Anticorrosion behaviour of amorphous silicon-based coatings prepared by remote cold plasma-assisted chemical vapour deposition process

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Abstract

Organosilicon films were deposited on carbon steel samples using remote microwave nitrogen plasma-assisted chemical vapour deposition. The deposits were obtained using TetraMethyDisoloxane monomer mixed with oxygen. The formed films were characterised using electron microprobe analysis, Fourier transformed infrared spectroscopy, contact angle measurements, scanning electron microscopy and atomic force microscopy. The electrochemical properties of the organosilicon coatings were evaluated using gravimetric experiments next to electrochemical tests. A significant increase in the corrosion resistance behaviour of the organosilicon coated carbon steel specimen was found when the samples were immersed in 3% aqueous sodium chloride solutions. Also, the surface pre-treatment process of carbon steel had an important influence on the morphological and electrochemical behaviour. Argon pre-treatment improves significantly the corrosion resistance or organosilicon coated steel samples. Gravimetric tests in particular showed that samples pre-treated with argon result in lower weight loss and decreased corrosion rates compared to interfaces pre-treated with nitrogen plasma.

Keywords: PACVD, carbon steel, organ silicon, corrosion, pre-treatment, electrochemical impedance spectroscopy.

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1. Introduction

Over the years, intense research efforts have been put into the protection of metals from corrosion, which prevents the use of some interesting metals and alloys on strategic applications such as aerospace or transport. Chromate conversion coatings were widely used over the years due to their simplicity [1–3]. Unfortunately, these approaches make use of toxic reactants and produce toxic wastes with important implications on the environment. Alternative technologies are thus being looked at. The process of plasma activated chemical vapour deposition (PACVD) is nowadays a key technology applied in a whole range of industries [4–6].

It enables deposition of thin films of controlled physico-chemical properties, using a variety of different organosilicon precursors. Its advantage over chemical processes is, besides being a dry process, it has a wide range of settings and changeable parameters such as the gas flow rates, gas ratio and type of plasma used, which enable to accurately control the growing film characteristics [7–10]. In addition, it allows to carry our substrate pre-treatment just before the coating process in order to improve the adhesion of coating. This together with the environmentally friendly character makes the process an interesting approach to increase the corrosion resistance of metals.

The organosilicon films formed using PACVD are mostly amorphous in nature and are associated with a high electrical resistivity (10^9–10^{15} Ω cm) [11, 12]. However, this depends strongly on the quality of deposits itself, which can be controlled by the conditions of preparation. A reduction in the amount of hydrogen in the coatings with an increased amount of Si-O links is believed to improve the barrier properties essential for application in corrosion [13, 14].

The aim of this work is to characterise and explain the efficiency of multifunctional coating to protect steel. This paper deals with the corrosion behaviour of carbon steel protected with a micrometer thick organosilicon films. The importance of the kind of surface pre-treatment carried out before depositon of the organosilicon film is discussed. Electrochemical measurements were used next to weight loss studies to identify the corrosive protective efficiency when the interfaces were immersed for 100 hour in 3% sodium chloride solution.

2. Experimental

2.1. Materials

The carbon steel substrates were obtained from Arcelor (France) and have the following chemical composition: C (0.37 %), Si (0.23 %), Mn (0.68 %), Ni (0.059 %), Cu (0.16 %), Cr (0.5 %), S (0.016 %), Ti (0.011 %) and Fe (97.9 %). Sodium chloride (NaCl) was purchased from Aldrich.

2.2. Surface coating

Organosilicon films were deposited on carbon steel using remote microwave nitrogen plasma-assisted chemical vapour deposition (MW-PACVD), following a similar process described previously [15]. The monomer precursor used was 1, 1, 3, 3, tetramethyldisiloxane (TMDS, purity 97%), which was premixed with oxygen (purity ≥ 99.5%). This mixture was injected into a cold remote nitrogen plasma (microwave generated, $P = 1,200$ W) through a coaxial injector.

