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To cite this article: Vera Sazavska *et al* 2016 *J. Phys.: Conf. Ser.* **715** 012012

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Plasmachemical Conservation of Corroded Metallic Objects

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Abstract: Plasmachemical process for conservation of metallic objects is a new way of effective and fast treatment of corroded objects. This process consists of two main steps: corrosion removal and deposition of a protecting film. Removal of corrosion products is based on plasmachemical reduction of corrosion layers by radio-frequency (RF) low pressure hydrogen plasma. Chosen barrier films are parylene (poly-para-xylylene) coatings and SiO₂-like high density films. Parylene coatings are prepared by a standard chemical vapor deposition (CVD) method. Plasma enhanced chemical vapour deposition (PECVD) enables preparation of SiO_x based thin films with higher flexibility due to variable incorporated organics groups. The coatings were characterized by various methods in order to obtain information about their chemical structure (FTIR) and barrier properties (OTR). The results from standard corrosion test were compared with those on samples treated by conventional conservation procedures.

1. Introduction

Plasmachemical removal of corrosion layers from metal samples is a relatively new technique for restoration of archaeological artefacts. The method is based on a partial reduction of the incrustation and corrosion layers by RF low pressure hydrogen plasma [1, 2]. The hydrogen molecule is dissociated to very reactive species like radicals, ions, and excited hydrogen in plasma discharge. These species react with compounds from corrosion layers. Corrosion products (like oxides, chlorides, etc.) can be reduced to the pure metal due to the reduction effect of hydrogen.

Surface of the treated object is highly reactive and inclines to rapid oxidation by air oxygen. To prevent this process, it is necessary to protect the surface by a barrier thin film preventing the penetration of oxygen (as well as the other corrosion agents) to the surface. The barrier film must not change optical properties of the object and have to be removable without damage of the object. Suitable barrier films are parylene (poly-para-xylylene) coatings and SiO₂-like high density films. Parylene coatings are chemically inert, conformal and transparent with excellent barrier properties [3], but relatively small adhesion. Parylene is one of the most well-known chemical vapor deposited (CVD) thin film polymers. SiO₂-like high density films have very good barrier properties and excellent adhesion. SiO_x layers were deposited by PECVD in a low pressure reactor with capacitively coupled plasma discharge. Mixture of hexamethyldisiloxane (HMDSO) with oxygen was used as a precursor of plasmachemical reactions. Hexamethyldisiloxane is another suitable monomer for the thin film preparation. The main advantages of these films are good barrier properties. Moreover, they are transparent, colourless, flexible, soft and inert [4].



2. Experimental setup

2.1 Plasmachemical treatment

The experiment was carried out in the Quartz cylindrical reactor (i.d. 95 mm, length of 90 cm) with outer copper electrodes (Figure 1). The capacitive coupled RF power supply (frequency of 13.56 MHz) gave the total power up to 600 W in a continuous or pulsed regime. We used pulses with a duty cycle of 75 %, 50 % and 25 %, and frequency was 1000 Hz (25% pulse means 0.25 ms discharge on and 0.75 ms off). Flowing plasma was created in pure hydrogen (gas flow of 50 sccm) at pressure of 200 Pa. The real temperature of samples was measured continuously by a thermocouple installed inside the model sample. The optical emission spectroscopy (OES) of OH radical was used for the process monitoring.

