

Influence of atmospheric pressure plasma treatments on the corrosion resistance of stainless steels

K. Brunelli, L. Pezzato, E. Napolitani, S. Gross, M. Magrini, M. Dabalà

In this study, the influence of treatments carried out with an atmospheric pressure plasma jet (APPJ) on the passive oxide films of different types of stainless steels and their corrosion properties was studied. The treatments were realized on a martensitic (AISI420) and a duplex (SAF2507) stainless steel using a plasma generated by air at 1.5 bar. The corrosion resistance of the samples was analyzed with potentiodynamic anodic polarization and electrochemical impedance spectroscopy tests in environments containing sulphates and/or chlorides. The effects of the treatment on the oxide layer were studied using secondary ion mass spectrometry and X-ray photoelectron spectroscopy. The plasma treatments allowed the growth of the passive film and improved the corrosion resistance of the stainless steels.

Keywords: Atmospheric pressure plasma jet - Stainless steel - Corrosion - EIS - SIMS - XPS

INTRODUCTION

Plasma is mainly constituted by electrons, ions and other extremely reactive particles, which can react with the surface of different types of materials (metals, polymers, etc) and change their surface characteristics and properties. In the industrial plants, plasma is often used for cleaning and activating the surfaces and/or for the deposition of different types of coatings.

In the past, the plasma technology required the use of low pressures and consequently of a vacuum chamber, which needed expensive automatic systems for the movement of the sample. [1-3] The development of plasma technologies that can work at atmospheric pressure overcomes the disadvantages of traditional vacuum operation and permits to apply this technology in a larger number of applications for example in continuous in line manufacturing. [4-5] Atmospheric pressure plasma sources can be divided

in three groups, using their excitation mode: i) the DC (direct current) and low frequency discharges; ii) the RF (radio frequency); iii) the microwave discharges. Several treatments can be carried out on the surfaces of different materials by atmospheric pressure plasma: cleaning (grease removal, decontamination); activation (adherence or anti adherence properties); etching; functionalization (electrical conductivity, chemical barrier). Atmospheric pressure plasma jet (APPJ) source is a RF plasma. It produces a stable discharge and avoids the arc transition. [6-8] Until now, the application of the atmospheric pressure plasma jet on metals was investigated mostly about the effects of the plasma on the adhesion, decontamination, hydrophilic properties and on the applications of coatings. [9-11] Nevertheless, knowledge regarding the thickness, the composition and the corrosion properties of the oxides formed on surface of metals after atmospheric pressure plasma jet treatment is lacking. Only one study was carried out on the effect of the atmospheric pressure plasma jet treatment on the oxide film of metals and its corrosion properties, and it showed that the treatment allowed the formation of a protective oxide film on the surface of AISI304 stainless steel. [12]

It is known that the passive layer formed on stainless steels is a double oxide layer, constituted by an inner protective layer consisting essentially of chromium oxide Cr_2O_3 and chromium hydroxide $\text{Cr}(\text{OH})_3$ and by an outer layer rich in iron oxide Fe_2O_3 , with spinel structure, containing also mixed oxides of chromium and molybdenum. [15-16] The total thickness of the oxide film is generally between 1 and 6 nm. Furthermore, in stainless steels, higher is the chromium content lower is the thickness of the passive layer. [17]

K. Brunelli, L. Pezzato, M. Magrini, M. Dabalà

*DII, University of Padua,
Via Marzolo 9, 35131 Padua, Italy*

E. Napolitani

*MATIS-IMM-CNR and Department of physics and
astronomy, University of Padua,
Via Marzolo 8, 35131 Padua*

S. Gross

*ISTM-CNR Padua and Dipartimento di Scienze
Chimiche, University of Padua,
via Marzolo 1, 35131 Padua, Italy*

