

Article

Article: Oxy-Nitriding AISI 304 Stainless Steel by Plasma Electrolytic Surface Saturation to Increase Wear Resistance

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Abstract: AISI 304 SS has good corrosion resistance in a variety of environments but does not have good resistance to wear. Aggressive marine environments require materials that can withstand both the biocorrosion and the wear associated with the impact of waves, ocean currents and suspended particles. Oxy-nitriding of stainless steels can be used to increase their hardness and wear resistance. The conventional oxy-nitriding process is lengthy, and the temperature involved can affect the corrosion resistance of the material. To mitigate these problems, it was decided to study an oxy-nitriding process in plasma electrolytic conditions, using aqueous solutions of 20, 30 and 40 wt% urea. The results showed that all the concentrations evaluated gave lower levels of wear than untreated stainless steel. However, considering the amount of urea used and the environmental emissions from the waste generated, a concentration of 20% by weight of urea in the electrolyte is considered sufficient to increase up to three times the wear resistance of stainless steel. XRD, XPS and microscopy analyses showed that, in the main, the outermost layer of the steel surface treated by electrolytic plasma has a morphology of small craters of chromium and iron oxy-nitrides. A nitrogen diffusion layer was also seen below the oxy-nitrided layer.

Keywords: oxy-nitriding; plasma electrolytic; wear resistance

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1. Introduction

In aggressive environments stainless steel is widely used, as it is very resistant to corrosion. However, the low wear resistance of stainless steel limits the range of applications it can be used in [1,2]. To increase wear resistance, processes involving nitriding, oxy-nitriding and oxy-carbonitriding can be used. These processes modify the surface microstructure of stainless steel, hardening its surface [2,3].

One of the most promising means of oxy-nitriding is saturating the surface with oxygen and nitrogen by plasma electrolytic process (SSONPE). This is a thermo-electrochemical process in which the reactive forms of oxygen and nitrogen react using the energy provided by the plasma and produce microstructures that improve the mechanical properties of the steel without affecting its corrosion resistance [4–6].

SSONPE treatment is carried out with various electrolytes, including ammonium carbonate [7], ammonium nitrate [8] and urea [5,6,8–15]. Essentially, the electrolyte composition used must have good electrical conductivity to generate the electrolyte plasma and provide appropriate concentrations of atoms and free radicals in the plasma electrolytic process. Of the reagents listed above, that most used is urea, as it is relatively inexpensive, environmentally friendly, non-hazardous, and readily available. Urea also has a high concentration of nitrogen, oxygen and carbon in its structure, permitting oxy-nitrocarburization. The only drawback is that urea is not an electroactive species, so a conductive salt, such as KOH or Na₂CO₃, must be added to increase its electrical conductivity.

Aliofkhazraei et al. [10] and Tavakoli et al. [11] have described the effect of urea concentration on microstructural characteristics and anti-corrosion properties, although

they only evaluated concentrations of over 50 wt%. Most of the published works concerning anti-wear properties using urea in their working solutions emphasize parameters such as operating voltage [5,6], processing time [5,6,8] or the presence of an additive that improves the system conditions [13]. To the best of the authors' knowledge, the effects of the urea concentration in aqueous solutions on anti-wear properties of stainless steel has not been studied.

The aim of this study was to investigate the effect of 10, 20, 30 and 40 wt% urea concentrations in aqueous solutions on the anti-wear resistance properties of stainless steels that have been oxy-nitrided in an SSONPE process. This work includes analyses of the modified surface of the steel, using X-ray photoelectron spectroscopy, X-ray diffraction and scanning electron microscopy.

2. Materials and Methods

Before carrying out the SSONPE process, the stainless steel specimens must be adequately prepared to eliminate their passive layer in order to improve their reactivity and facilitate the diffusion process of the active species into their crystalline structure. AISI 304 SS disks, diameter 2.7 cm $\times$ thickness 1 mm, were used as working electrodes (cathodes). These specimens were polished by roughing their surface with silicon carbide sandpapers number 80, 220, 500, 800, 1000 and 2200 and then polished to a mirror finish using 3 and 1 micron diamond paste on cloth. Finally, the samples were cleaned ultrasonically for 5 min in ethanol. A plate of AISI 304 SS, 5 cm $\times$ 5 cm $\times$ 1 mm, was used as a counter electrode (anode). Both electrodes were submerged inside a tempered glass container of 1 L capacity, in which 500 mL of the aqueous urea solution (20, 30 and 40 wt%) was added. To increase the conductivity of the electrolyte, 0.3 wt% ammonium nitrate was also added. To compensate for the loss of evaporated solution, fresh solution of the same composition was replenished at a rate of 50 mL/min.

The SSONPE treatment was performed in two stages using a 6 kW power supply. During the first stage, the electrical potential was brought up to 180 V, and it was kept at this value for two minutes. Subsequently, the voltage was increased to 370 V to attain the plasma electrolytic condition, keeping the electrolyte at this value for 10 min. Finally, the treated part was washed in water and cleaned ultrasonically for 5 min in ethanol. Figure 1 shows how the pieces and the equipment were placed during the experiment.

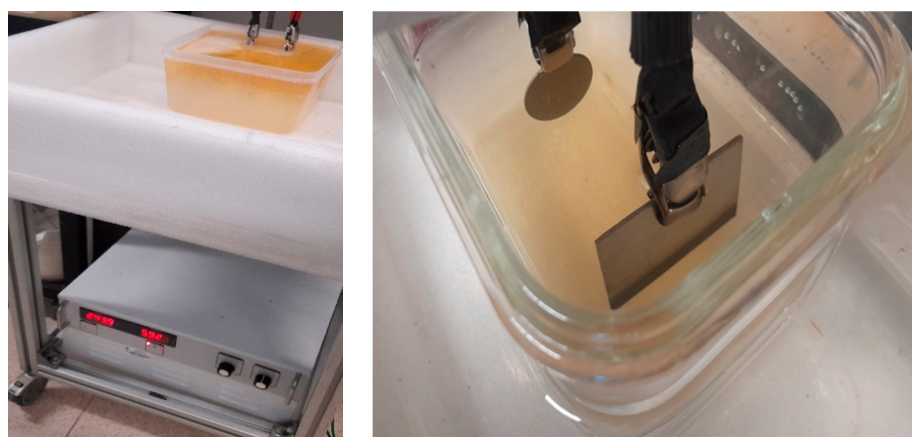


Figure 1. System used to achieve oxy-nitriding by the SSONPE process.

The treated surfaces were characterized by XPS, using a Thermo Scientific k-AlphaTM spectrophotometer with an internal pressure chamber of 6.5×10^{-8} mbar, a monochromatic Al-K α X-ray source ($h\nu = 1486.68$ eV) and a 400 μ m analysis radius. The crystalline phases on the treated steel surfaces were determined by DRX, using a Bruker AXS D8 AdvanceTM diffractometer. The operation conditions were a CuK alpha wavelength of 1.5418 Å, a voltage of 40 kV, a current density of 30 mA, and an aperture of 0.02° (2 θ) per second.