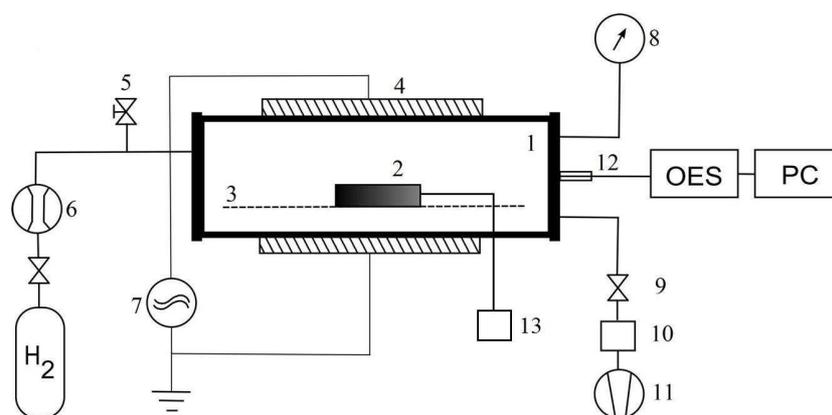


Figure 1: Experimental set-up: 1 – Quartz discharge reactor (90 cm long, i.d. 95 mm); 2 – corroded sample; 3 – glass sample holder; 4 – outer copper electrodes; 5 – air-inlet valve; 6 – mass flow controller; 7 – RF power supply and matching network; 8 – pressure gauge; 9, 10 – valves; 11 – rotary oil pump; 12 – optical fibre; 13 – thermocouple

2.2 Parylene deposition

The apparatus for chemical vapour deposition uses the Gorham process consisted of the following parts: vaporizer, pyrolytic chamber, cooling section and deposition chamber. The vaporizer consists of a brass cartridge where the defined amount of Parylene C is placed. The pyrolytic chamber is about 1.5 m long and its inner diameter is 38 mm. The cooling chamber is shorter than the pyrolytic chamber and also has the bigger inner diameter. The deposition chamber is a vertical cylinder of diameter of 35 cm and a height of approximately 50 cm. Vacuum inside the deposition chamber is up to 10 Pa and it is produced by a mechanical vacuum pump. The last main part of the apparatus is a cold trap with temperature about -20°C which serves for removal of the rest of monomer to prevent clogging of the mechanical vacuum pump.

Defined amount of Parylene C (42 g for the barrier thickness of $20\ \mu\text{m}$) was placed into the vaporizer. Temperature of the vaporizer was gradually increased up to about 120°C when the process began and further to 180°C when process was finished. Because of the vacuum gradient, molecules of the dimer went through the pyrolytic chamber which was heated to temperature of about 680°C . The dimer was fragmented into reactive monomer particles. Monomer particles came into the cooling section which served for the gas temperature decrease (150°C). Pressure in the deposition chamber was kept constant at the value of 10 Pa. The whole process of the deposition lasted for 4.5 hour.

2.2 pp-HMDSO deposition

The apparatus for SiOx depositions is designed as a high-vacuum bell jar reactor with pressure of about 10^{-4} Pa. The system consists of a glass reactor with volume of 30 L. It is equipped by two thermal evaporators and a capacitive coupled system of electrodes connected to the plasma generator (working frequency of 13.56 MHz). The system also allows monomer vapour deposition and it is equipped with mass flow controllers. Reactor space is evacuated by a rotary oil pump in the first step,

and by a turbomolecular pump, subsequently. It is possible to change the pumping velocity of the whole pumping system continuously by a manually controlled gate valve (DN100) in order to achieve the desired working pressure. The radiofrequency capacitive coupled glow discharge is created between two plan-parallel electrodes with the diameter of 170 mm which are placed in the centre of the reactor. The inlet of working gases is located under the lower grounded electrode. The upper electrode can be settled by substrates (Quartz polished on both sides, silicon wafer, a foil or another deposited sample). Radiofrequency voltage is supplied to this electrode from the generator with an automatic matching network.

The deposition process was done on a silicon wafer and a PP foil as a substrate. The PP foil was cleaned by ethanol. Liquid hexamethyldisiloxan ($C_6H_{18}OSi_2$) was used for plasma polymerization as a precursor. It was placed in a glass flask and only the monomer vapour was let flowing into the apparatus. Pressure inside the deposition chamber was $2 \cdot 10^{-3}$ Pa. Then, the chamber was purged with the mixture of the monomer (0.54 sccm) and oxygen (10 sccm). The deposition time was 6 minutes for all samples and power was 50 W.

3. Results and discussion

3.1 Integral intensity of OH radicals

The optical emission spectroscopy of created OH radicals was used for the process monitoring. Atomic hydrogen reacts with oxygen from corrosion layers and forms OH radical (in excited state) [5]. OH radical emits in the spectral region of 305–325 nm, and its integral intensity was used for the quantitative analysis of oxygen removal from the corrosion layer [6, 7]. Simultaneously, rotational temperature was calculated from emission spectra. The rotational temperature was more or less constant during the plasma treatment (600 K).