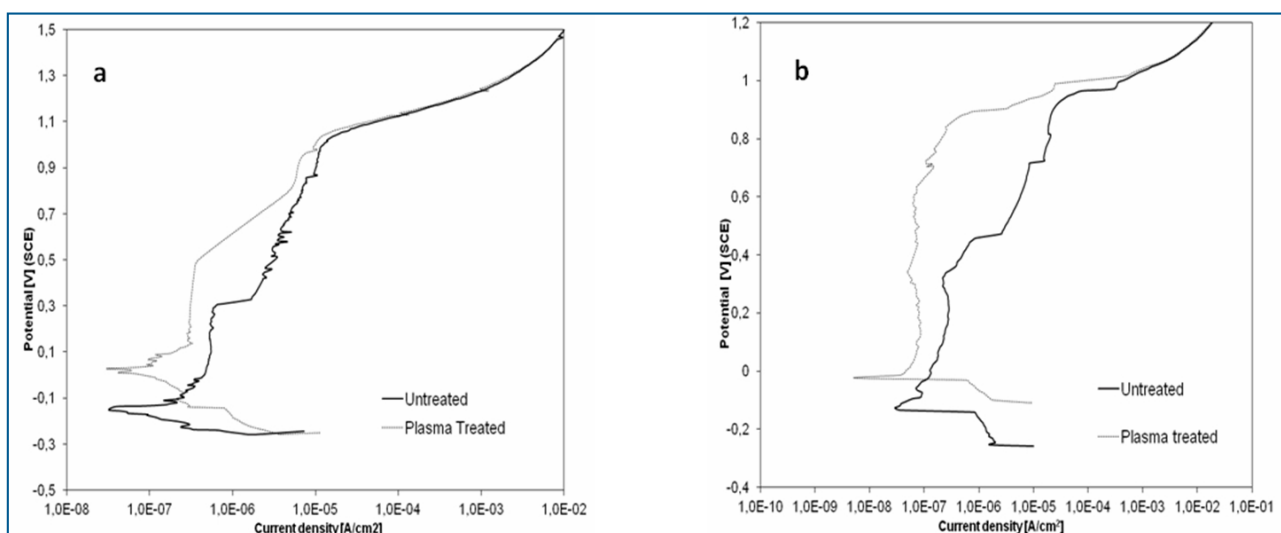


Fig. 1 - Potentiodynamic polarization curves in 0.3M NaCl (a) and 0.5M H₂SO₄ (b) solution of untreated sample and plasma treated sample of SAF2507

Fig. 1 - Prove di polarizzazione anodica per l'acciaio SAF2507, sottoposto a trattamento con plasma atmosferico, in soluzione 0.3M NaCl (a) e soluzione 0.5M H₂SO₄ (b)

The main goal of this work is to study the effect of treatment with atmospheric pressure plasma on the surface of two different stainless steels (martensitic and duplex) and to correlate the surface modifications with the corrosion resistance. Potentiodynamic anodic polarization and electrochemical impedance spectroscopy (EIS) were used to investigate the effect of the plasma treatment on corrosion protection properties of the passive film in solutions containing NaCl or H₂SO₄.

EXPERIMENTAL

The samples of the two stainless steels (AISI 420 and SAF2507) were taken from bars and their surfaces polished according to standard metallographic procedures. The nominal compositions of the steels were 0.3% C, 13% Cr, 1% Si, 1% Mn for AISI420 and 0.019% C, 25% Cr, 7%Ni, 0.28% N and 3.8% Mo for SAF2507.

The surfaces of the samples were treated with a Flume RD1400 atmospheric pressure plasma jet, which worked at a frequency between 16 and 20 kHz and generated a plasma with a power of 2.7 kW (230V, 12A). The plasma was generated by ionizing compressed air at 1.5 bar of pressure. The ionized gas was directed onto the sample surface through a torch, which can be moved at different speeds. In this work, the treatments were performed moving the torch with a speed of 2×10^{-3} m/s. The distance between the torch and the samples was 30 mm. The treated samples were exposed to air for 1 hour before performing the surface characterization and the electrochemical tests. The analysis of the thickness and composition of the oxide layer was performed with a SIMS CAMECA IMS- 4f spectrometer using a Cs⁺ 14.5 keV 3 nA primary beam rastered over an area of $100 \times 100 \mu\text{m}^2$, while collecting