The deposition process was carried out in two steps: first, samples were treated for − 10 minutes by the cold remote nitrogen plasma (N_2 flow rate = 2,500 mL/min, microwave power = 1,000 W) in order to increase the adhesion quality of the polymer. Second, the deposition step was performed without air exposure using following parameters: flow rate of TMDS = 15 mL/min; flow rate of oxygen = 150 mL/min, flow rate of nitrogen = 2,500 mL/min, microwave power = 1,000 Watts. In the case of argon pre-treatment the following parameters were used before the deposition: flow rate of argon = 500 sccm

and time $=$ 15 minutes. In the case of nitrogen, pre-treatment following parameters were used before the deposition: flow rate of nitrogen $=$ 2,500 sccm and time $=$ 5 minutes.

3. Results and discussion

3.1. Preparation and characterisation of the organosilicon film

Remote MW-PACVD using TMDS as monomer precursor was used for the formation of an organosilicon coating on polished carbon steel specimens. The thickness of the deposited film was controlled by the time of deposition, which was in our case 20 minutes. From profilometric measurements, the thickness of the organosilicon film was determined as 2.5 ± 0.1 μm.

Prior to the deposition of the coating, two different pre-treatment steps were performed on the interfaces: nitrogen plasma and argon plasma treatment. The kind of surface pre-treatment of carbon steel had a significant influence on the finingnal wetting properties of the coated sample. Polished uncoated carbon steel shows a static contact angle of 89 ± 2. Coating with an organosilicon film of 2.5 μm without any special one pre-treatment and with nitrogen plasma treatment increased the water contact angle slightly to 95 ± 2 and 98 ± 2, respectively. However, in the case of argon pre-treatment a hydrophobic water contact angle of 117 ± 2 was found. The wetting properties of the argon pre-treated interface is highly stable in time. Indeed, after 20 days, no change in the wetting properties was recorded.

The morphology of the interfaces was investigated using scanning electron microscopy (SEM, Figure 1) electron microprobe analysis (Figure 2). While nitrogen pre-treated and untreated carbon steel interfaces show that the deposited organosilicon film has a globular structure, in the case of an argon-pre-treated interface a smooth polymer film with grains of very small size are formed. Images of backscattered electrons obtained by electron microprobe analysis confirm the SEM results. A smooth surface with reduced defects is obtained in the case of argon pre-treatment, while cracks are observed on untreated and with nitrogen plasma pre-treated samples. This might have important consequences for the protective efficiency against corrosion. Indeed, the presence of defects such as holes and cracks will allow the infiltration of solutions more easily and thus attack the underlying carbon–steel interface.
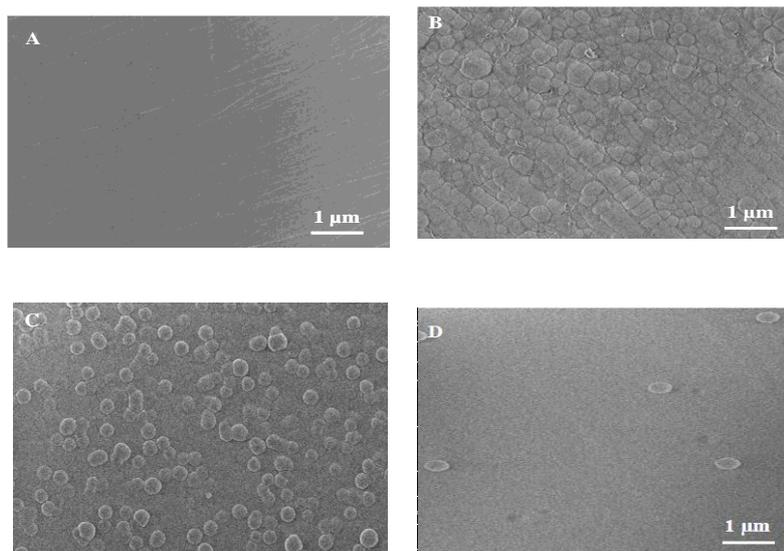
Figure 1. SEM images of carbon steel coated with organosilicon films of 2.5 μm in thickness using different surface pre-treatments. (a) Polished carbon steel. (b) No pre-treatment. (c) Nitrogen pre- treatment. (d) Argon pre-treatment
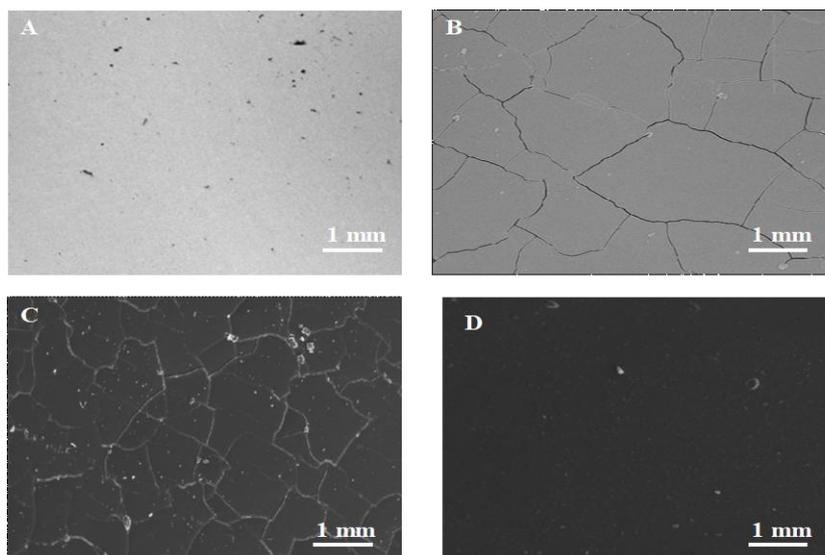
Figure 2. Images in the backscattered electrons mode of a carbon–steel interface. (a) When coated with organosilicon films of 2.5 μm in thickness using different surface pre-treatments pre-treatment. (b) No re-treatment. (c) Nitrogen pre-treatment. (d) Argon pre-treatment