Integral intensity of OH radicals during plasma removal of corroded objects is shown in Figure 2. OH intensity quickly increases to the maximum then the reduction process slow down. Plasma treatment was stopped when the value of relative intensity of OH radicals reached one tenth of maximum OH radical intensity [7]. Maximum OH radical intensity shows extent of reduction of oxides from corrosion layers. We can see in the Figure 2 maximum OH radical intensity is lower in pulsed regime (200W 75% pulse) thus reduction process is less strong in the pulsed regime than in continual regime. Advantage of pulsed regime is lower heating stress of treated objects. Pulsed regime is suitable for metal objects sensitive to the heating stress. The plasma treatment duration was 60–120 minutes depending on the duty cycle.

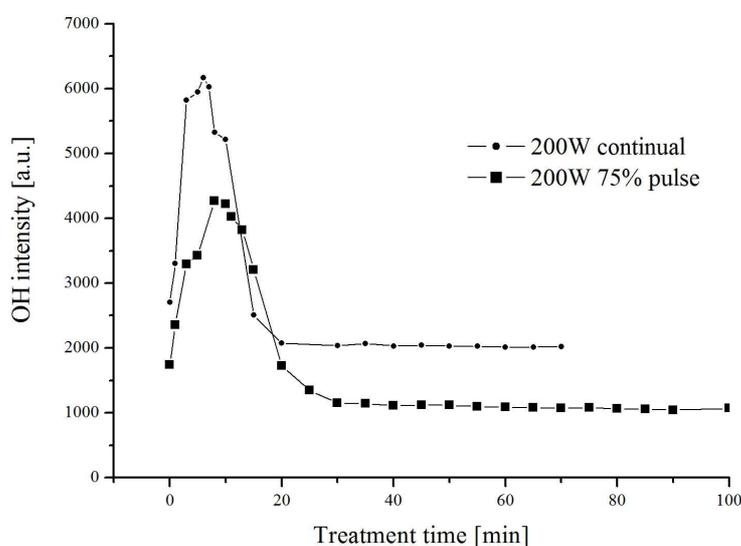


Figure 2. Relative intensity of OH radicals in the dependence on treatment time

3.2 Energy dispersive X-ray spectroscopy of treated samples

Corroded and treated objects were analyzed by a SEM-EDX method in order to determine changes of their surface elemental composition caused by hydrogen plasma. We can see decrease of amount of elements from corrosion layer and increase of abundance of elements from metals (in Figure 3). Thus partial removal of corrosion layers was proved.

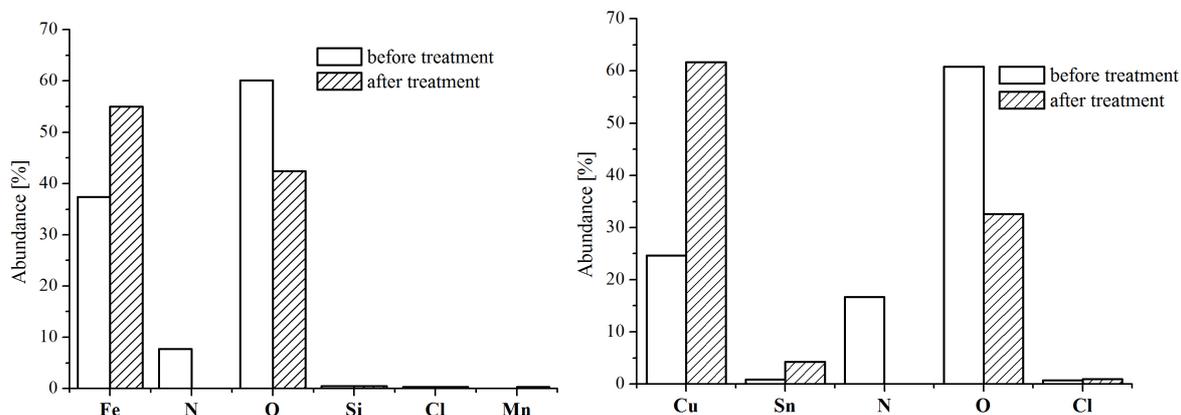


Figure 3: Results of the SEM-EDX analysis of iron (left) and bronze (right) samples