A morphological analysis was carried out at the center of the cathode using a KeyenceTM optical microscope model VHX 6000, while the thickness analysis was measured by a PHILIPS XL30ESEM scanning electron microscope with an accelerating voltage of 20 keV. Electron back scattered spectroscopy (EDS) was used for the surface chemical analysis.

The wear behavior of the oxy-nitrided part were evaluated at the center of the cathode by a Micro-TestTM pin-on-disk Tribometer according to the G99 standard. The test conditions were a 4 mm diameter WC pin, a distance traveled of 60 m, a speed of 50 rpm and an applied weight of 5 N. The footprint width was measured at the four cardinal points using the Keyence microscope. The reported value was the average of the four measurements.

3. Results

3.1. Optical Microscopy (Keyence)

Figure 2 shows the surface finish obtained by SSONPE at center of the cathode for the three urea concentrations.

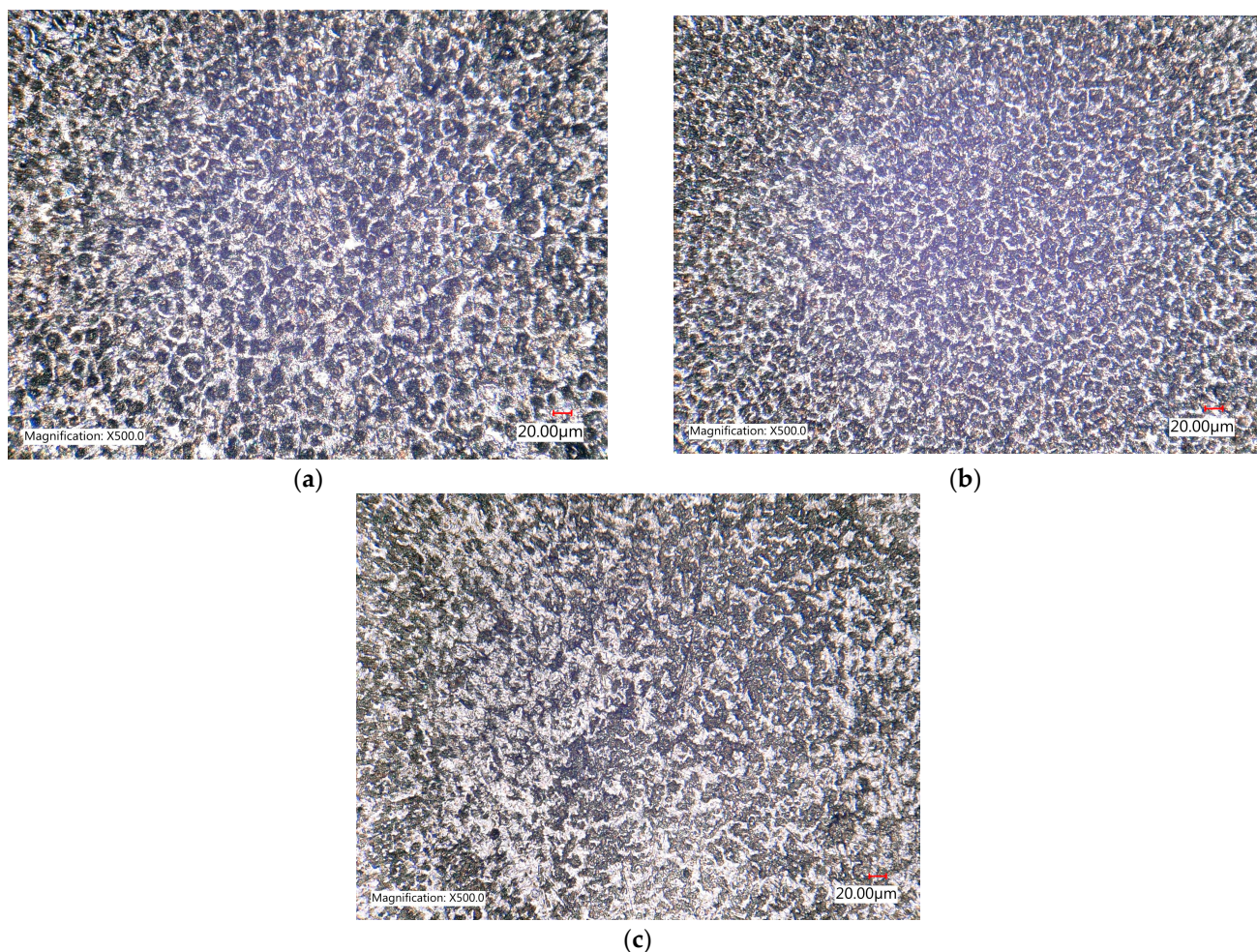


Figure 2. Typical surface microstructure of AISI 304 SS specimens oxy-nitrided by SSONPE in aqueous solutions of 0.3% NH_4NO_3 and urea at concentrations of: (a) 20 wt%, (b) 30 wt% and (c) 40 wt%.

In Figure 2a network of homogeneously distributed craters is seen. These are probably formed when gas bubbles collapse, due to the pressure generated in the plasma electrolytic process. Microscopic observations show a slightly different finishing morphology for the three urea concentrations, the ridge-valley distance of these craters is 1.2–2.0 μm . Direct observations during the experimental work showed that as the urea content increased in the SSONPE process, the gaseous emissions increased radically; making the maintenance

of the plasma arc more difficult. These differences during the process originated physical and chemical changes in the oxy-nitrided surfaces.

It is possible that this microstructure is so because the process involved a static system, i.e., there was no external agitation in the electrolytic cell and the hydrodynamic conditions were dominated only by the convective currents formed by the boiling of the solution and the surge formed when plasma conditions were reached. Most works reported in the literature [8,11,12] use electrolyte solutions in dynamic conditions, i.e., they use a device to move the solution towards the face of the working electrode.

3.2. Scanning Electron Microscopy (Thickness Analysis)

In Figure 3 the cross-sectional analysis of oxy-nitrided AISI 304 SS shows the thicknesses of the layers obtained with the various solutions of urea. Firstly, it is seen that as the urea concentration in the aqueous solution increases, the thickness of the modified layer decreases (6.84 μm for 20 wt%, 6.5 μm for 30 wt% and 2.7 μm for 40 wt%), This is probably related to the fact that as the urea concentration increases, less water is available to form the gaseous envelope around the working electrode. Therefore, the amount of urea volatilized and integrated into the gaseous envelope decreases as the water is depleted faster.

