenite) without chromium nitride precipitates. Nanoindentation and reduced modulus measurements of the DLC coatings were carried out on a Hysitron Ti 950 TriboIndenter at a maximum load of 10 mN. The load was selected so that the indentation depth of the indenter did not exceed 1/5 of the thickness of the coating in order to eliminate the elastic interaction of the substrate. The morphology of the surface of the nitrided layer and the coatings was examined using a Veeco atomic force microscope with a MultiMode V controller, while the roughness of the tested surfaces was determined using a WYKO NT9300 optical profilometer. Nitrogen content in the coating was measured with a Thermo Noran energy dispersive spectrometer (EDS) at an acceleration voltage of 10 kV. The set voltage made it possible to determine the content of nitrogen in the DLC coatings without affecting the nitrogen content in the nitrided layer and other elements contained in the steel. Before the test, the materials were thoroughly cleaned with acetone in an ultrasonic washer, rinsed in distilled water and dried with air. The samples prepared for microscopic observation were cut and ground along their cross-sections using SiC abrasive paper (up to 1200 grit) and then polished with a diamond suspension containing 1 µm abrasive particles. The etching of 316L steel was performed using a reagent with the following composition: 50% HCl + 25% HNO_3 + 25% H_2O. The thickness and microstructure of the layer and coatings was measured along the cross-section of the specimens using a Nikon Eclypse LV150N optical microscope. Coating adhesion tests were carried out on a CSM scratch-test device using a Rockwell diamond indenter with a tip radius of 0.8 mm. The test specimen was moved at a constant speed perpendicular to the tip. The coatings' adhesion was alanysed by observing scratches using a Nikon Eclipse LV150N microscope. The scratches had a length of 5 mm, while the contact force varied linearly from 1 to 20 N. Corrosion resistance was tested in a 0.5 M NaCl solution with a pH of 7 by means of the potentiodynamic method from a potential 0.2 V lower than corrosive potential up to 1.5 V. The system consisted of three electrodes: the examined electrode, a saturated calomel electrode (SCE), i.e. the reference electrode, and a platinum gauze as a counter electrode. Prior to the test, the samples were held in solution for 2 hours for stabilisation and to determine their corrosive potential. The polarisation resistance was determined using the Stern method by polarising the test material from a potential 10 mV lower to 10 mV higher than the corrosion potential, at a sweep rate of 0.2 mV/sec. The R_{pol} polarisation resistance was determined on the basis of the angle of the slope gained from the $E = f(i)$ dependence. Corrosion potential E_{corr}, and corrosion current density i_{corr} were determined using the Tafel method. After corrosion testing, the samples were analyzed using a Hitachi S-3500N scanning electron microscope.

3. Results and discussion

Fig. 1 shows the microstructures of DLC coatings deposited on a nitrided layer of 316L steel. The S-phase layer had a thickness of about 9 µm. Thanks to a carefully selected process temperature, no nitride precipitates were visible [25]. The thickness, nitrogen concentration, hardness and reduced modulus of the produced DLC coatings are presented in Table 1. Investigations carried out on the cross-section of the tested materials revealed that the thickness of the coating produced under DC glow discharge conditions (Fig. 1a) was almost twice that of the coating obtained under pulsed conditions (Fig. 1b).

It is noted that a change in the glow discharge conditions has a major impact on the coating deposition rate, which was 6,6 µm/h and 2,7 µm/h respectively for DC and pulsed glow discharge coatings. These differences may be due to the different voltages and currents used during the coating process. In order to maintain the required temperature when coating under pulsed discharge conditions, the current intensity was 0.1 A