¹⁸O, ²⁷Al, ²⁴Mg, ⁶³Cu secondary ions from a central area of 60 μm diameter. The determination of the depth of the crater produced by the primary ion beam, used for the calculation of the average speed of excavation, was performed with a profilometer TENCOR P10. The XPS experiments were conducted using a PERKIN ELMER $\Phi 5600\text{ci}$ X-Ray Photoelectron spectrometer with an AlK _{α} anode X-ray source (1486.6 eV) with an energy of 14 kV and an electron current of 20 mA. A CHA (Concentric Hemispherical Analyser) was used to collect the output signals. Analysed areas were circles of 0.8 mm in diameter. Survey scan mode acquired spectra stepping every 1.0 eV (pass energy 187.85 eV), while multiplex scan mode required 0.2 eV steps (pass energy 58.70 eV). A charge neutralizer was used to avoid spectral shift in insulating samples and all spectra were corrected according to charging effect, assigning to C1s peak 284.8 eV binding energy. Deconvolution of the peaks was performed with XPSpeak 4.1 software.

The anodic polarization tests were realized with a potentiostat AMEL 2049 coupled with a function generator 568 AMEL. The scanning speed was 1 mV/s. A calomel electrode and a Pt electrode were used as reference and counter electrode, respectively. Corrosion tests were carried out both in aqueous solution containing sulfates and chlorides. In detail a 0.3M NaCl solution and a 0.5 M H₂SO₄ solution were used.

The EIS tests were carried out using a Schlumberger Solartron 1255 FRA spectrometer connected to a EG&G potentiostat 273. The tests were performed at the open circuit potential, with an amplitude of oscillation of 10 mV, in the frequency range $10^4 - 10^2$ Hz. Electrolytes, geometry of the cell and electrodes were the same of the anodic polarization tests. The fitting of the experimental data were carried out using the software ZView and the Randles circuit as equivalent circuit.

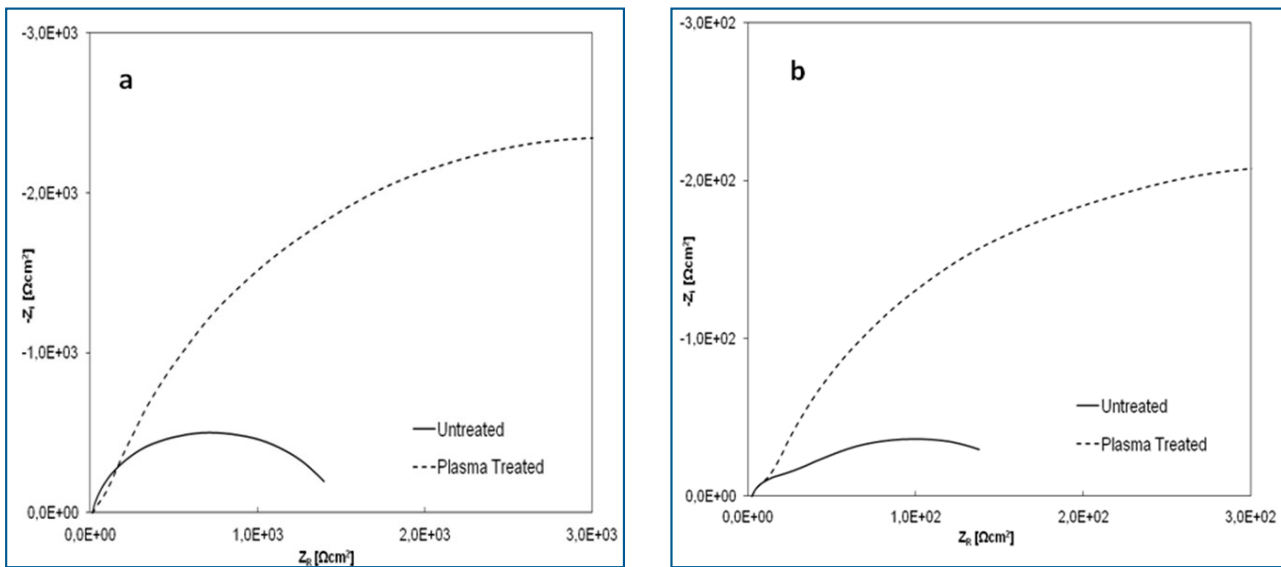


Fig. 2 - Nyquist plots of EIS data in 0.3M NaCl (a) and 0.5M H₂SO₄ (b) solution of untreated sample and plasma treated sample of SAF2507; equivalent circuit used for quantitative evaluation of EIS spectra (c)