3.2. FTIR and Raman characterisation

Figure 3(b) shows the FTIR spectra in reflection mode of the polished steel interface after coating with 2.5 μm thick organosilicon films using different surface pre-treatments. The main groups are $Si(CH_3)_x$ and Si-O-Si in accordance with the literature [15]. The asymmetric vibration band of Si-O-Si is located towards 1,000–1,200 cm^{-1} and is the strongest band observed [16]. Argon pre-treatment considerably increased the absorption intensity of the Si-O-Si band, which is linked to an increase in the dissociation of the monomer precursor TMDS. The asymmetric v (CH_3) bans are seen at 2,963 and 2,910 cm^{-1} and at 840 cm^{-1}. The bands at 1,258 and 1,417 cm^{-1} are attributed to v (CH_3) due to $Si(CH_3)_x$ with $x = 1$, 2 or 3. The absorbance intensity at 1,258 cm^{-1} is also affected by the surface pre-treatment. Nitrogen and argon plasma pre-treatment results in a significant increase. However, the band is smaller than the Si-O-Si one. Indeed, the dissociation of TMDS starts rather by the loss of methyl functions as the binding energy between silicon and carbon is smaller than that between silicon and oxygen [3, 17]. The contribution of Si-H stretching bands observed at ≈ 2,090 cm^{-1} is rather weak. However, the broad band cantered at 3,321 cm^{-1} is characteristic of OH stretching modes from either surface hydroxyl groups and/or absorbed water.

In addition, Raman spectra were recorded [Figure 3(a)]. The bands at 486 and 701 cm^{-1} are due to Si-O-Si, while the one centred at 183 cm^{-1} is assigned as structure lattice mode due to the pseudo-amorphous nature of the deposit [18].The CH deformation modes are observed in the spectral range between 750 and 860 cm^{-1} [19]. Indeed, the amorhous nature of the coating was confirmed by EDS analysis (Table 1) [20]. The argon pre-treatment results in a slight decrease in the Si/C ratio, while the Si/O content stayed rather unchanged.