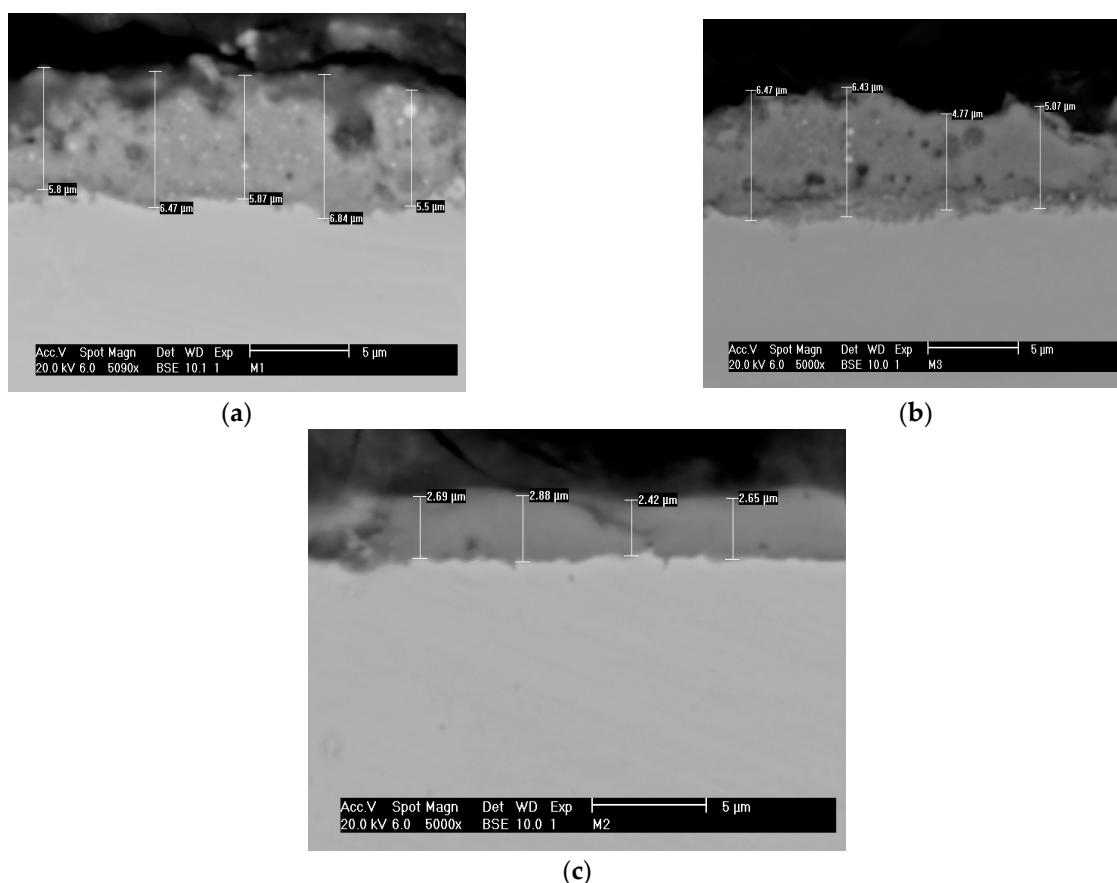


Figure 3. Cross-sectional analysis of oxy-nitrided AISI 304 SS using: (a) 20 wt% urea, (b) 30 wt% urea and (c) 40 wt% urea, 5000 $\times$ magnification using the scanning electron microscope and backscattered electrons.

Figure 4 shows a cross section analysis by secondary electrons in SEM for the specimen treated with 20% urea. This Figure shows a double layer composed by an outer porous layer of oxy-nitrides (subsequently confirmed by XPS) and an innermost layer of nitrogen diffusion (confirmed by elemental mapping). The thickness of this double layer was almost 10 μm .

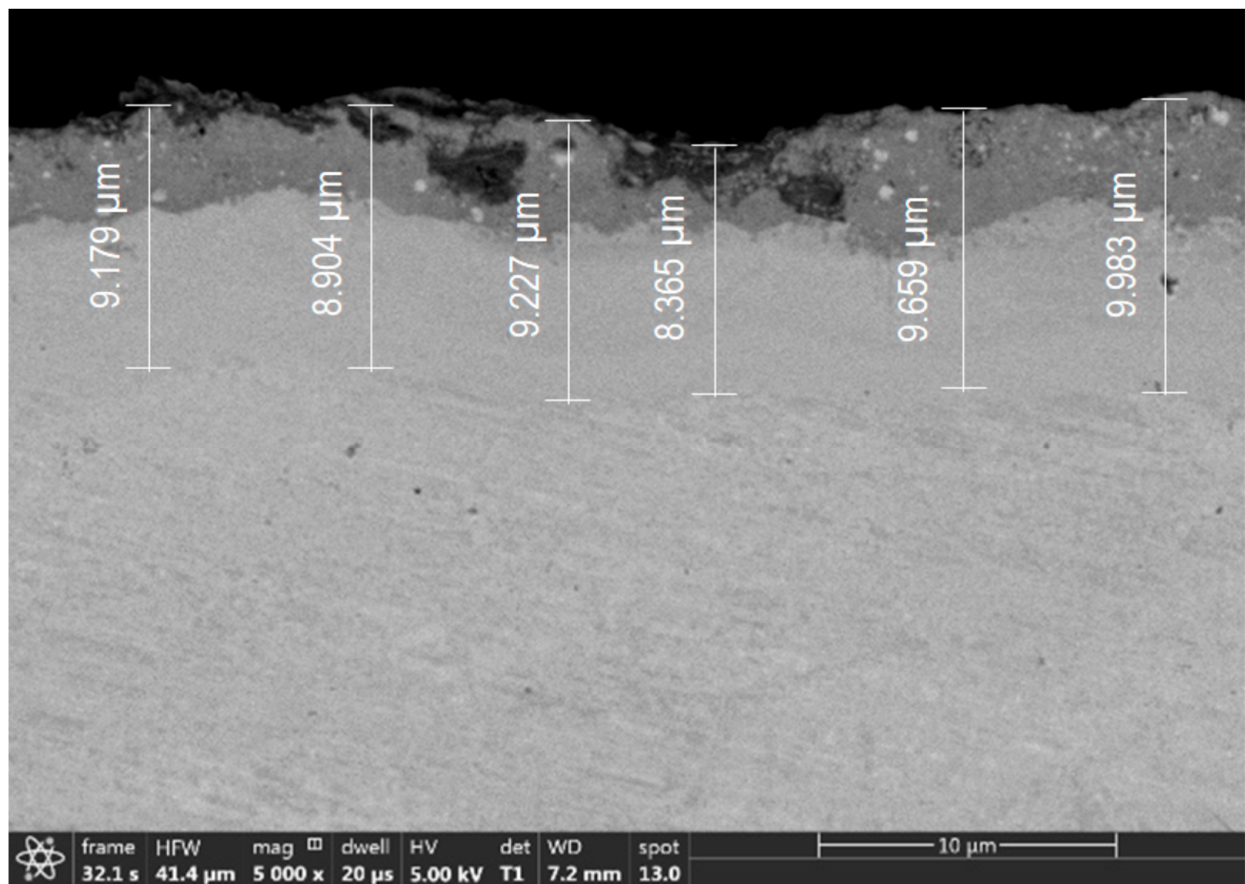


Figure 4. Cross-sectional analysis of oxy-nitrided AISI 304 SS with 20 wt% urea, viewed under the SEM at 5000 $\times$ using secondary electrons.

3.3. X-ray Photoelectron Spectroscopy (XPS) Analysis

To evaluate the chemical composition of the layer formed on the surface of AISI 304 SS after the oxy-nitriding process, an analysis was carried out by XPS. The XPS analyses are shown in Figures 5–8.