Fig. 2 - Diagrammi di Nyquist dei dati EIS dei campioni di SAF2507 per l'acciaio SAF2507, sottoposto a trattamento con plasma atmosferico, in soluzione 0.3M NaCl (a) e soluzione 0.5M H₂SO₄ (b); modello del circuito equivalente usato per il fitting dei dati sperimentali (c)

RESULTS AND DISCUSSION

The anodic polarization curves of the SAF2507 samples are shown in Fig. 1a and Fig. 1b, respectively. An ennoblement of the corrosion potential E_{corr} of about 200 mV was observed for the plasma treated sample in all the solutions considered. After the treatment, a decrease in the anodic current was also measured, whereas no significant variations in the corrosion current i_{corr} was observed. The potential break-down wasn't influenced by the plasma treatment in the tests with 0.3M NaCl solution, whereas an increase of approximately 100 mV was observed in the case of 0.5 M H₂SO₄ solution.

The results obtained in the polarization tests of the AISI420 samples in 0.3M NaCl and 0.5M H₂SO₄ solutions were similar (figures not reported). Also in this case, the plasma treatment improved the corrosion resistance of the steel and this improvement was much more observable in the solution containing sulfates than in the one containing chlorides. In fact, an increase in the corrosion potential E_{corr} can be observed in both the solutions, whereas a significant reduction in the corrosion current i_{corr} can be noted only in the tests carried out in the solution containing sulphates.

The untreated and the plasma treated samples of the two stainless steels were also analysed with EIS test. The Nyquist impedance spectra of the samples of SAF2507 are shown in Fig. 2a and Fig. 2b. The data obtained by EIS measurements were fitted with the equivalent circuit shown in Fig. 2c, called Randles circuit, and the results are reported in Tab. 1. In this circuit R_1 represents

SOLUTION 0.3M NaCl				
	SAF2507 Untreated	SAF2507 Plasma treated	AISI420 Untreated	AISI420 Plasma treated
R1 [Ω*cm²]	15	13	12.89	15.01
Q [F*Hz¹⁻ⁿ]	1.3x10 ⁻⁴	7.6x10 ⁻⁵	8.8x10 ⁻⁵	4.96x10 ⁻⁵
n	0.79	0.825	0.83	0.89
R2 [Ω*cm²]	1395	6500	5785	17045
SOLUTION 0.5M H ₂ SO ₄				
	SAF2507 Untreated	SAF2507 Plasma treated	AISI420 Untreated	AISI420 Plasma treated
R1 [Ω*cm²]	11	15	2.6	2.25
Q [F*Hz¹⁻ⁿ]	1.591x10 ⁻³	9.06x10 ⁻⁴	2.2x10 ⁻⁴	1.7x10 ⁻⁴
n	0.81	0.78	0.86	0.859
R2 [Ω*cm²]	120.3	783.2	35.5	400.41

Tab. 1 - Equivalent circuit values for samples of AISI420 and SAF2507 treated with APPJ and tested in solutions containing chlorides or sulphates.

Tab. 1 - Risultati della simulazione dei dati sperimentali per i campioni di AISI420 e SAF2507 trattati con plasma atmosferico e testate in soluzioni contenenti cloruri o solfati.

the resistance of the electrolyte, R_2 is the polarization resistance, which strongly depends on the passive film and is a measure of the corrosion resistance of the material, and CPE is a constant phase element, used instead of a capacitance because the measured capacitance is not ideal. The chosen equivalent circuit is suitable to fit EIS data of stainless steels tested in chlorides and sulphates

