

EFFECT OF PLASMA TREATMENT ON CORROSION LAYER OF IRON

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Plasmachemical process for conservation of metallic objects is a new way of effective and fast treatment of corroded objects. Removal of corrosion products is based on plasmachemical reduction of corrosion layers by radio-frequency (RF) low pressure hydrogen plasma. The analyses XRD and SEM/EDX on corroded and treatment samples were done.

1. Introduction

For the last twenty years the application of hydrogen plasma in the conservation and restoration of metallic objects has been investigated in order to determine its potential and limits for culture heritage objects treatment. The method is still under development, and model samples under various experimental conditions are tested.

The method is based on reduction of the corrosion products on the metal objects (model samples or excavated archeological objects) by reactive hydrogen atoms in low pressure radio-frequency (RF) hydrogen glow discharge plasma at low temperature. The reduced layer on objects becomes brittle and can be removed easily by the conservators. The application of RF discharge plasma for removing of corrosion layers mainly from iron objects was developed by Prof. Veprek during the 1980s [1,2].

This work extends our recent experiments with plasmachemical treatment of metal objects [3]. The presented contribution describes new experiments with model iron samples and results of analyses by X-ray diffraction (XRD) and Scanning Electron Microscopy (SEM) / Energy Dispersive X-ray Spectroscopy (EDX).

2. Experimental set-up

The samples used in our experiments were made of low doped construction steel (98.9% Fe), dimensions of 10 mm x 10 mm x 5 mm, see Fig.1a. Then the samples were corroded in HCl solution for five weeks, see Fig. 1b.

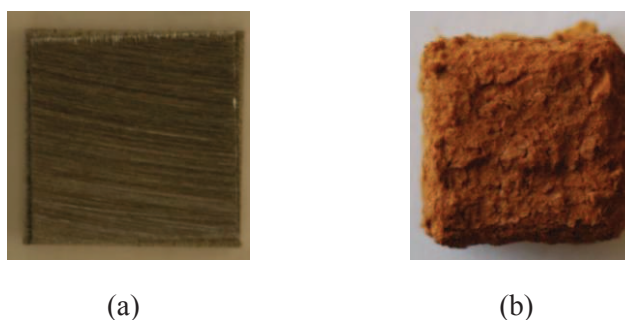


Fig. 1: The samples: a-before corrosion, b-corroded sample.

The simplified schematic drawing of our experimental device is shown in Fig. 2. The plasma reactor was cylindrical with inner diameter of 95 mm and length of 900 mm made of quartz glass. The copper electrodes were placed out of the reactor on the reactor wall opposite each other. The capacitive coupled RF power supply with frequency of 13.56 MHz delivered 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 pulse frequency was 1000 Hz. 25% pulse means 0.25 ms discharge on and 0.75 ms off. The plasma was created in pure hydrogen with gas flow of 50 sccm at pressure of 200 Pa.

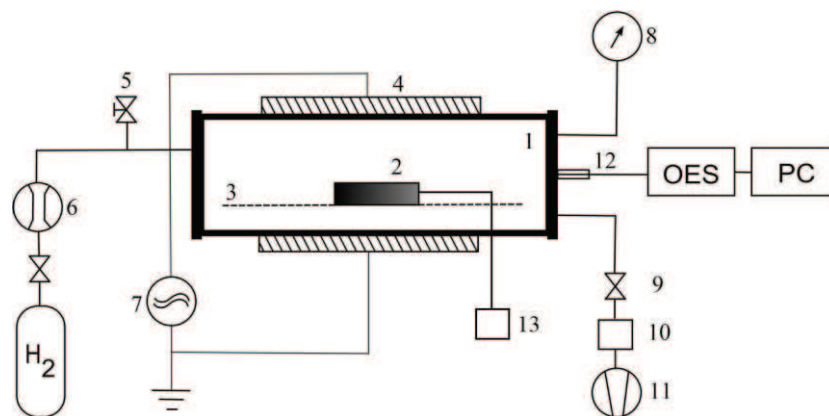


Fig. 2. Experimental set-up: 1 – Quartz discharge reactor (90 cm long, i.d. 95 mm); 2 – corroded sample; 3 – glass sample holder; 4 – outer copper electrodes; 5 – air-inlet valve; 6 – mass flow controller; 7 – RF power supply and matching network; 8 – pressure gauge; 9, 10 – valves; 11 – rotary oil pump;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

The real temperature of sample was measured during the treatment by a thermocouple installed inside the model sample. The optical emission spectroscopy (OES) of OH radical was used for the process monitoring. Optical emission spectra of OH radicals were measured by an Ocean Optics HR 4000 spectrometer with 2400 gr/mm grating. Atomic hydrogen reacts with oxygen from corrosion layers and forms OH radicals in excited states. OH radicals emit in the spectral region of 305–325 nm, and integral intensity over this region was used for the quantitative analysis of oxygen removal from the corrosion layer. The plasma treatment was stopped when a value of relative intensity of OH spectrum reached one tenth of the maximum OH spectrum intensity [4]. The plasma treatment duration was 60–120 minutes depending on the duty cycle.