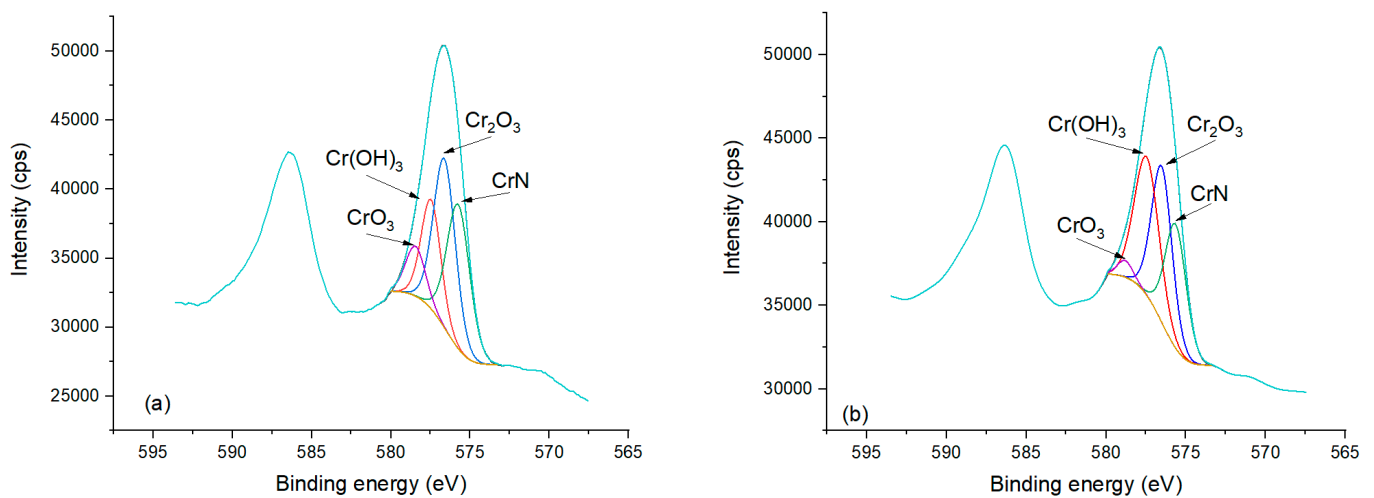


Figure 5. Cont.

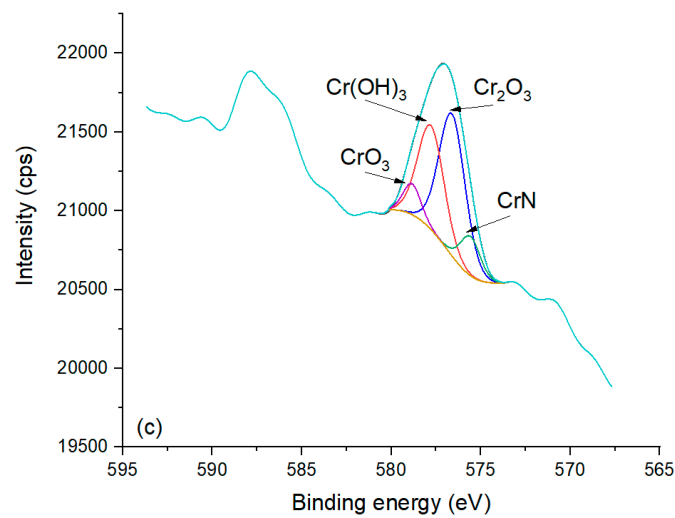


Figure 5. Cr2p3/2 XPS spectra (and its deconvolution) of the oxy-nitrided AISI 304 SS samples using: (a) 20 wt% urea, (b) 30 wt% urea and (c) 40 wt% urea.

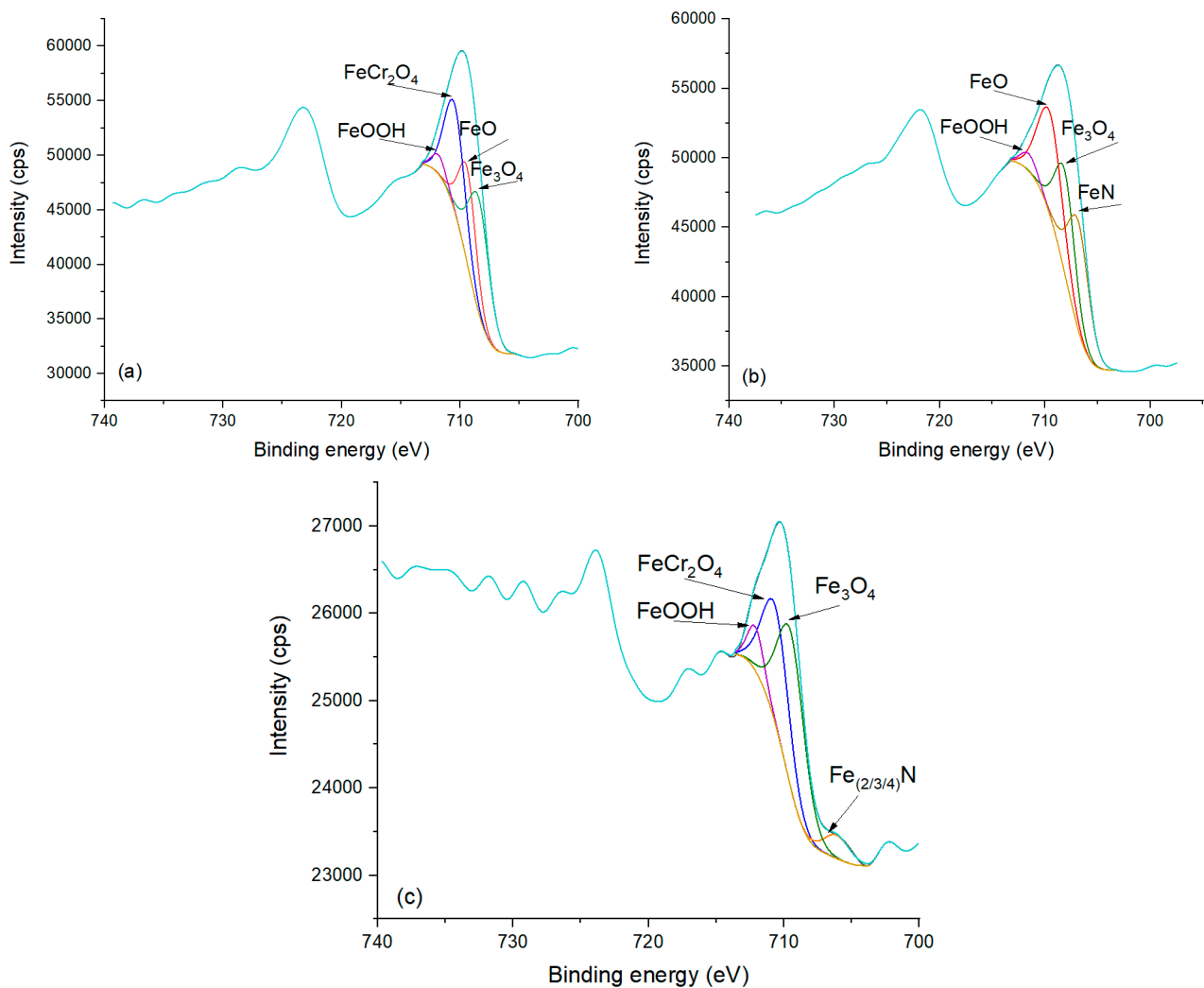


Figure 6. XPS spectra of Fe2p3/2 (and its deconvolution) of the samples processed by SSONPE using (a) 20 wt% urea, (b) 30 wt% urea and (c) 40 wt% urea.