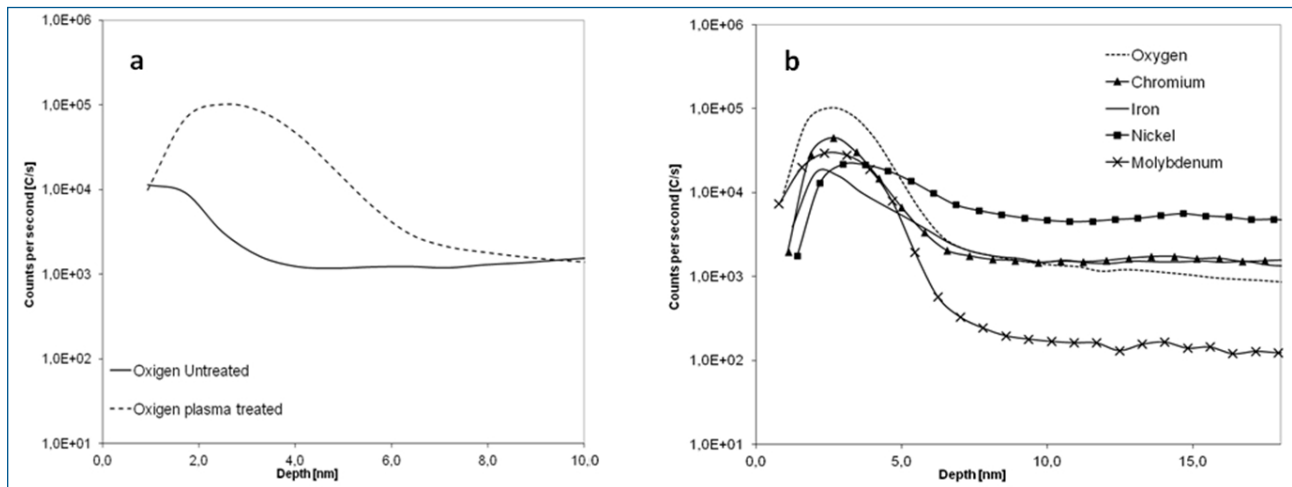


Fig. 3 - SIMS depth profiles of oxygen in untreated and plasma treated sample of SAF2507 duplex stainless steel (a); SIMS depth profiles of the sample of SAF2507 treated with APPJ at $2 \times 10^{-3} \text{ m/s}$ (b)

Fig. 3 - Profilo chimico SIMS dell'ossigeno per i due campioni di SAF2507 (a); profilo chimico SIMS per il campione di SAF2507 trattato con plasma atmosferico con velocità di movimentazione della torcia di $2 \times 10^{-3} \text{ m/s}$ (b)

solutions, as can be found in literature for similar trends [12], and good fitting quality was obtained.

The double layer capacitance can be calculated using the values of Q , n and R_2 reported in Tab. 1, using Eq.1 [13-14]:

$$C = n \sqrt{\frac{Q}{R_2^{n-1}}} \quad (1)$$

Therefore, the decreasing of Q passing from the untreated samples to the plasma treated samples implies a decrease of the values of C . From Eq. 2, this decrease can be correlated to the increase of the oxide layer thickness.

$$C = \frac{\epsilon_0 \epsilon S}{d} \quad (2)$$

where C is the capacitance, ϵ_0 is the permittivity of vacuum, ϵ is the dielectric constant, S the area and d the thickness of the oxide layer.

The polarization resistance of the SAF2507 plasma treated samples was significantly higher than the one of the untreated samples, in both the solutions examined. Since the polarization resistance is a measure of the corrosion resistance of the material (it is inversely proportional to i_{corr}), these values showed the higher corrosion resistance of the plasma treated sample in comparison with the untreated sample, in agreement with the results obtained by polarization tests. Similar results were obtained for the AISI420 steel (Tab. 1).

The SIMS analysis were carried out to study the effect of plasma treatment on the surface of the two stainless steels. The oxygen chemical profiles of the untreated and plasma treated samples of SAF2507 are shown in Fig. 3a, where it is possible to observe that the treatment with atmospheric plasma induced the oxidation of the surface and the formation of a thicker oxide layer. The thickness of the oxide, that can be estimated as the depth at which the oxygen concentration falls down to 50% of its maximum

value, was 1.5 nm for the untreated sample and 4 nm for the plasma treated sample. The SIMS profiles of the other elements for the plasma treated sample (Fig. 3b) showed that the passive layer was constituted by a double layer, with the outer one rich in iron and the inner one rich in chromium and molybdenum, in agreement with literature. [15-16]. In fact, the peak of iron is more external than the ones of chromium and molybdenum. It can be also observed that the peak of nickel is more internal with respect to the passive layer, confirming that this element is not involved in the formation of the oxide film. [18] The SIMS analysis carried out for AISI420 showed that the plasma treatment induced the formation of a thicker layer.