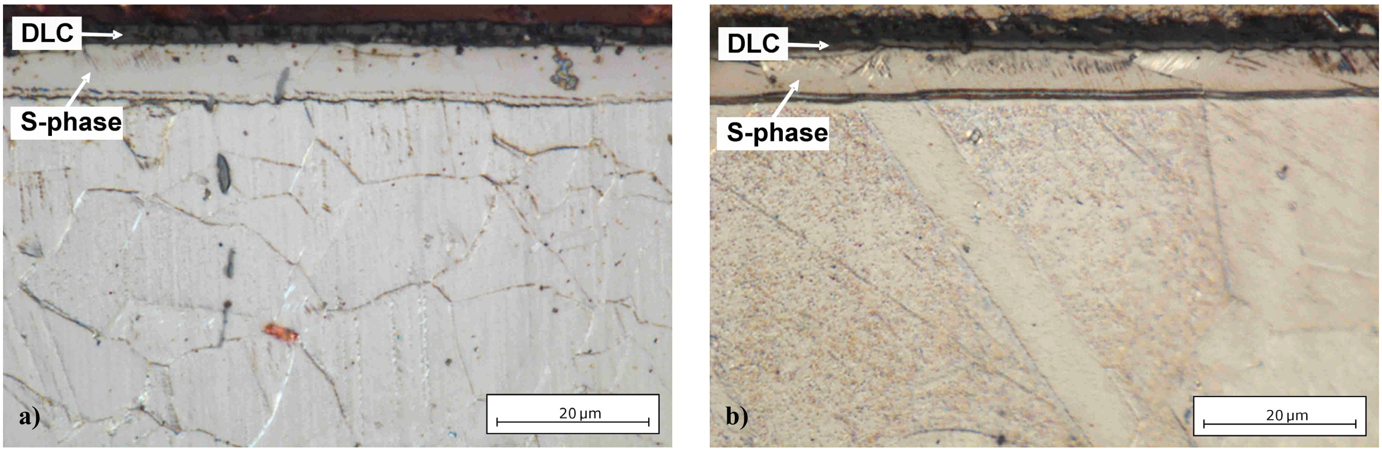

Fig. 1. Microstructure of DLC coatings produced in (a) DC and (b) pulsed glow discharge conditions on nitrided 316L steel

higher while the voltage 440 V greater than in the DC discharge process. Under these conditions, intensified cathodic sputtering may occur while the coating is deposited, resulting in less effective coating thickness gain. The change of discharge type also affected the amount of nitrogen deposited from the atmosphere that was present in the working chamber. A significant difference in the concentration of this element in both the coatings can be observed. For DC discharge, its concentration in the coating was 14.8 at.%, while for the coating deposited using pulsed discharge, the nitrogen content was 9.7 at.%. The hardness and reduced modulus amounted to 2.3 and 27 GPa for coatings with a higher nitrogen content (14.8 at.%) and 9.2 and 111 GPa for coatings with a lower nitrogen content (9.7 at.%). The low hardness and reduced modulus are mainly due to the presence of nitrogen in the coating. This relationship has already been observed by Ruijun et al. [20].

TABLE 1

Thickness (d), nitrogen concentration (N), hardness (H), reduced modulus (Er) of DLC coatings produced in DC and pulsed glow discharge conditions

Sample	d [µm]	N [at%]	H [GPa]	Er [GPa]
DC	2.16±0.09	14.8±1.9	2.3±0.1	27±1
Pulsed	0.90±0.03	9.7±1.0	9.2±0.6	111±3

Figure 2 shows the surface topographies obtained with the AFM microscope and the *Ra* parameters measured with the optical profilometer. It was observed that glow discharge nitriding significantly changes the appearance and roughness of the surface, which increased from *Ra* = 62 nm to 158 nm (Fig. 2a,b). The increase in the roughness of the layers is mainly due to the relief that appears at the grain boundaries of nitrided steel. The formation of a coating under DC conditions results in a slight increase of the Ra parameter to 162 nm (Fig. 2c) as compared to a nitrided layer. On the other hand, the coating with a lower thickness and nitrogen content, produced under pulsed glow discharge conditions, showed the highest roughness, i.e. *Ra* = 182 nm (Fig. 2d). It was also observed that the morphologies of both coatings differ significantly from each other. Studies by Srinivasan et al. [23] show that the presence of nitrogen may lead to the coating surface becoming smoother. Coatings produced under DC conditions, where a higher concentration of nitrogen is observed, showed lower roughness values compared to coatings applied under pulsed discharge conditions containing a lower concentration of nitrogen (Table 1).