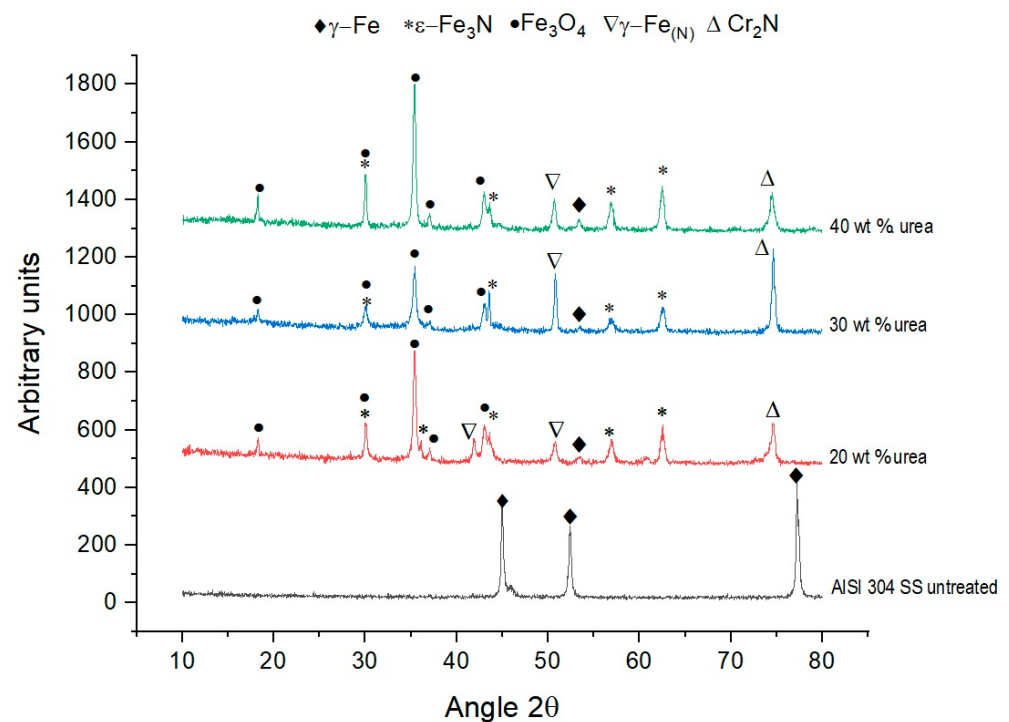


Figure 7. Diffraction patterns of oxy-nitrided AISI 304 SS, using different urea concentrations.

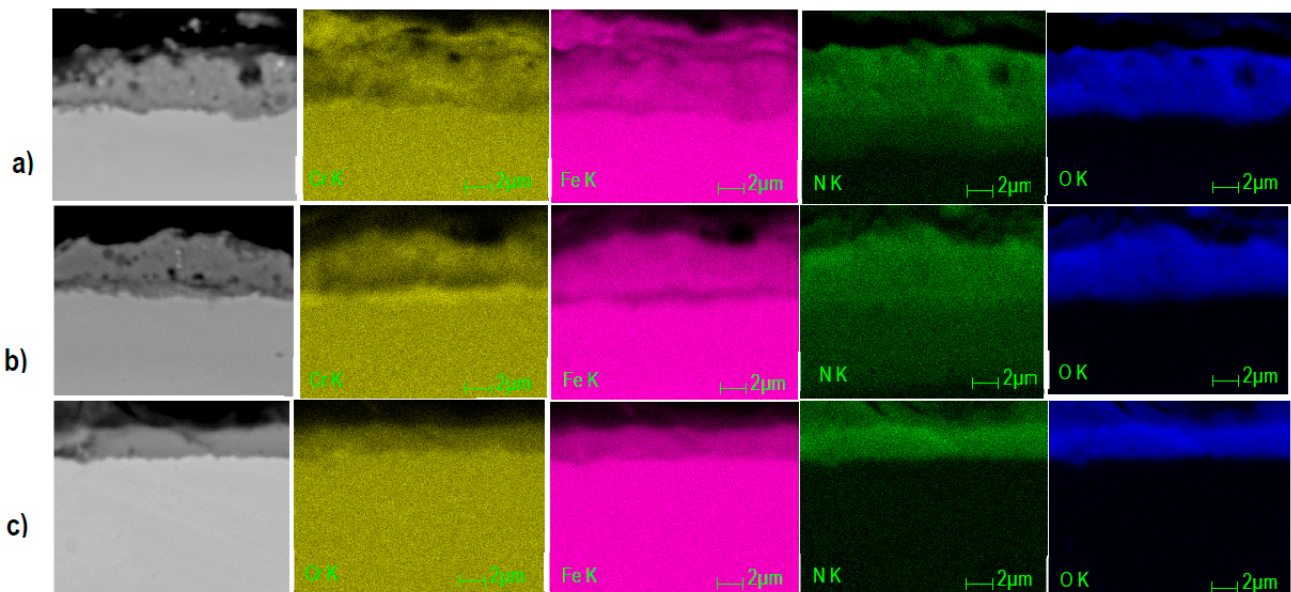


Figure 8. Chemical mapping by SEM-EDS on oxy-nitrided AISI 304 SS with: (a) 20 wt% urea, (b) 30 wt% urea and (c) 40 wt% urea.

Figure 5 shows the Cr2p XPS spectra of the samples processed by SSONPE using 20 wt%, 30 wt% and 40 wt% urea. The presence of chromium nitride (CrN), chromium oxides (Cr_2O_3) and chromium hydroxides ($\text{Cr}(\text{OH})_3$) were observed for the different urea solutions evaluated.

The presence of chromium nitrides (CrN) was observed in all the concentrations tested. The Cr_2O_3 and CrO_3 oxides form a passive layer that contributes to the increased corrosion resistance on the surface, while $\text{Cr}(\text{OH})_3$ is associated with the surface hydration caused by the aqueous solution. The concentration of each chromium species found was calculated from the XPS spectra. The molecular percentage is shown in Table 1.

Table 1. Molecular percentages of chromium species of the oxy-nitrided AISI 304 SS samples using: (a) 20 wt% urea, (b) 30 wt% urea and (c) 40 wt% urea.