In order to obtain information about the oxidation state of the elements present in the oxide layer of the stainless steels, XPS analysis (without sputtering) was performed before and after the plasma treatment on the SAF2507 sample. Figure 4a shows high resolution single peak O 1s spectra for untreated and plasma treated SAF2507 samples. The oxygen spectra can be deconvoluted in two components: the peak located at 530.7 eV BE corresponds to metallic oxides; the peak located at 531.8 eV BE corresponds to metallic hydroxides. Observing the plots of the deconvoluted peak, it resulted that the plasma treatment caused an increase of the metallic oxides to the detriment of metallic hydroxides (the ratio oxides/hydroxides was 1.1 for the untreated sample and 3.2 for the plasma treated sample). From the deconvolution of the Fe $2p_{3/2}$ peak (Fig. 4b), where the peak located at 709.2 eV BE corresponds to the Fe(II) species and the peak located at 710.6 eV BE to Fe(III) species, it resulted that the surface plasma treatment induced the oxidation of the iron from Fe(II) to Fe(III). In fact, the plasma treated sample was characterised by a higher amount of Fe(III) species in comparison with the untreated sample (51% and 62% for the untreated and plasma treated sample, respectively).

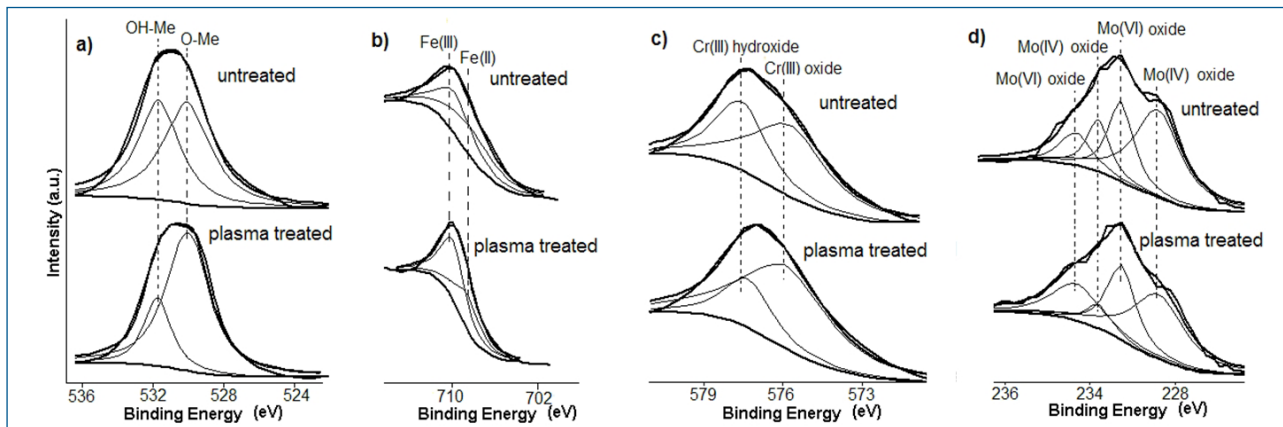


Fig. 4 - XPS high resolution single peak spectra of the O 1s (a), Fe 2p_{3/2} (b), Cr 2p_{3/2} (c) and Mo 3d (d) of SAF2507 sample.

Fig. 4 - Risultati della deconvoluzione dei picchi O 1s (a), Fe 2p_{3/2} (b), Cr 2p_{3/2} (c) e Mo 3d (d) dell'analisi XPS del campione SAF2507.

The deconvolution of the peak of the Cr 2p_{3/2} spectra is reported in Fig. 4c, both for the untreated and plasma treated sample. The peak at 576.2 eV BE correspond to Cr(III) oxide, the peak at 577.4 eV BE to Cr(III) hydroxides, CrOOH and Cr(OH)₃. The plasma treatment caused an increase of the oxides species to the detriment of the hydroxides species: the ratio oxide/hydroxide of Cr(III) was 1.1 for the untreated sample and 2.9 for the plasma treated sample.

