

PLASMA ELECTROLYTIC SATURATION OF 316 L STAINLESS STEEL IN AN AQUEOUS ELECTROLYTE CONTAINING UREA AND AMMONIUM NITRATE

PLAZEMSKO ELEKTROLITSKO NASIČENJE NERJAVNEGA JEKLA 316 L V VODNEM ELEKTROLITU S SEČNINO IN AMONIJEVIM NITRATOM

Levent Cenk Kumruoglu, Ahmet Özel

University of Sakarya, Engineering Faculty, Metallurgy and Materials Department, Esentepe-Sakarya, Turkey
lkumruoglu@sakarya.edu.tr

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Plasma electrolytic saturation (PES) is an environmentally friendly electrochemical process that allows altering the surface chemistry and grain size of metallic substrates, negatively biased in an aqueous electrolyte containing ionic species such as N, O and C. Wear- and corrosion-resistant nanocrystalline layers consisting of carbides, nitro carbides, borides and nitro-carbon oxides could be fabricated with PES in short treatment durations. In this study, PES was performed on 316 L stainless steel in an electrolyte containing urea and ammonium nitrate with several treatment durations from 5 s to 30 min. The surface morphology, topography and microstructure were investigated with X-Ray diffraction, optical microscopy, scanning electron microscopy with energy dispersive spectroscopy, a surface profilometer and microhardness testing. The wear and friction properties were evaluated using a ball-on-plate, linear, reciprocating wear test at 1 N to 3 N applied loads with an alumina ball against both the treated and untreated substrates. It was found that PES can increase the wear resistance and mechanical properties of 316 L stainless steel.

Keywords: plasma electrolysis, saturation – diffusion, nitriding, wear, 316 L

Plazemsko elektrolitsko nasičenje (PES) je okolju prijazen elektrokemijski postopek, ki omogoča spreminjanje površinske kemije in velikost zrn v kovinski podlagi, ki je neustrezna v vodnem elektrolitu, ki vsebuje ione N, O in C. V kratkem času je mogoče s PES izdelati obrabno in korozijsko obstojne nanokristalne plasti iz karbidov, nitrokarbidov, botidov in nitro-karbo-oksidi. V tej študiji je bil PES uporabljen pri nerjavnem jeklu 316 L v elektrolitu, ki je vseboval sečnino in amonijev nitrat in so bili časi obdelave od 5 s do 30 min. Preiskovana je bila morfologija površine, topografija in mikrostruktura z rentgensko difrakcijo, svetlobno mikroskopijo, vrstično elektronsko mikroskopijo, energijsko disperzijsko spektroskopijo, s površinskim profilometrom in meritvijo trdote. Obraba in torne lastnosti so bile ocenjene z metodo kroglica na plošči z linearnim izmeničnim obrabnim preizkusom pri obtežbi od 1 N do 3 N s kroglico iz Al₂O₃ na obdelani in neobdelani površini. Ugotovljeno je bilo, da PES lahko poveča odpornost proti obrabi in izboljša mehanske lastnosti nerjavnega jekla 316 L.

Ključne besede: plazemska elektroliza, nasičenje – difuzija, nitriranje, obraba, 316 L

1 INTRODUCTION

To improve and alter the surface properties of metallic substrates with a plasma-electrolytic-saturation process,¹⁻⁷ interstitial atoms like C, N, O and species are diffused into the surface of a biased substrate from an aqueous medium containing interstitial atoms under the appropriate plasma conditions like specific temperature, potential, duration.¹⁻⁵ Plasma electrolysis is a special thermo-chemical-mechanical process employing electrolysis in an aqueous solution under particular conditions, for instance specific potential, current, electrolyte and durations.¹⁻⁷ Plasma electrolysis is a complex process, which couples physical metallurgy and electrochemical events, such as heating a work piece in a cathodic regime^{2,4} (gas liberation, spark ignition, continuous plasma envelope, and arcing regime), where phase transformations and deformations occur simultaneously.

For the PES process, the selection of an electrolyte is relatively simple; for example, for the nitrocarburing the electrolyte is composed of C/N-containing organic com-

pounds in a conductive solution, e.g., KCl or Na₂CO₃. In contrast to conventional pack and liquid-based treatments using cyanide, various ecologically friendly organic compounds can be used to provide, with plasma thermal decomposition, desirable carbon/nitrogen ions and/or atoms for the treatment. PES can have a considerable strengthening effect on steel substrates. Even though a wide range of materials has been treated using a plasma-electrolytic-saturation technique,² very few studies exist in the literature that report on the wear resistance of oxy-nitrided or oxy-carbon-nitrided 316 L stainless steel. To evaluate the saturation phenomena and wear behaviour of the oxy-nitrided layer, different electrolytes, process durations and dry, reciprocating, sliding tests have been conducted. The modified phases on the surface were investigated with XRD (Rigaku) applying the standard 2θ -scan from 20 to 90 degrees and cross-sections of saturated layers were revealed with optical microscopy (Nikon) and scanning electron microscopy (JEOL 6600) with energy dispersive spectroscopy. The

surface roughness and microhardness of the samples were measured using a surface profilometer (Tencor P6) and a microhardness tester (Shimadzu HMV).

