

# Plasmachemical Treatment on Corrosion Layer of Iron

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## Summary

Plasmachemical process for conservation of metallic objects is a new way of effective and fast treatment of corroded objects. Removal 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 discharge plasma at low temperature. The reduced layer on objects becomes brittle and can be removed easily by the conservators. 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).

## 1 Introduction

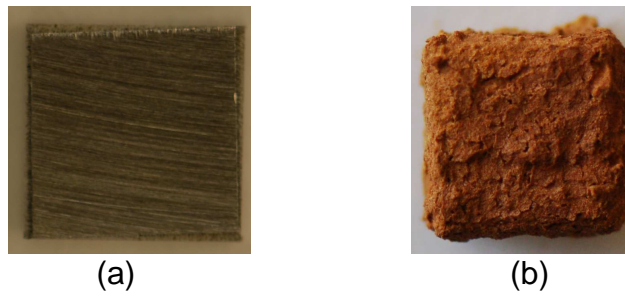
For the last twenty years the application of hydrogen plasma in the conservation and restoration of metallic objects has been investigated in order to determine its potential and limits for culture heritage objects treatment. The method is still under development, and model samples under various experimental conditions are tested. This process is still under development for conservation of archeological artefacts made of various materials, and it is used in several technical musea [1].

The method is based on a partial reduction of the incrustation and corrosion layers by hydrogen discharge plasma. 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. The application of RF discharge plasma for removing of corrosion layers mainly from iron objects was developed by Prof. Veprek during the 1980s [2,3].

Plasmachemical treatment is much more shorter than the mechanical or chemical treatment that have been commonly used till this time. The main advantage of this method is the fact that it is possible to treat the artefact of big size, the hollow artefacts or artefacts with broken relief [4, 5].

## 2 Experimental part

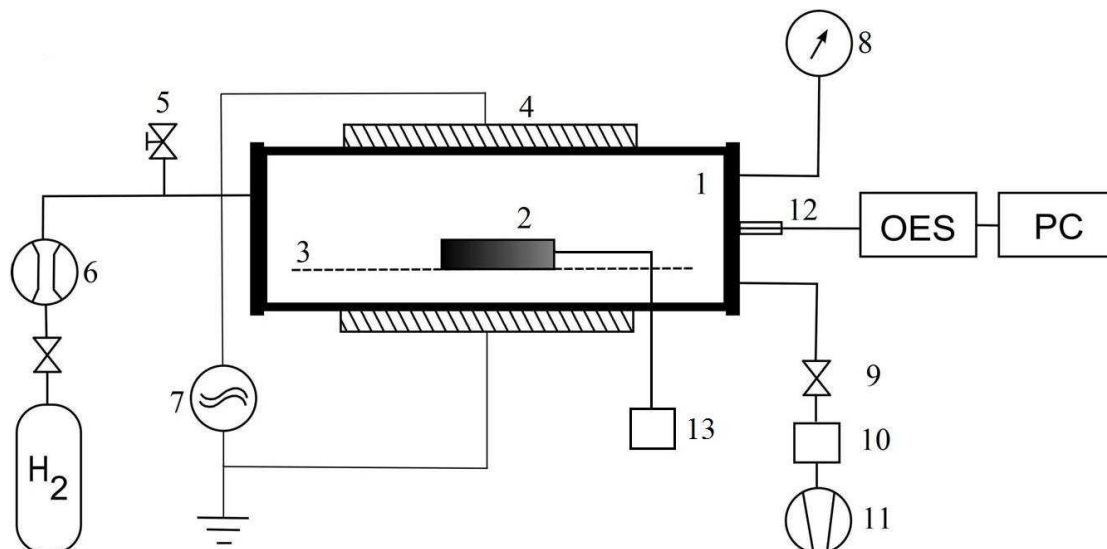
The samples of size (10x10x5) mm used in our experiments were made of low doped construction steel (98.9% Fe) that were corroded in vapor of concentrated hydrochloric acid for five weeks (see in Figure 1) in dessicator. After this corrosion process, the samples were kept for 24 hours in vacuum dryer and then the plasmachemical treatment was applied.