3.3 Fourier Transform Infrared Spectroscopy

Chemical structure analysis of protective films was done by a spectrometer Nicolet iS10 with OMNIC software. The FT-IR measurements give information about the coating composition. The obtained spectrum of Parylene C is in Figure 4 and the spectrum of pp-HMDSO is in Figure 5.

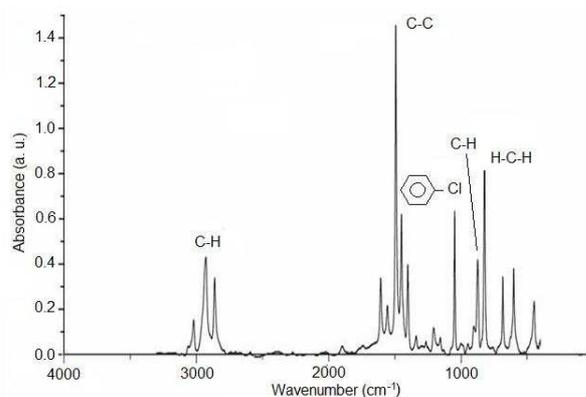


Figure 4: Infrared spectrum of Parylene C

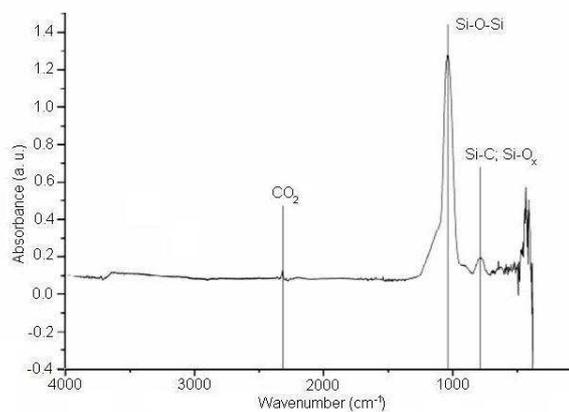


Figure 5: Infrared spectrum of pp-HMDSO

In the spectrum of Parylene C, the 1494 cm^{-1} peak represents the aryl carbon vibrational movement (C – C). Peak at 1050 cm^{-1} is attributed to the chlorine bonding to the ring. The 825 cm^{-1} peak is a representative of two neighbouring hydrogen atoms bonded to the ring (CH_2), and the peak at 877 cm^{-1} is a representative of the single hydrogen to the ring (CH) which is neighbouring chlorine and ethyl group in this case. Additional characteristic peak of CH_2 on the benzene ring is at 1452 cm^{-1} . A pair of peaks at 2861 and 2927 cm^{-1} indicates the vibrational movement of the C–H bond in methyl groups and C–H bond vibrational movement in the aromatic ring at 3019 cm^{-1} [8].

There are smaller peaks in addition to the peaks described in the spectrum. These peaks can be caused by noise or various contaminants contained in the deposition precursor of Parylene C or added substances, such as 3-(trimethoxysilyl)propyl methacrylate.

In the spectrum of the pp-HMDSO, there is the peak at 2330 cm^{-1} which represents the molecule of CO_2 . Peak at 1069 cm^{-1} is a representative of Si-O-Si, and the peak at 790 cm^{-1} represents Si-O_x bonds [9]. It means that we have prepared a layer with minimum amount of carbon.

3.3 Oxygen Transmission Rate

Transmission rate of the PP foil for oxygen was measured. We have measured foils with the thin layer (Parylene C or pp-HMDSO) as well as clean PP foils. As you can see in Table 1, the values for Oxygen Transmission Rate measurements are very different. In case of pp-HMDSO, the transmission rate is of the same order as the clean PP-foil. It is in contrast to Parylene C where the transmission rate is about 20 times lower than the permeability of the PP-foil.