2 EXPERIMENTAL STUDIES

The testing coupons (10 mm × 20 mm × 1.5 mm) made from 316 L stainless steel were used as the substrate materials. The nominal composition of a substrate in mass fractions was Cr 18 %, Mn 1.6 %, Ni 10 %, C 0.02 %, Mo 2.1 %, N < 0.02 %, Fe balance. Prior to PES, the substrates were polished to $R_a \approx 0.05 \mu\text{m}$ from 240 to 1200 grit with the emery paper and then with the alumina solution. The PES was carried out by using 24 kW DC power supply and in a specially designed instrumented rig shown in **Figure 1**. Two types of electrolyte at 25 °C were chosen as given in the following formulas, $m(\text{E1}) = 4 \text{ kg urea, } 40 \text{ g KOH and } 4 \text{ l di-water (cond. } 8 \text{ mS)}$ and $m(\text{E2}) = 4 \text{ kg ammonium nitrate, } 4 \text{ l di-water, } 20 \text{ g KOH (cond. } 180 \text{ mS)}$. The substrates were biased negatively and treated for 5 s and (1, 15 and 30) min at the potentials varying from 100 V (for E2) to 300 V (for E1). The breaking potentials were 550 V for E1 and 350 V for E2. The electrolyte was pumped from the container to the bottom surface of the samples and then the potential was increased manually to fix the plasma envelope. The treated surfaces were tested using the following parameters: the normal loads of 1 N and 3 N, the track length of 10 mm, the frequency of 5 Hz, the sliding speed of 0.1 m s^{-1} and the sliding distances of 100 m and 1200 m. The average value of the friction coefficient was measured in both reciprocating directions of the bearing ball. The CSM tribometer was used for the wear tests. Before and after each test, both the sample and the alumina ball (10 mm) were cleaned ultrasonically in acetone and dried with hot air.