The hardness and nitrogen content values obtained correlate with the scratch-test results (Fig. 3). It is observed that the coating with a higher nitrogen content, lower hardness and higher smoothness sustained almost no damage. In Fig. 3a, only a slight abrasion of the coating by the indenter is observed due to a deformation of surface irregularities. The coating had not delaminated in the test. For the coating produced under pulsed discharge conditions, a distinct permanent deformation of the coating took place at 4.7 N, while the first single chips formed at approx. 15 N as shown in Fig. 3b. It is noted that this coating is characterized by lower nitrogen content and increased hardness (brittleness), which contributes to its weaker adhesion. However, the coating did not undergo complete delamination during the test,which was conducted up to a load of 20 N.

Ruijun et al. [20] conducted a study of nano-scratch DLC coatings doped with 4.1 to 7.8 % at. nitrogen produced by the ECWR-CVD method. The study was carried out at much lower loads, i.e. from 1 mN to 10 mN using a conical diamond indenter. The coatings did not chip and mainly underwent plastic deformation. It was noted that the degree of coating deformation increased with nitrogen concentration. The coating with the lowest nitrogen content was characterized by the highest hardness value (9.07 GPa).

The formation of a nitrided layer consisting of expanded austenite caused a very significant increase in the corrosion resistance of 316L steel in a 0.5 M NaCl solution, as shown in Fig. 4. In turn, Table 2 summarizes the electrochemical parameters for 316L steel in initial state, after glow discharge nitriding and after coating deposition. The increase in breakthrough potential from 377 to 1500 mV and decrease of anodic current density of the nitrided layer are particularly noticeable. The surface of 316L steel underwent pitting corrosion from 377 mV,