Species	Urea Concentration					
	20 wt%		30 wt%		40 wt%	
	Binding Energy	%	Binding Energy	%	Binding Energy	%
CrN	575.74 eV	32.64	575.64 eV	27.69	575.58 eV	10.14
Cr ₂ O ₃	576.62 eV	36.5	576.5 eV	33.72	576.6 eV	47.91
Cr(OH) ₃	577.46 eV	21.1	577.45 eV	35.86	577.78 eV	34.94
CrO ₃	578.45 eV	9.76	578.81 eV	2.73	578.84 eV	7.01

Table 1 shows that as the concentration of chromium nitride decreased, the urea concentration in the solution increased. On the other hand, the layer of oxides and hydroxides behaved inversely, i.e., the concentration of these oxides and hydroxides increased as the urea concentration increased.

Figure 6 shows the XPS spectra of Fe2p of the samples processed by SSONPE using 20, 30, and 40 wt% urea. Among the iron species found, the spinel-type oxides present in all the concentrations evaluated stand out; these species provide the treated surface with great hardness and wear resistance. Oxides and hydroxides were also seen to be present [16,17]. The presence of iron nitride was observed only when electrolytes with 30 and 40 wt% urea were used.

The concentrations of each iron species present on the surface are shown in Table 2. The highest number of spinel-type oxides (Fe₃O₄, FeCr₂O₄) was obtained in the sample treated with 40 wt% urea (84.7%). It is inferred that in the treatment with 20 wt% urea all the nitrogen was used in the formation of chromium nitride and the formation of iron and iron-chromium spinels was favored by the presence of oxygen in the aqueous urea solution.

Table 2. Molecular percentages of iron species present on AISI 304 SS surfaces treated with each urea concentration.

Species	Urea Concentration					
	20 wt%		30 wt%		40 wt%	
	Binding Energy	%	Binding Energy	%	Binding Energy	%
Fe _x N _y		0	706.82 eV	32.1	706.09 eV	7
Fe ₃ O ₄	708.41 eV	36.78	708.1 eV	28.72	709.45 eV	48.82
FeO	709.37 eV	25.34	709.51 eV	35.2		0
FeCr ₂ O ₄	710.46 eV	33.65		0	710.61 eV	35.88
FeOOH	711.78 eV	4.23	711.51 eV	3.98	712.08 eV	8.3

3.4. X-ray Diffraction Analysis

Figure 7 shows the X-ray diffraction signals of the crystalline phases ϵ -Fe₃N, Cr₂N, Fe₃O₄ and expanded austenite (γ -FeN). It is important to mention that the spinel type oxides not only include Fe₃O₄, but also FeCr₂O₄ [5] and NiFe₂O₄ [9]. These additional oxides have the same structure as Fe₃O₄, so their diffractograms are very similar [5,8,9]. The presence of these phases confirms and complements the information obtained by XPS analysis.

Similar peaks were observed for each urea concentration. However, changes in intensity were observed at angles between 42–45 angle 2 θ . Only in the treatment with 20 wt% urea, were two new peaks observed, one for gamma iron and the other for iron nitride.

3.5. SEM-EDS Surface Chemical Mapping

In the chemical mapping seen in Figure 8, chromium, iron, nitrogen, and oxygen are visible on the surface of all oxy-nitrided specimens, which confirms the presence of chromium and iron oxy-nitrides. Below the oxy-nitrided layer, a region rich in nitrogen was observed only in samples processed with 20 and 30 wt% urea. The sample processed with 40% urea did not show the nitrogen diffusion region possibly due to the instability of the electric arc during the SSONPE process.

3.6. Wear Analysis of Oxy-Nitrided AISI 304 SS Specimens

According to the results shown by Figure 9, the wear of the untreated steel is about 3 times (0.0008 g) higher than the oxy-nitrided sample with 20 wt% urea (0.0003 g) both for a sliding distance of 60 m. Samples treated with higher urea contents did not further improve wear resistance. The greater resistance to wear of the oxy-nitrided specimens with 20% urea can be explained by the higher content of hard chromium-based compounds obtained under these conditions (see Table 1). Consequently, SSONPE treatments with a maximum of 20 wt% of urea in aqueous solutions will give economic savings and reduce the waste emitted to the environment, compared with treatments using higher concentrations of urea.

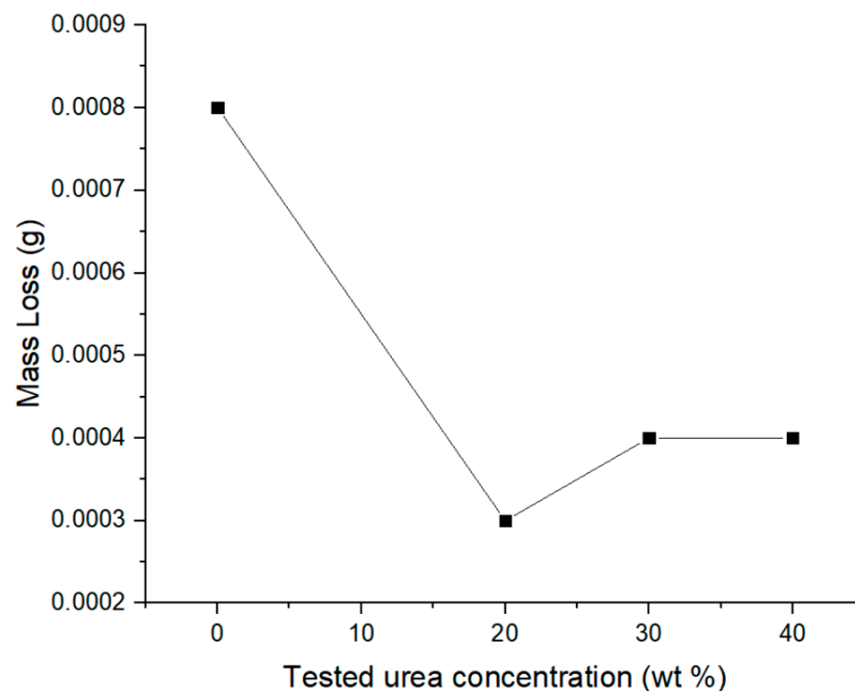


Figure 9. Wear of the oxy-nitrided samples according to the ASTM G99 standard for a sliding distance of 60 m.

During the wear test by the “pin-on-disk” technique a track is generated on the specimen surface, the greater its width and depth, the greater wear of the sample. For a sliding distance of 60 m the track of 527 μm in width seen in Figure 10a shows a severe adhesive and abrasive wear for the untreated stainless steel. The oxy-nitrided samples using 20 wt% urea seen in Figure 10b showed lighter abrasive wear (tracks of 141 μm in width). At 30 wt% urea seen in Figure 10c (253 μm of track width) and 40 wt% urea seen in Figure 10d (241 μm of track width) the worn surfaces exhibited higher abrasion than the 20 wt% urea. These results confirm the mass wear data shown by Figure 9.