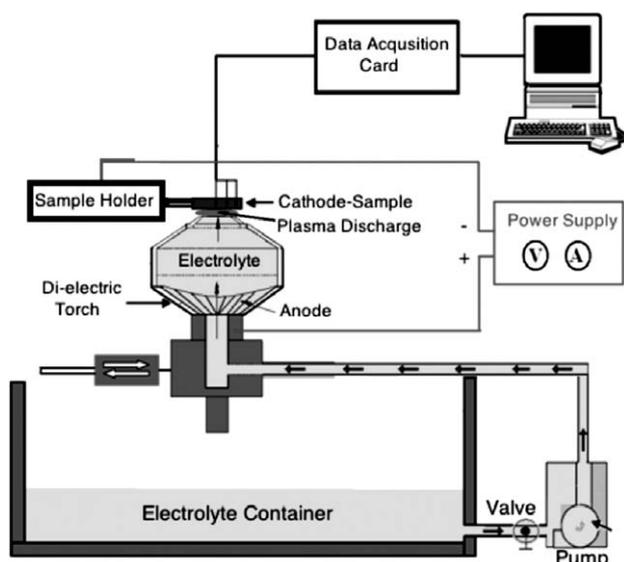


Figure 1: Schematic drawing and picture of the PES setup

Slika 1: Shematski prikaz PES-sestava

3 RESULTS AND DISCUSSION

Recent studies have revealed that plasma saturation can produce compound nitrides and oxide phases, e.g., $(\text{Fe,Cr})_2\text{O}_4$, $\text{Fe}_3\text{O}_4 + \text{FeN}$, CrN , $\gamma_{(\text{N})}$.³⁻⁶ The XRD patterns of the samples treated with E1 and E2 are given in **Figures 2a** and **b**. SEM and OM studies revealed that the surfaces consist of Fe, Cr_2O_4 , Fe_3O_4 , $\text{FeN}_{0.076}$ and a γ_{N} saturated layer that is $3 \mu\text{m}$ to $40 \mu\text{m}$ thick. In addition to the mixture phases, Fe_2O_3 was detected in the sample saturated in urea for 5 s. According to the Fe-O binary system and the phase-stability diagram, Fe_2O_3 and Fe_3O_4 can be formed at 400 °C, depending on the oxygen concentration, and FeO is not stable below 570 °C. In the Fe-O system, a larger amount of oxygen causes a formation of hematite at high temperatures. However, in the H_2 atmosphere, Fe_2O_3 may be reduced to Fe_3O_4 .⁸ In plasma electrolysis hydrogen can be produced at the cathode.³ Hence, longer plasma durations may cause the formation of larger and thicker amounts of Fe_3O_4 and a broadening of the XRD lines. SEM-EDS analyses proved the nitrogen, oxygen and carbon diffusions for both plasma processes (**Figure 3**). The microhardness testing was performed on the saturated layers. The maximum value of 535 HV was observed for the PES using the urea electrolyte for 30 min. However, the hardness testing

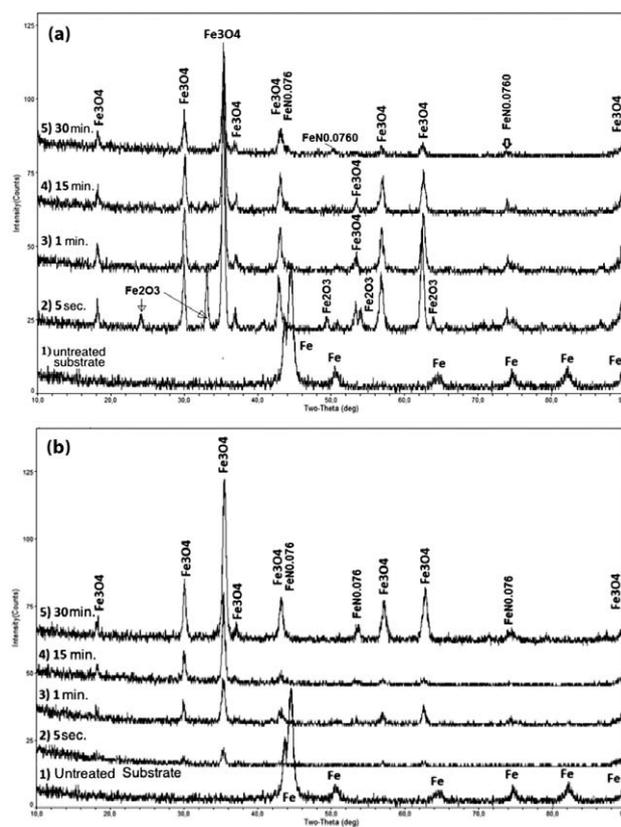
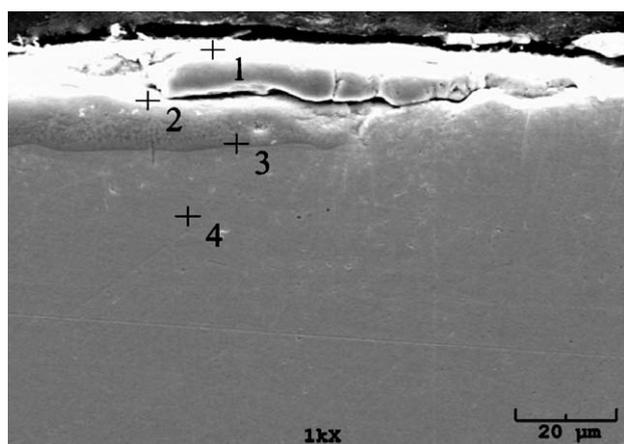


Figure 2: XRD of substrates saturated with electrolytic plasma with: a) urea and b) with ammonium nitrate

Slika 2: XRD podlage, nasičene z elektrolitsko plazmo: a) s sečnino in b) z amonijevim nitratom



| 1 | w/% | 2 | w/% | 3 | w/% | 4 | w/% |
|----|-------|----|-------|----|--------|----|-------|
| C | 21.41 | C | 1.007 | C | 3.120 | C | 3.385 |
| N | 0.000 | N | 0.678 | N | 0.498 | N | 0.000 |
| O | 41.10 | O | 38.96 | O | 19.400 | O | 2.017 |
| Fe | 35.06 | Cr | 9.472 | Cr | 22.418 | Cr | 18.07 |
| Ni | 1.898 | Fe | 47.94 | Fe | 44.217 | Fe | 68.78 |
| Mo | 0.519 | Ni | 1.579 | Ni | 9.984 | Ni | 7.540 |
| | 100.0 | Mo | 0.354 | Mo | 0.363 | Mo | 0.199 |
| | | | 100.0 | | 100.0 | | 100.0 |