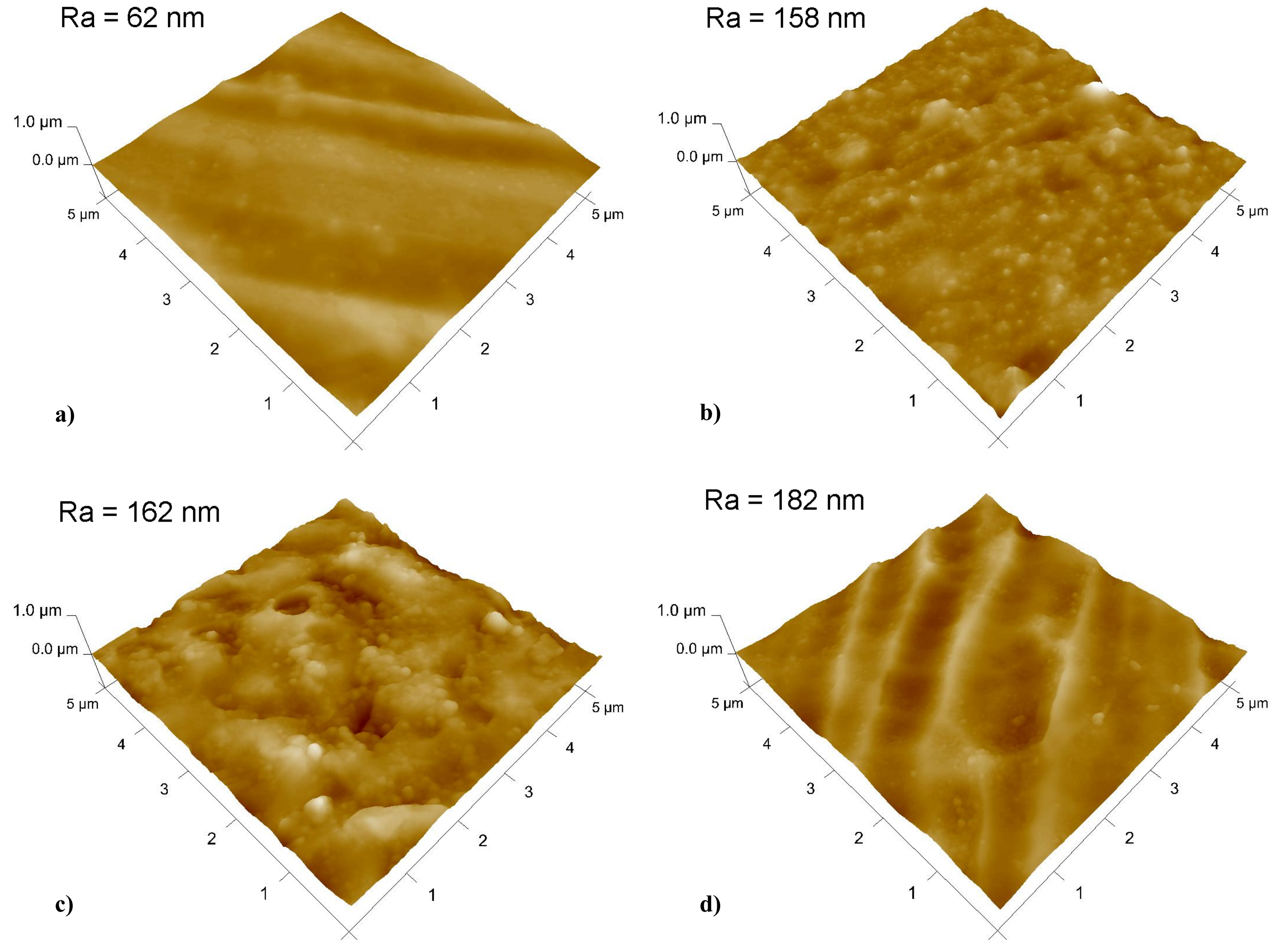

Fig. 2. AFM images and roughness of 316L steel (a) in initial state, (b) after glow-dischare nitriding and DLC coating produced in (c) DC and (d) pulsed glow discharge conditions

as observed in Fig. 5a. Comparing the steel in its initial state and with a nitrided layer, no significant changes in the corrosion potential (E_{corr}) and corrosion current density (i_{corr}) were observed, while the polarization resistance (R_{pol}) decreased 3-fold from 1.09 to 0.36 MΩ·cm^2. However, the change of the R_{pol} did not affect the durability of the passive film formed on the expanded austenite layer as no pits were observed in the entire polarization range up to 1500 mV, as shown in Fig. 5b.

The deposition of DLC coatings on the nitrided layer resulted in an additional improvement of the corrosion resistance of steel. For the coating produced under DC glow discharge condi-

TABLE 2

Electrochemical parameters for 316L steel in initial state (IS), after glow dischare nitriding (PN) and coatings produced in DC (C-PN-DC) and pulsed (C-PN-Pulsed) glow discharge conditions

Sample	E_{corr} [mV]	i_{corr} [μA/cm^2]	R_{pol} [MΩ·cm^2]	E_{pit} [mV]
IS	–143	0.021	1.09	377
PN	–146	0.015	0.36	≥1500
C-PN-DC	–75	0.056	1.40	chipping ~1300
C-PN-Pulsed	60	0.001	6.39	delamination ~1100

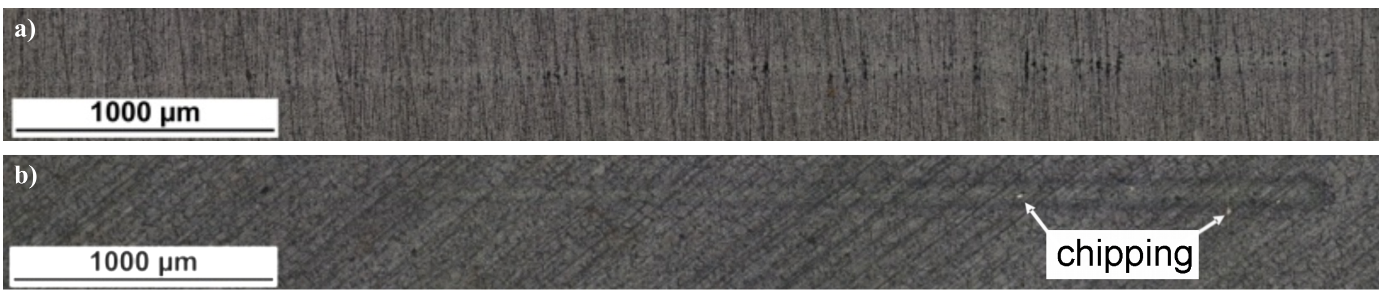

Fig. 3. Scratch images of DLC coatings produced in (a) DC and (b) pulsed glow discharge conditions on nitrided 316L steel