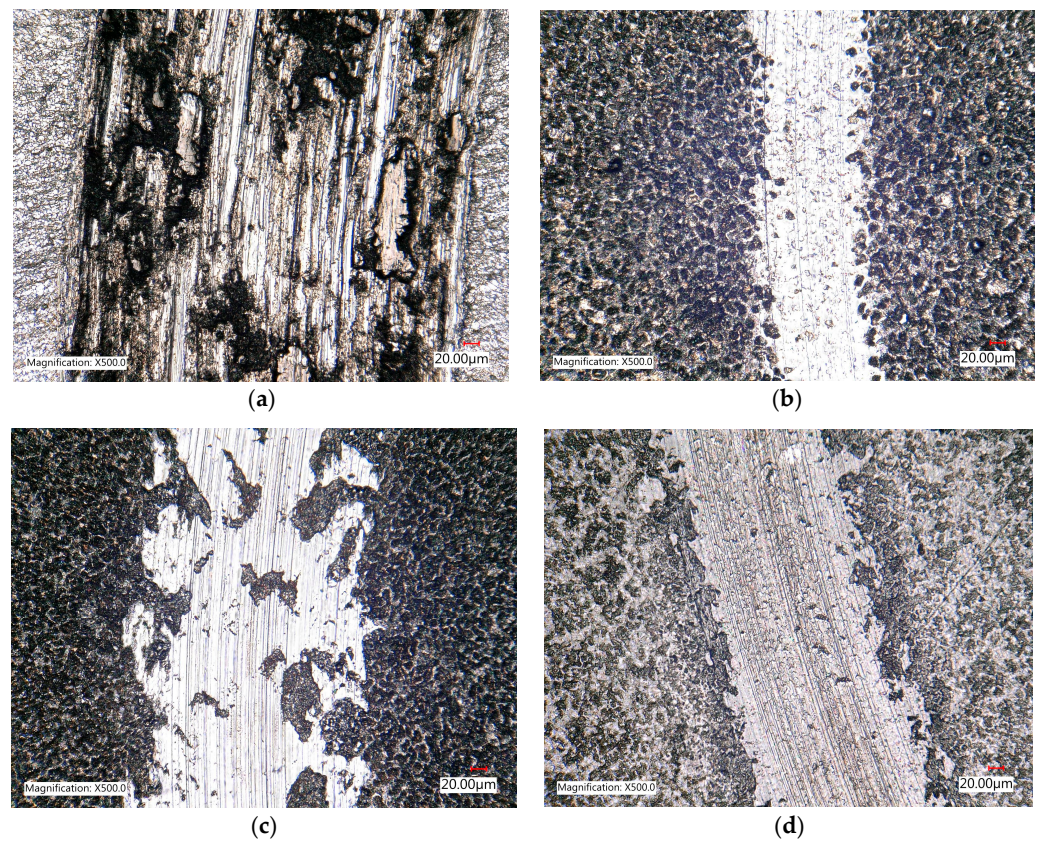


Figure 10. Wear tracks on the different steel surfaces, at $500\times$ magnification for a sliding distance of 60 m on: (a) untreated steel, (b) oxy-nitrided with 20 wt% urea, (c) oxy-nitrided with 30 wt% urea and (d) oxy-nitrided with 40 wt% urea.

4. Discussion

The SSONPE oxy-nitriding process. The voltage and current behavior of the SSOMPE process is shown in Figure 11.

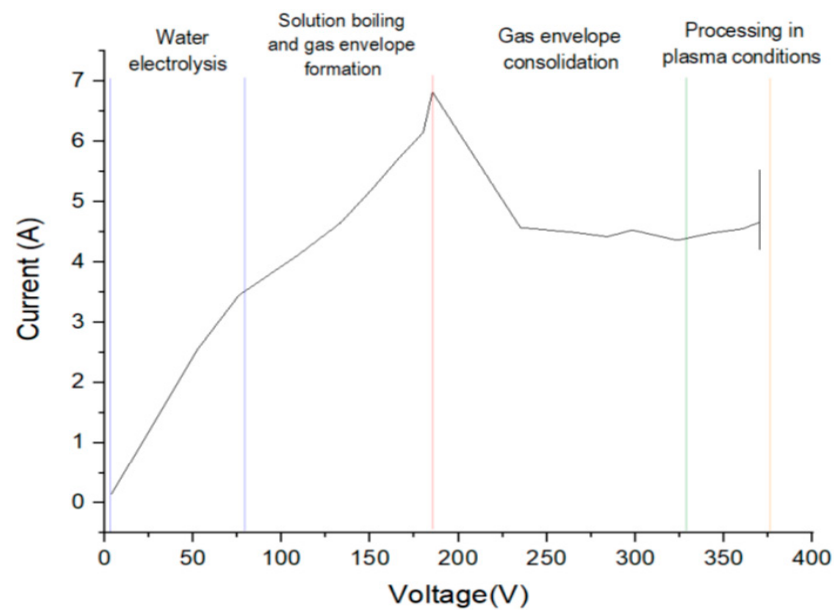


Figure 11. Current/voltage behavior during the SSONPE nitriding process of AISI 304 SS using aqueous solutions of urea and NH_4NO_3 .

Up to 80 V, water electrolysis occurs, with a continuous release of hydrogen bubbles (at the cathode) and oxygen bubbles (at the anode). Beyond 80 V, boiling of the solution takes place. At 180 V, the increase in the voltage was paused, to avoid overheating the working electrode. At this voltage, the system starts to behave in a predominantly non-ohmic way i.e., like a capacitor, with the voltage drop taking place as it accumulates electric current. This non-ohmic behaviour is due to the formation of a film of vapour around the working electrode, which becomes thicker over time.

Between 180 and 329 V, the gaseous layer becomes more consolidated, preventing electrical conduction. As the capacitor fills up, the voltage increases again, until it reaches what is known as dielectric breakdown voltage (approx. 280 V). At this point, small holes form in the vapour sheath where current leakage occurs in the form of electrical discharges.

Between 330 and 370 V, plasma operation begins, where the current in the system tends to decrease between 19% (5.5 A) and 38% (4.2 A) with respect to the maximum current (6.8 A). When the voltage is 330 V, the system has enough energy to build up an electrical arc. From preliminary experimental observations, we believe this arc still does not have enough energy to carry out the oxy-nitriding process. The process continues until the system reaches 370 V. At this value the electrical arc is consolidated and has enough energy for the oxy-nitriding process to take place.

Figure 12 shows the schematic representation of the oxy-nitriding process at interfaces.

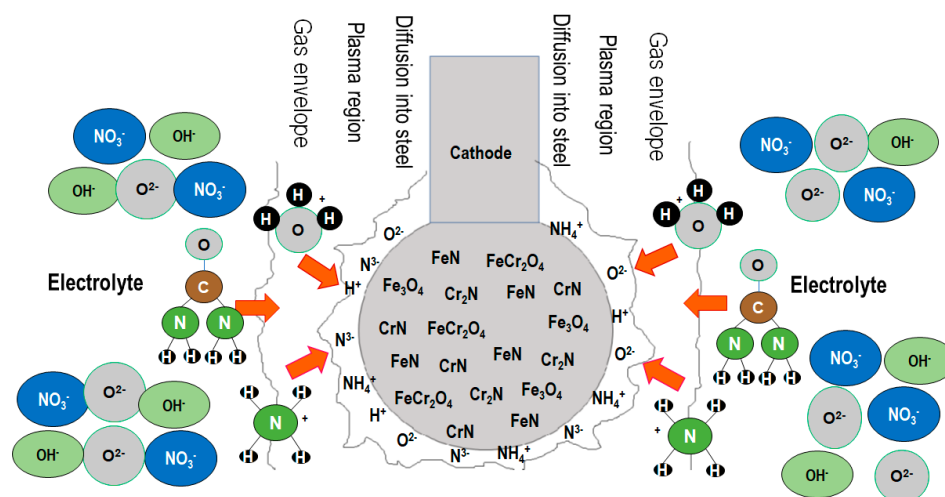


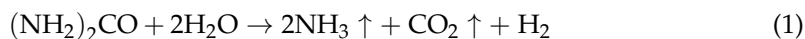
Figure 12. Schematic representation of the phenomena occurring at the electrolyte/gas envelope/plasma region/working electrode interfaces, during the SSONPE process.