Figure 3: Cross-section SEM view and EDS analysis of a saturation layer (1 min with E1)

Slika 3: Prerez (SEM) in EDS-analiza nasičene plasti (1 min z E1)

cannot be performed on the PES substrates using an ammonium nitrate electrolyte because of the rough and thin hardened layer. On the other hand, the surface hardness was measured as 550 HV using light indentation loads such as 10 g (**Figure 4**). Recently, the post-oxidation treatment was studied on nitrided layers.⁹ The studies suggest that a thin Fe_3O_4 layer improves the wear resistance of a nitrided layer.⁹ PES may be described as a single-step compound diffusion process that enables both nitriding and post oxidation. Nitriding can be performed in a relatively low temperature range of 400–600 °C.^{2,3} In PES, the surface of the substrate may reach this temperature in a few seconds.³ It is possible to heat a substrate

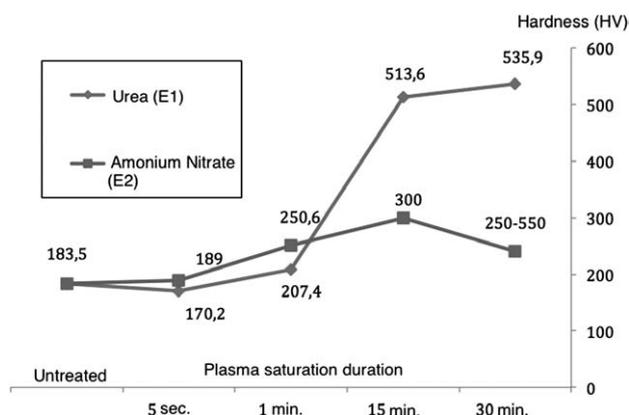


Figure 4: Cross-sectional microhardness profile of saturated samples
Slika 4: Mikrotrdota na prečnem prezu nasičenih vzorcev

above the nitriding temperatures; if the temperatures increase the oxidation may occur on the nitrided layer because of the oxygen atoms in the electrolyte. The wear behavior and the friction coefficient of the saturated layers sliding against the alumina ball 10 mm under a load of 3 N is shown in **Figures 5a** and **b**, respectively. It can be seen that the wear resistance of the substrate saturated for (1, 15 and 30) min in the E2 electrolyte is much greater than that of the untreated substrate. The untreated sample was marked with the symbol "0". Also, there are a small drop for the PES 1 min and sharp drops for the PESs 15 min and 30 min in the friction coefficient over the sliding distance 1200 m. The Fe_3O_4 layer on the saturated steel may cause this kind of friction behavior.⁹ The wear resistance of the substrate treated with the urea electrolyte was improved after the PES 15 min. On the other hand, a good result was observed for the PES 3 min. This may be related to both an increase in the surface hardness and the thickness of the oxynitrided layer. The thin layers (treated for 5 s) were probably delaminated at the onset of the wear test because there was no significant change in the friction coefficients of both electrolyte groups. Below the sliding distance 100 m the wear resistance of the PES layers treated for 5 s in the ammonium nitrate electrolyte was 2.5 times better than that of the untreated substrate, while for the sample treated for 30 min the wear resistance was 10 times higher than that of the untreated one and the worn track was very thin and hardly

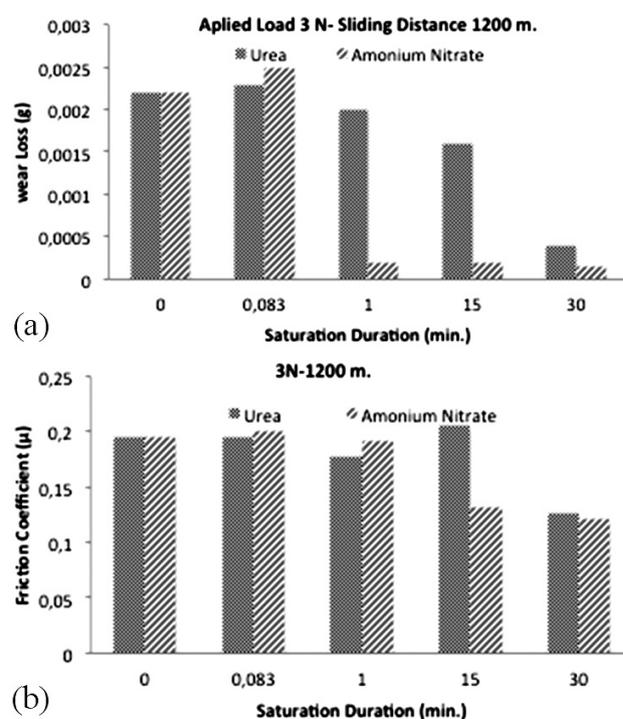


Figure 5: a) Wear properties of PES layer for 3 N and 1200 m sliding distance and b) the friction coefficient