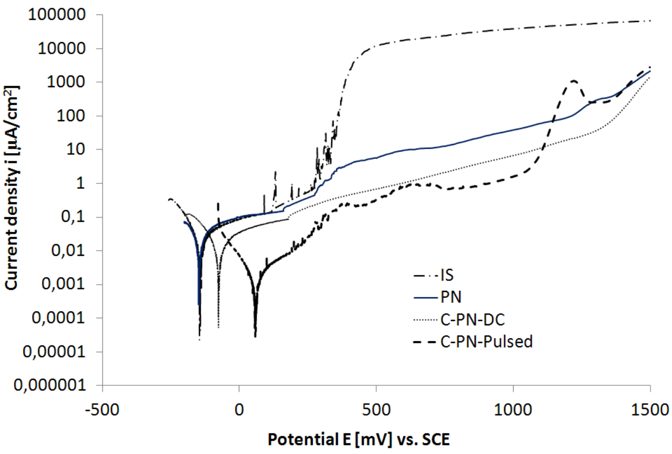

Fig. 4. Anodic polarization curves for 316L steel in initial state (IS), after glow-dischare nitriding (PN) and coatings produced in DC (C-PN-DC) and pulsed (C-PN-Pulsed) glow discharge conditions

tions, there was an increase in corrosion potential up to –75 mV, corrosion current density up to 0.056 μA/cm^2 and polarization resistance up to 1.40 MΩ·cm^2. The results in Fig. 4 show that current densities are lower than those of the nitrided layer in the entire anodic polarization range. At a value of about 1300 mV, an increase in current density is observed, which is most likely the result of the coating slowly beginning to chip, as shown in Fig. 5c. This coating exhibits very good adhesion to the nitrided substrate (Fig. 3a), but due to the action of aggressive Cl^- ions, which penetrate discontinuities in the structure of the coating, it may undergo local delamination. In this case, however, no pits were observed. Deposition of the coating under pulsed glow discharge conditions increased the corrosion potential to 60 mV and decreased the corrosion current density to 0.001 μA/cm^2. It also significantly increased the polarization resistance to 6.39 MΩ·cm^2. This coating was found to have the lowest anodic current density in the range up to 1100 mV. Above this value, an increase in current density is observed, which, however, is not related to the formation of pits, but to the delamination of the DLC coating, as shown in Fig. 5d. The chipping of the pulsed discharge deposited coating during the potentiodynamic tests is related to its weaker adhesion to the substrate, which was confirmed in the scratch-test (Fig. 3b). A higher concentration of nitrogen in the structure of the DLC coating produced via DC glow discharge leads to the graphitization of the structure, i.e. an increase of sp^2 bonds [18]. Under such conditions, the