The deconvolution of the peak of Mo 3d spectrum is shown in Fig. 4d, where the peaks at 229.8 eV BE (Mo3d_{5/2}) and 233.4 eV BE (Mo3d_{3/2}) corresponds to Mo(IV) oxide species, whereas 231.8 eV BE (Mo3d_{5/2}) and 235.0 eV BE (Mo3d_{3/2}) to Mo(VI) oxide species. It is possible to observe that the plasma treatment induced also in this case the oxidation of Mo(IV) to Mo(VI): a total amount of Mo(VI) oxide species of 37% was calculated for the untreated sample vs. a value of 50% for the plasma treated sample. From SIMS and XPS analysis it resulted that the plasma treatment allowed the formation of a passive layer thrice thicker than the layer of the untreated sample and promoted the oxidation of the elements constituting the passive layer (Fe, Cr and Mo). Therefore, the improvement in the corrosion resistance of the plasma treated samples, can be attributed to the thicker passive layer and to the presence of a higher amount of Cr(III) and Mo(VI) oxide species.

CONCLUSIONS

In this work the effects of surface treatment with an atmospheric pressure plasma jet on the passive film and on the corrosion resistance of two different stainless steels, were investigated. The potentiodynamic anodic polarization and the electrochemical impedance spectroscopy tests showed that the plasma treatment induced an improvement in the corrosion resistance of SAF2507 and AISI420 stainless steels. The enhancement in the corrosion properties is more visible in the 0.5M

H₂SO₄ solution than in 0.3M NaCl solution. From SIMS and XPS analysis it resulted that the plasma treatment promoted the oxidation of the surface and the formation of a thicker oxide layer, 4.5 nm thick, with a higher presence of metallic oxides, in comparison with the untreated sample. The native passive layer, 1.5 nm thick, was constituted mainly by oxides of Fe, Cr and Mo. The plasma treatment induced an increase of the Cr(III), Fe(III) and Mo(IV) oxides species. The improvement in the corrosion resistance of the plasma treated samples is probably due to the presence of a thicker passive layer and to the presence of a higher amount of Cr(III) and Mo(VI) oxide species.

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Influenza di trattamenti con plasma atmosferico sulla resistenza a corrosione di acciai inossidabili

Parole chiave: Acciai inox - Corrosione - Trattamenti superficiali - Caratterizzazione dei materiali

In questo studio è stato studiato l'effetto del trattamento con plasma atmosferico sullo strato di ossido superficiale di due acciai inossidabili (l'acciaio inossidabile martensitico AISI420 e l'acciaio duplex SAF2507) e la loro resistenza a corrosione. I campioni metallici sono stati trattati mediante plasma generato utilizzando aria alla pressione costante di 1.5 bar e con una velocità di passata della torcia di 2×10^{-3} m/s. Lo strumento utilizzato per generare il plasma è un APPJ (Atmospheric Pressure Plasma Jet). Le variazioni della composizione superficiale sono state studiate mediante XPS e SIMS. I risultati dell'analisi al SIMS hanno evidenziato come lo spessore dello strato di ossido triplichi a seguito del trattamento con plasma atmosferico; inoltre è stata confermata la presenza di un doppio strato di passivazione, con il ferro e il molibdeno nella parte esterna e il cromo in quella interna. Le analisi XPS hanno rilevato che il trattamento con il plasma aumenta il contenuto degli ossidi di Cr(III), Fe(III) e Mo(VI) nello strato di passivazione. Per valutare la resistenza a corrosione, sono state eseguite prove di polarizzazione anodica e di spettroscopia di impedenza (EIS) in ambienti contenenti solfati o cloruri. È stato osservato un incremento della resistenza a corrosione a seguito del trattamento con plasma in entrambe le soluzioni considerate; il miglioramento è però più marcato nel caso della soluzione 0.5M H₂SO₄ poiché questa, meno aggressiva, consente di evidenziare meglio le differenze tra i due campioni. Il miglioramento della resistenza a corrosione può essere spiegato con l'aumento di spessore dello strato passivante, con l'aumento del contenuto di ossidi di Cr e con la presenza di una maggiore quantità di MoO₃.