Slika 5: a) Obrabne lastnosti PES-plasti pri 3 N in 1200 m drsne poti b) torni koeficienti

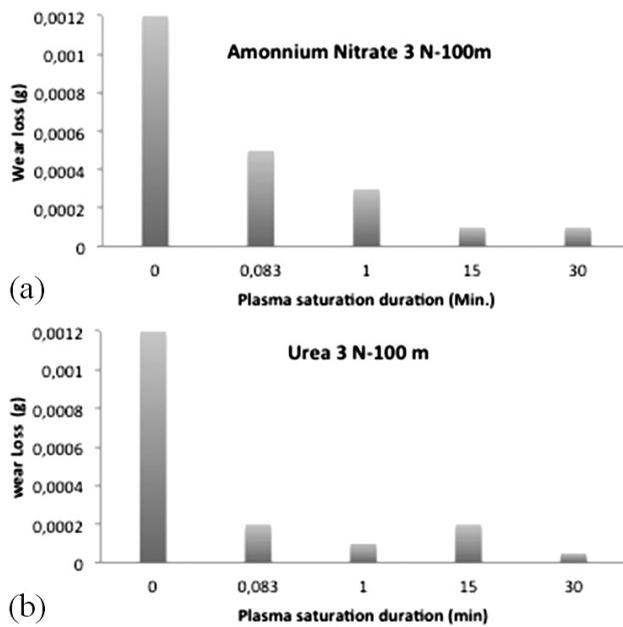


Figure 6: Wear properties of PES layer for 3 N and 100 m sliding distance for both electrolytes

Slika 6: Obrabne lastnosti PES-plasti pri 3 N in 100 m drsne poti za oba elektrolita

observed (**Figure 6a**). On the other hand, the wear-test results for the samples treated with the urea solution were slightly better than the results for the ammonium nitrate electrolyte (**Figure 6b**).

4 CONCLUSIONS

The electrolytes containing urea and ammonium nitrate can be used for the surface saturation of 316 L stainless steel. The PES layers consist predominantly of the FeCr_2O_4 , FeN and Fe_3O_4 phases. In short PES dura-

tions, Fe_2O_3 was observed with the other phases because of the low substrate temperature. At the beginning of PES, the expanded austenite can be formed with an atomic diffusion; however, an increase in the temperature of the substrate gives rise to a formation of metal (nitro) oxides. The H_2 gas at the cathode causes a reduction of hematite; so a stable mix of the FeCr_2O_4 , $\text{FeN}_{0,076}$ and Fe_3O_4 phases can be formed on the surface. These phases increase the hardness and reduce the friction coefficient, thus increasing the wear resistance. There was no scaling or delaminating of the oxide layers under the all-mechanical tests.

The value of the breaking potential depended on the conductivity of the electrolyte. The breaking potentials of the electrolyte were 550–600 V for the conductivity of 8 mS (E1) and 300–350 V for the conductivity of 180 mS (E2).

The layer thickness increases with the treatment time, resulting in an associated increase in the surface hardness.

5 REFERENCES

- ¹ M. Aliofkhaeze, A. S. Rouhaghdam, T. Shahrabi, *Journal of Alloys and Compounds*, 460 (2008), 614–618
- ² A. L. Yerokhin et al., *Surface and Coatings Technology*, 122 (1999) 2–3, 73–93
- ³ C. Cionea, PhD thesis, The University of Texas At Arlington, 2010
- ⁴ T. Paulmier, J. M. Bell, P. M. Fredericks, *Thin Solid Films*, 515 (2007), 2926–2934
- ⁵ P. Taheri, C. Dehghanian, *Transaction B: Mechanical Engineering*, 16 (2009) 1, 87–91
- ⁶ L. C. Kumruoğlu, A. Özel, *Materials and Manufacturing Processes*, 25 (2010) 9, 923–931
- ⁷ L. C. Kumruoğlu, D. A. Becerik, A. Ozel, A. Mimaroglu, *Materials and Manufacturing Processes*, 24 (2009), 781
- ⁸ Lin et. al., *Thermochimica Acta*, 400 (2003), 61–67
- ⁹ M. L. Fares, K. Chaoui, J. Le Coze, *Surf. Interface Analysis*, 41 (2009), 4549–4559