(a) (b)
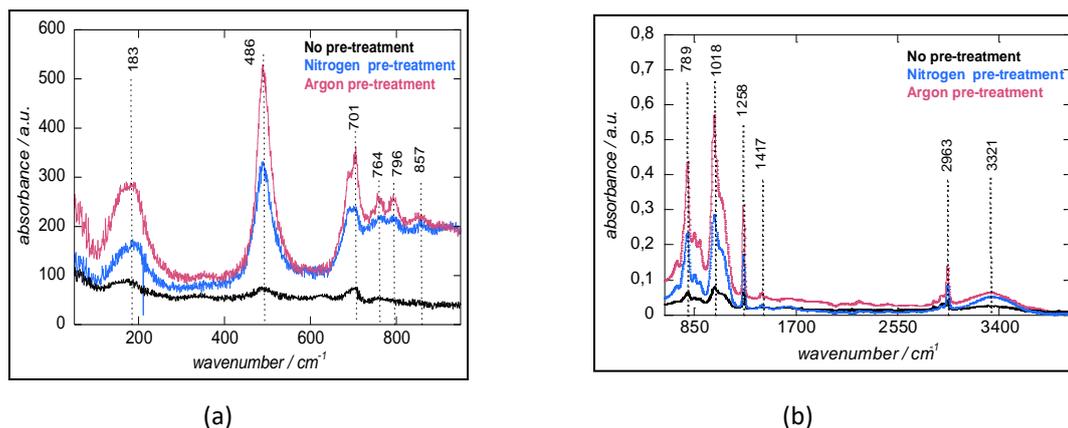
Figure 3. Influence of the carbon steel pre-treatment on (a) Raman spectra and FTR and (b) when coated with organosilicon films of 2.5 μm in thickness: no pre-treatment (black), nitrogen (blue), argon (magenta)

3.3. Investigation of the corrosion protection efficiently

In order to understand better the corrosion protection mechanism of the organosilicon coating formed on carbon steel using different surface pre-treatment electrochemical investigations were performed next to gravimetric experiments in aqueous solutions of 3% NaCl.

3.3.1. Gravimetric analysis

Weight loss experiments were performed on carbon steel and protected carbon–steel interfaces for 30 days at 30°C. The corrosion rate (v_{corr}), expressed in millimetres per year (mpy), of uncoated and coated specimens steel can be determined using Eq. (1) [21, 22]

$$v_{corr} \, (mpy) = \frac{3.45 \times 10^6 W}{ADt} \tag{1}$$

where W is the weight loss (g), D is the density of the carbon steel specimen (7.85 g cm^{-3}), A is the area of the coupon (cm^2) and t is the exposure time (h). From the values of weight loss of uncoated (W_0) and coated specimens steel (W), the protective efficiency (PE%) can be determined using Eq. (2) [23, 24]

$$PE \, (\%) = \left(1 - \frac{W}{W_0}\right) \times 100 \tag{2}$$

The results of the gravimetric determinations of coated and uncoated carbon steel with different pre-treatment in 3% NaCl are summarised in Table 2. Coated and in particular argon pre-treatment interfaces present excellent corrosive protection. In the case of argon, pre-treated samples have a PE of 81% determined after corrosion for 30 days in 3% NaCl solutions.

Table 1. Results of weight loss studies

Interface	Immersion time days	Weight loss g × 10⁻³	v_{corr} mpy	PE %
Carbon steel	7	3.04 ± 0.03	1.51	0
	15	5.13 ± 0.04	1.19	0
	30	28.71 ± 0.04	3.33	0
Coated steel	7	0.95 ± 0.03	0.47	69
No pre-treatment	15	2.66 ± 0.03	0.61	48
	30	19.01 ± 0.03	2.20	34
Coated steel	7	0.27 ± 0.03	0.18	91
nitrogen pre-treatment	15	0.21 ± 0.03	0.48	59
	30	20.72 ± 0.03	2.40	28
Coated steel	7	0.19 ± 0.03	0.09	99
argon pre-treatment	15	0.38 ± 0.03	0.08	93
	30	0.55 ± 0.03	0.63	81

3.3.2. Measurements of the open circuit potential (EOCP)

The evolution of the (E_{OCP}) with time provides information about the corrosion activities of a metal interface [24, 25]. Figure 4 shows the evolutions of E_{OCP} when uncoated and coated carbon steel substrates were immersed into saline aqueous solution (NaCl 3%). In the case of unprotected steel, a decrease in E_{OCP} is observed after about 40 hour immersion into NaCl 3%. This is attributed to the dissolution of iron [26]. The behaviour was different for the steel coated with organosilicon films. The E_{OCP} was shifted to more positive potential values and no obvious fluctuation of E_{OCP} was observed in the measurement time frame, indicating that these interfaces seem to have an increased corrosion resistance.
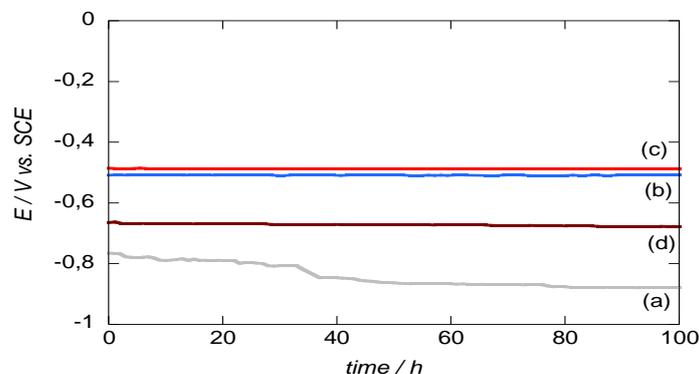
Figure 4. Change of E_{OCP} versus time carbon steel (a) and when coated with organosilicon films of 2.5 μm in thickness using different surface pre-treatments pre-treatment: (b) no re-treatment, (c) nitrogen pre-treatment, (d) argon pre-treatment; solution: 3% NaCl