Corroded and treated samples were analysed by a SEM-EDX and XRD method in order to determine changes of their surface elemental composition caused by hydrogen plasma.

3. Results and discussion

Results from XRD spectra of corroded samples shows presence of rookhite ($\text{FeCl}_2 \cdot 2\text{H}_2\text{O}$) and akageneite ($\text{Fe}^{3+} \text{O}(\text{OH}, \text{Cl})$). These compounds are typical products of HCl corrosion. Example of measured XRD spectra is shown in Fig. 3.

The corrosion layers were analysed before the plasma treatment by electron microscopy with elementary X-ray spectroscopy. The same analysis was repeated after the plasma treatment. The microphotography of treated sample (400 W, pulse 50%) showed relatively complicated surface structures (see Fig. 4) and also demonstrated non-homogeneity of the corrosion layer.

The elementary analysis of surface layers showed a significant difference of corrosive elements abundance depending on treatment conditions as it is shown in Fig. 5. There is also the comparison of the pulsed and the continual regime of plasma treatment. It can be seen that the amount of oxygen and chlorine decreases with increasing power in the continual regime. The same dependence can be seen in pulsed regime, the amount of oxygen and chlorine decreases with increasing pulse duration.

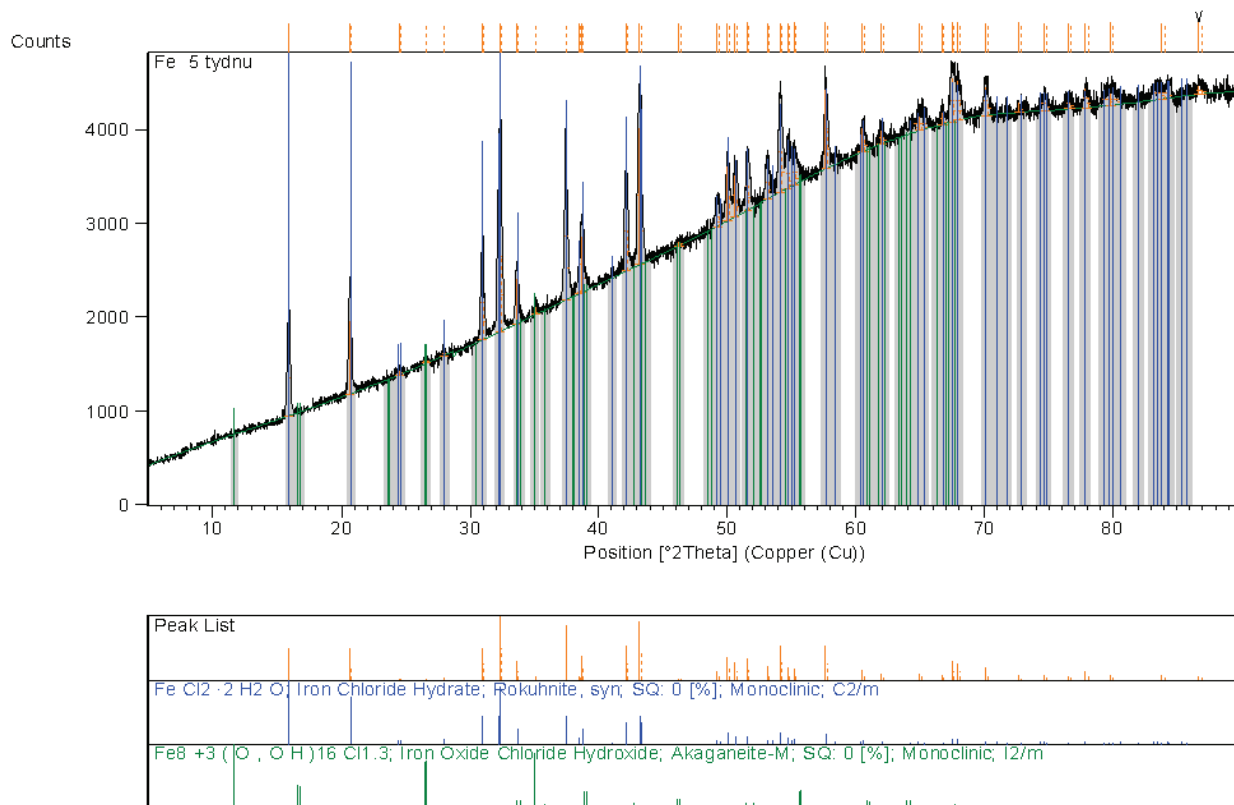


Fig. 3. XRD spectra of sample corroded in HCl for five weeks.

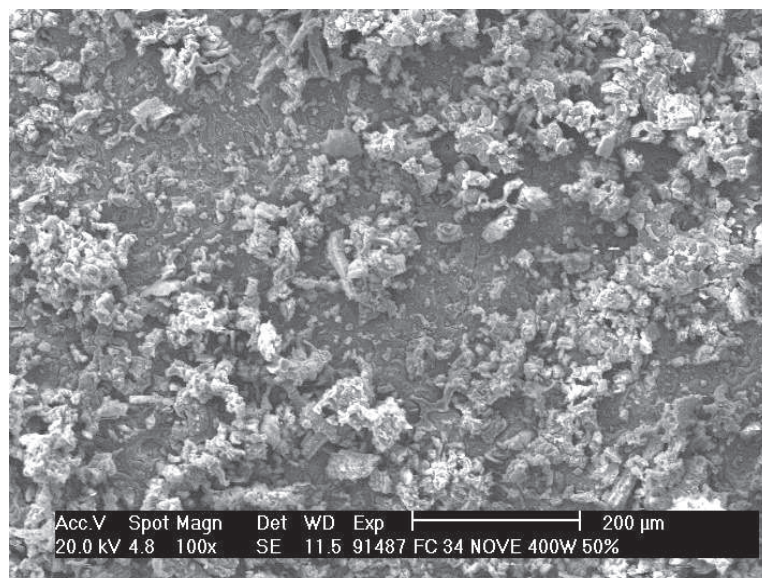


Fig. 4. The SEM image of the surface of corroded sample.

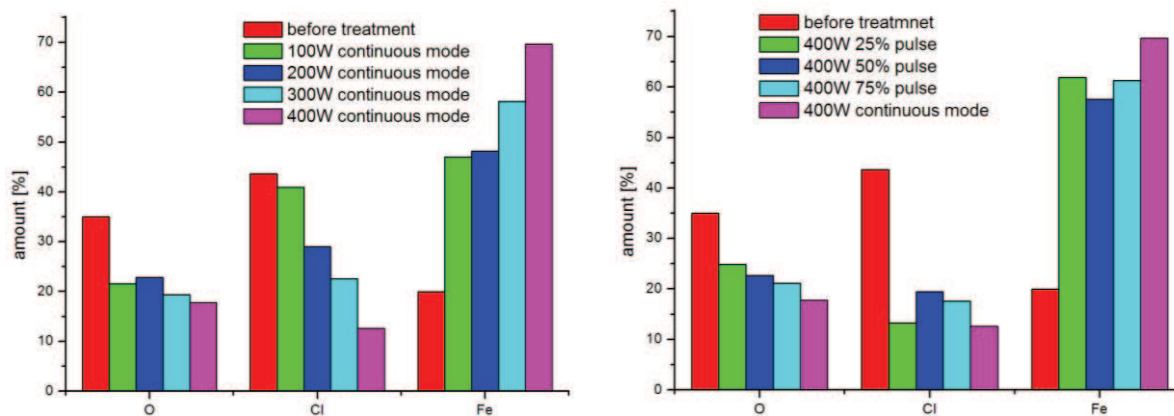


Fig. 5. A result of material analyzes of HCl vapor corroded samples after plasma treatment at different powers in continuous mode (left) and at 400W in pulsed regime (right).

4. Conclusion

The corrosions as well as their removal are a very complex problem. Plasma chemical treatment of performed model corroded iron samples was arranged by RF hydrogen low pressure plasma. Our experiment was realized in different regimes. The duty cycle was varied from continuous to 25% pulse. The analyses XRD and SEM/EDX on corroded and treatment samples were performed. The analyses show that the decrease of main corrosion agents as chlorine and oxygen was achieved by hydrogen plasma treating.

5. Acknowledgement

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6. References

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