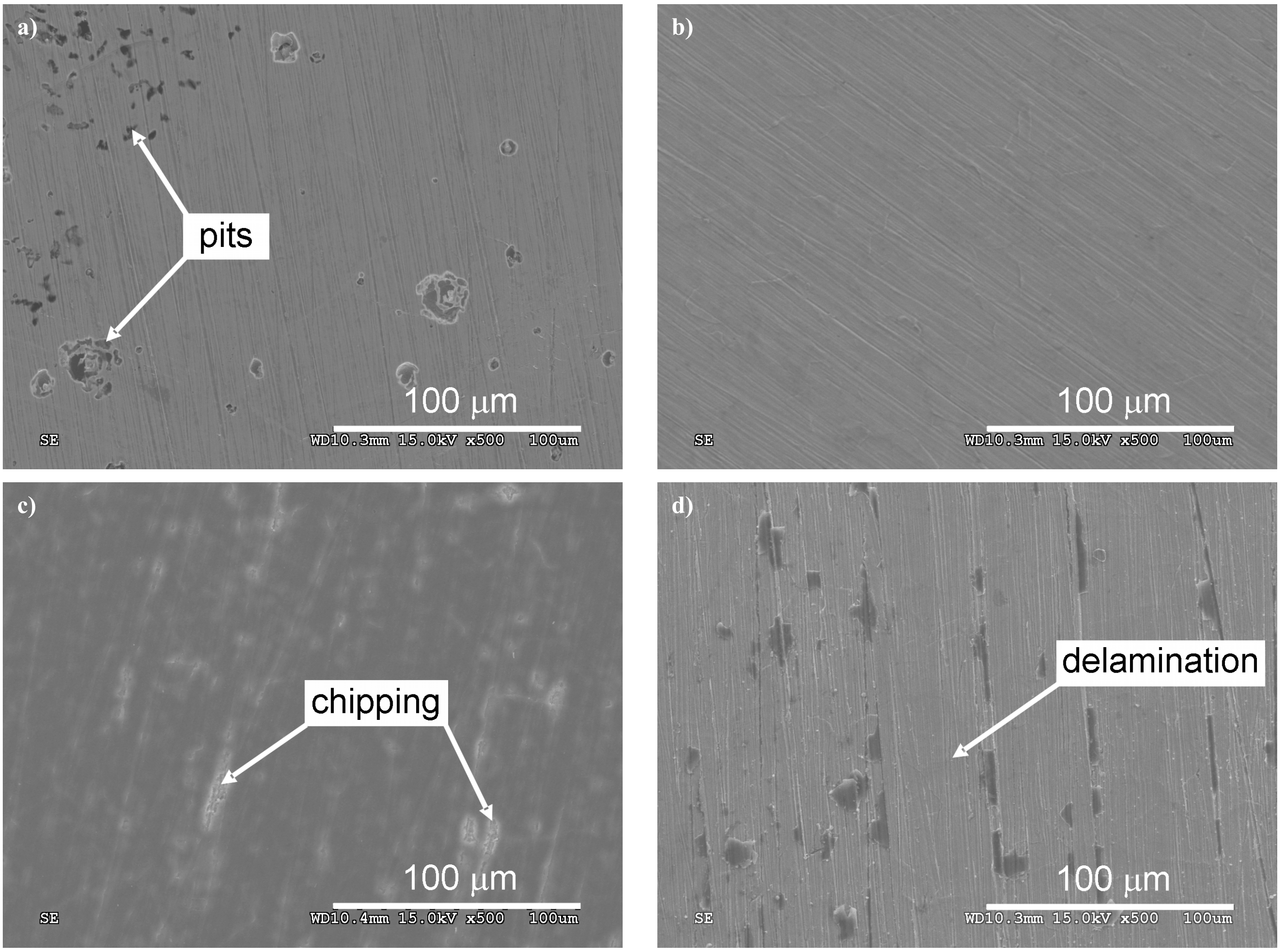

Fig. 5. SEM images of surfaces after corrosion tests of 316L steel (a) in initial state, (b) after glow dischare nitriding and coatings produced in (c) DC and (d) pulsed glow discharge conditions

residual stresses in the coating are also reduced, as is the hardness of the coating (Table 1), which leads to an improvement in its adhesion. The increase of sp^2 bonds in the DC deposited coating is evidenced by lower polarization resistance compared to the pulsed glow discharge coatings. Sharifahmadian et al. [21] conducted corrosion tests of a DLC coating doped with nitrogen, which was produced in the PACVD process on nitrided 316 steel. The corrosion medium used consisted of a 3.5% NaCl solution. The result was a shift in corrosion current density and corrosion potential towards lower values in comparison to the coating without added nitrogen. It is noted that the corrosion potential of the coating was lower (–391 mV) and the corrosion current density higher (5.24 $\mu A/cm^2$) compared to the electrochemical values of coatings produced in this study (Table 2).

4. Conclusion

It can be concluded that DC glow discharge treatment produces thicker coatings with higher nitrogen concentrations. Such coatings also show a lower hardness and roughness of the surface compared to coatings produced in the pulsed discharge process. The above parameters have a very big influence on coating adhesion to the substrate and on corrosion resistance. The coating produced under pulsed glow discharge conditions delaminated at a potential of 1100 mV, most likely because of the lower content of nitrogen and weaker adhesion. The coating was characterized by the highest polarisation resistance value, which most likely resulted from a greater share of sp^3 bonds in the coating structure. However, in order to guarantee very good corrosion resistance of 316L steel and good coating adhesion, direct current glow discharge treatment appears to be a more reliable solution.

In order to characterize the coatings more precisely and to determine the influence of the type of glow discharge process on their properties, the results of structural studies obtained using Raman spectroscopy will be the subject of the next studies.

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