3.3.3. Quasi-steady-state linear polarisation measurements

Figure 5 shows representative potentiodynamic polarisation curves of the different interfaces and shows clearly that the pre-treatment has a strong influence on the corrosion potential. The corrosion potential of carbon steel sample after immersion for 7 days in NaCl 3 % was found to be around −880 mV with a corrosion current density $j_{corr} = 7.2 \times 10^{-6}$ A·cm⁻² (Table 3). A strong shift in corrosion potential, compared to unmodified steel is observed for organosilicon coated carbon steel. The presence of the film decreased additionally both the anodic and cathodic current densities due to a restricted supply of oxygen and water, limiting their reduction. Consequently, the corrosion currents

are as in Table 3. The PE of the coating can be determined using Eq. (2) by replacing W and W_0 by j_{corr} and $j^0_{corr,}$ denoting, respectively, the corrosion currents densities for coated and uncoated steel [27, 28].The results are comparable with those obtained from weight loss studies. Indeed, the argon pre-treated interface shows again the best corrosive protection.
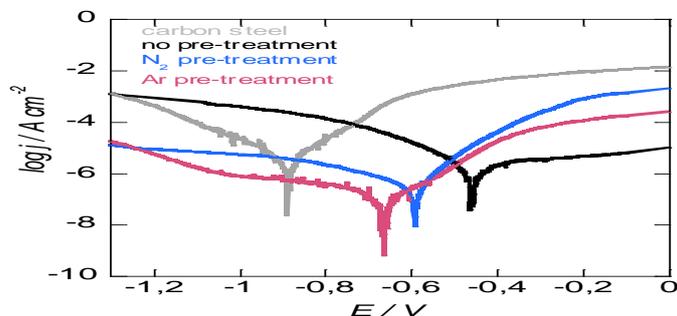
Figure 5. Potentiodynamic polarisation curves of carbon steel (grey) and when coated with organosilicon films of 2.5 μm in thickness using different surface pre-treatments: no re-treatment (black), nitrogen pre-treatment, (blue) and argon pre-treatment (magenta): solution: 3 % NaCl aqueous solution, immersion for 7 days

Table 2. Electrochemically determined parameters from potentiodynamic polarisation curves

Interface	Immersion time days	E_{corr}/V	j_{corr} /A cm^{-2}	PE %
Carbon steel	7	−0.88	7.2×10^{-6}	0
	15	−0.88	3.5×10^{-5}	0
	30	−0.88	1.1×10^{-4}	0
Coated steel	7	−0.46	2.5×10^{-6}	65
No pre-treatment	15	−0.46	3.6×10^{-6}	50
	30	−0.48	4.7×10^{-6}	37
Coated steel	7	−0.58	4.5×10^{-7}	93
nitrogen pre-treatment	15	−0.59	2.9×10^{-6}	59
	30	−0.59	5.3×10^{-6}	26
Coated steel	7	−0.67	2.7×10^{-7}	96
argon pre-treatment	15	−0.67	5.3×10^{-7}	92
	30	−0.67	1.3×10^{-6}	82