Since urea is not an electroactive species, even at high voltages, it was necessary to add ammonium nitrate. The resulting conductivity allows the plasma state to develop. During boiling, the gaseous envelope starts to form when water and urea become gaseous, improving the transfer of oxygen, nitrogen, and hydrogen reactive species towards the working electrode.

The urea concentration increases as the gaseous sheath consolidates. When the first luminescent discharge occurs, sufficient energy is available to start the ionization process of urea, water, and ammonium nitrate, generating active nitrogen, oxygen, and hydrogen species.

Once the plasma state is reached, the system has enough energy to activate and accelerate the diffusion process of the reactive species (oxygen and nitrogen) towards the surface of the steel, where they react with the available iron and chromium to form the oxy-nitrides, as shown in Figure 13.

First the ionization of the urea molecule occurs, forming molecular hydrogen, which, as stated by Osetrova (reported in Nie [5]), only takes place in SSONPE in cathodic mode by the reaction (1):



The dissociation of the reaction products continues if the reactive nitrogen, oxygen, hydrogen, and carbon species are available. Due to the large amount of energy generated in the plasma region these species become ionized.

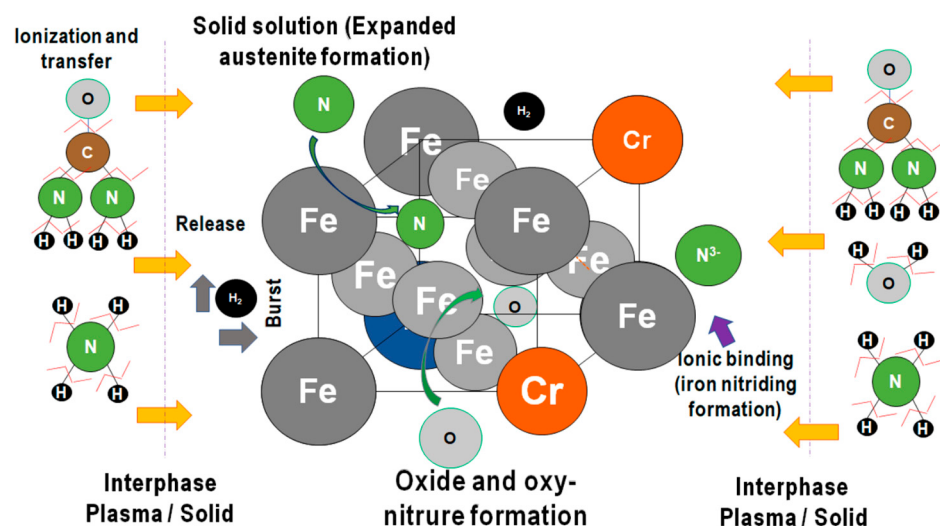


Figure 13. Transfer of reactive species towards the surface of the working electrode and its surface modification in the SSONPE process of AISI 304 SS.

This hydrogen gas is responsible for forming the craters on the surface of the treated steel, giving it the typical microstructure shown in Figure 2. The mechanism involved is explained by Pogrebnyak [18]. The shock waves are generated due to the collapse of hydrogen bubbles on cooling, leaving craters on the surface of the steel.

According to Dong [19], the expanded austenite, which is a modification in the lattice parameters of austenite caused by the formation of a solid solution of nitrogen in this structure, can contain up to 10 wt% nitrogen. The solid solution in the stainless steel is made by diffusing reactive nitrogen through defects and voids in the austenite structure.

Iron and chromium nitrides and oxy-nitrides are produced by chemical reactions between ionic species of nitrogen, oxygen, iron and chromium. Iron and chromium are activated by the electric current at the surface of the working electrode. The iron and chromium oxy-nitrides give the steel surface increased hardness and wear resistance.

Spinel-type oxides such as FeCr_2O_4 or $\text{NiFe}_{0.5}\text{Cr}_{1.5}\text{O}_4$ are complex oxides of the type $\text{A}^{2+}\text{B}^{3+}\text{O}_4$. Their formation is associated with the octahedral and tetrahedral sites formed by oxygen and Fe^{2+} and Cr^{3+} ions. The resulting spinels give high mechanical strength, and consequently, good wear resistance.

Protection mechanism. The increase in wear resistance is associated with three fundamental aspects:

An increase in the number of atoms present on the surface of the steel, i.e., an increase in the surface density of the steel.

The presence of hard chromium nitrides.

The presence of chromium and iron spinels.

This protection was confirmed by the small amount of wear that occurred on the oxy-nitrided parts by the SSONPE process, compared to that seen on the untreated stainless steel. According to Yerokhin, et al. [6] and Kong et al. [15], the oxides and nitrides generated on

the surface can significantly increase the surface hardness, meaning much less deformation of the steel, fewer cracks, as well as a reduced rate of wear.

5. Conclusions

The wear of the untreated steel was about 3 times (0.0008 g) higher than the oxy-nitrided sample with 20 wt% urea (0.0003 g) both for a sliding distance of 60 m. Samples treated with higher urea contents did not further improve wear resistance.

Untreated stainless steel showed a severe adhesive and abrasive wear. A wear track of 527 μm in width by the pin-on-disc testing was observed. The oxy-nitrided samples with 20 wt% urea showed lighter abrasive wear (tracks of 141 μm in width). At 30 wt% urea (253 μm of track width) and 40 wt% urea (241 μm of track width) the worn surfaces exhibited higher abrasion than the samples processed with 20 wt% urea.

Direct observations during the experimental process showed that as the urea content increased above 20 wt%, the gaseous emissions increased radically; in addition the maintenance of the plasma arc under these conditions became difficult. These differences during the process originated physical and chemical changes in the oxy-nitrided surfaces.

The greater resistance to wear of the oxy-nitrided specimens with 20% urea can be explained by the higher content of hard chromium-based compounds obtained under these conditions.

Oxy-nitriding under electrolytic plasma process with a maximum of 20 wt% of urea in aqueous solutions will give economic savings and reduce the waste emitted to the environment, compared with treatments using higher concentrations of urea.

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Informed Consent Statement: “Not applicable” this study has not involved humans.

Data Availability Statement: Not applicable.

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Conflicts of Interest: The authors declare that they have no conflict of interest.

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