Table 1: Transmission rate of the PP-foil

Substrate	Permeability ($\text{cm}^3/(\text{m}^2 \cdot \text{atm} \cdot \text{day})$)
PP-foil	665
PP-foil with pp-HMDSO	127
PP-foil with Parylene C	32

3.3 Corrosion test in salt spray chamber

The new protective film (Parylen C) and a barrier film (paraloid B44) commonly used in restoration practice were compared. The metal samples with both films were tested in the salt spray chamber Ascot 450 according to the CSN EN ISO 9227 norm. The tested samples were exposed to the salt spray for 300 h. The salt spray had contained 5% NaCl solution mixed with air in the nozzle. The temperature was $25\text{ }^\circ\text{C}$ in the salt spray chamber.

The result of the corrosion test for paraloid B44 is in Figure 6. The protective varnish paraloid B44 have not perfect resistance to corrosion. The Parylen C layer is shown in Figure 7. Only few corrosive spots are presented on the surface. The result is clear that the new Parylen C layer has much better corrosion resistance than commonly used varnish paraloid B44.

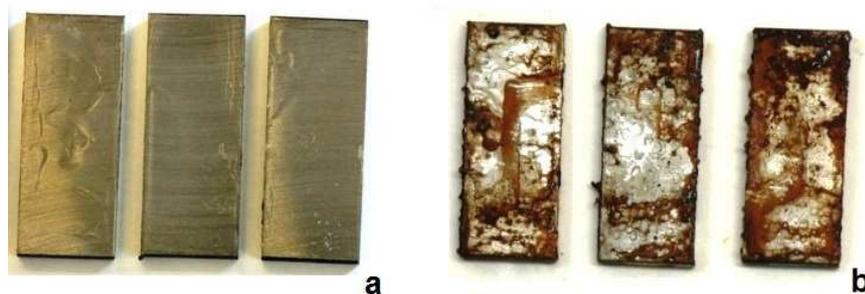


Figure 6. Results of the test CSN EN ISO 9227 in the salt chamber for the iron sample with the protective film paraloid B44 (**a** before test, **b** after 300h in the salt chamber)

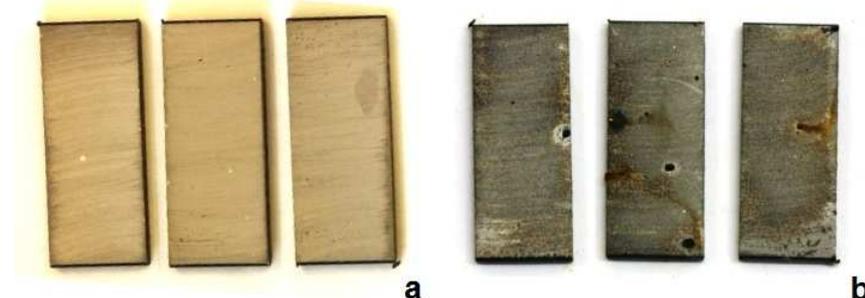


Figure 7. Results of the test CSN EN ISO 9227 in the salt chamber for the iron sample with the protective film Parylen C (**a** before test, **b** after 300h in the salt chamber)

4. Conclusion

We proved partial remove of corrosion compounds by SEM-EDX and OES. We characterised thin protective films (Parylen C and SiO_x) by FTIR and OTR. Elemental composition was investigated by the infrared spectroscopy. We determined that thin layers of pp-HMDSO did not contain carbon, which indicated that we had prepared the thin layer really similar to the SiO₂ like layer. Oxygen permeability through the protective films was investigated by oxygen transmission rate. The thin film of Parylene C had a four times smaller permeability than the thin film of pp-HMDSO.

Parylen C layer was compared with the conventional varnish paraloid B44 by the corrosion test in the salt spray chamber. The corrosion test proved much better protective properties of Parylen C.

Acknowledgements:

This research has been supported by the Czech Ministry of Culture, project No. DF11P01OVV004.

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