3.3.4. Electrochemical impedance spectroscopy (EIS)

Electrochemical Impedance analysis between 2 MHz and 100 kHz with an amplitude of 10 mV at E_{OCP} was in addition performed. Nyquist plots of the steel specimen coated with organosilicon polymers in 3% NaCl are shown in Figure 6(a). Two time constants at the high and medium frequency ranges are clearly observed in the case of coated steel, while only one time constant is observed for carbon steel. The first high-frequency loops are related to the film properties, while the second loop at lower frequencies is linked to the substrate surface. Such results are best presented by the equivalent circuit shown in Figure 6(b), where R_S is the electrolyte resistance; R_C and CPE_C the resistance and capacitance of the coating; R_{CT} the charge transfer resistance and C_{DL} is the capacitance of the substrate/coating interface. Indeed, such a circuit is commonly employed for simulation of coating/substrate systems [2, 29].
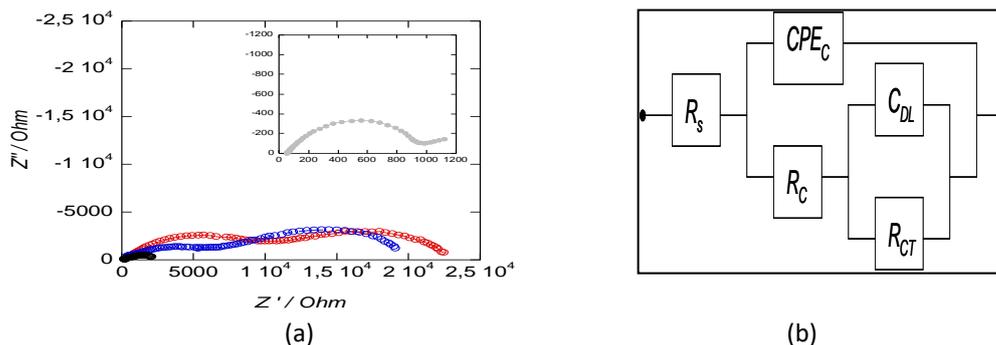
Figure 6. (a) Nyquist plots of carbon steel (inset, grey) and the same substrate when coated with organosilicon films of 2.5 μm in thickness using different surface pre-treatments: no pre-treatment (black), nitrogen pre-treatment, (blue) and argon pre-treatment (red): solution 3% NaCl aqueous solution. (b) Equivalent circuit used to simulate the EIS results

The charge transfer resistance is increased on the coated carbon steel interfaces being 2.6 kΩcm^2 for coated carbon steel without any pre-treatment and 18.1 and 22.4 kΩ cm^2 for interfaces with nitrogen and argon plasma pre-treatment, respectively. Figure 7 shows the change in the charge transfer of the coated steel specimens when immersed in 3% NaCl. The argon and nitrogen treated samples show a charge transfer resistance of about 6 kΩ cm^2 over the 100 hour immersion and seems to stabilise. The coated carbon steel sample where no additional surface pre-treatment was performed, shows an initial lower charge transfer resistance value, which changes only by 6 kΩ cm^2 over the 100 hour immersion.
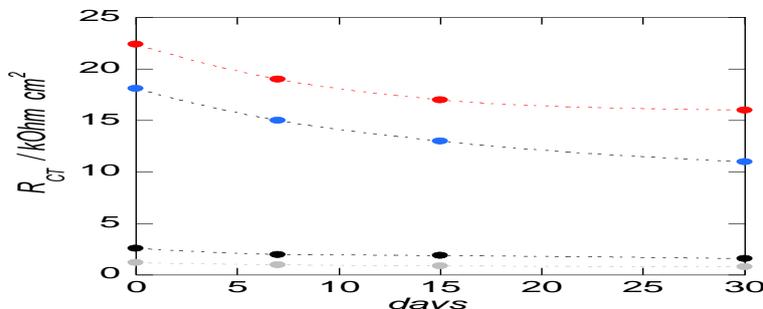
Figure 7. Change of the charge transfer resistance over time when immersed in 3% NaCl aqueous solution. Carbon steel (grey), coated with organosilicon films of 2.5 μm in thickness using different surface pre-treatments: no pre-treatment (black), nitrogen pre-treatment, (blue) and argon pre-treatment (red)

4. Conclusion

Amorphous organosilicon films of 2.5 μm in thickness were deposited on carbon steel samples using remote MW-PACVD. The barrier properties of the coatings against corrosion were investigated. A significant increase in the corrosion resistance behaviour of the organosilicon coated carbon steel specimen was found when the carbon steel interface was pre-treated with argon plasma. Gravimetric tests were cooperated by electrochemical corrosion tests.

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