**Figure 1:** The Samples: (a) before corrosion; (b) corroded sample.

The simplified schematic drawing of our experimental device is in Figure 2. The cylindrical quartz plasma reactor was with inner diameter of 95 mm and length of 900 mm. The outside copper electrodes were placed on the opposite sides (top and bottom) of the reactor wall. 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. The real temperature of sample during the plasma processing was measured by a thermocouple installed inside the model sample. Sample temperature did not exceed 200°C during all these experiments.

The optical emission spectroscopy (OES) of OH radical was used for the process monitoring by an Ocean Optics HR 4000 spectrometer with 2400 gr/mm grating. The OH radical spectra in the spectral region of 305–325 nm were used for the process monitoring because atomic hydrogen reacts with oxygen from corrosion layers and forms OH radicals in excited states [6]. Thus OH spectrum reflects the efficiency of the corrosion removal process [8]. The plasma treatment was stopped when a value of relative intensity of OH radicals reached one tenth of the maximum OH radical intensity [7].



**Figure 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 – gas-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.

### 3 Results and discussion

The model samples were treated 90–120 minutes under different experimental conditions. The dependencies of OH radical integral intensity and sample temperature on treatment time were evaluated for all treatment samples. Results for discharge power of 400 W are shown in Fig. 3 and Fig. 4.

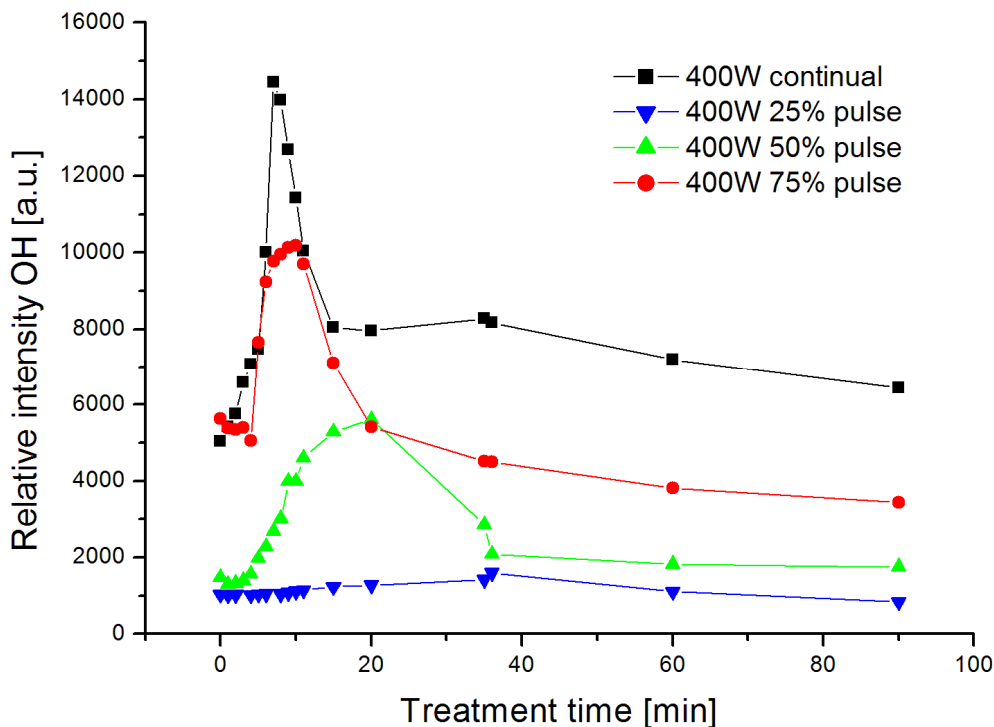


Figure 3: Dependencies of relative OH radical intensity on treatment time.

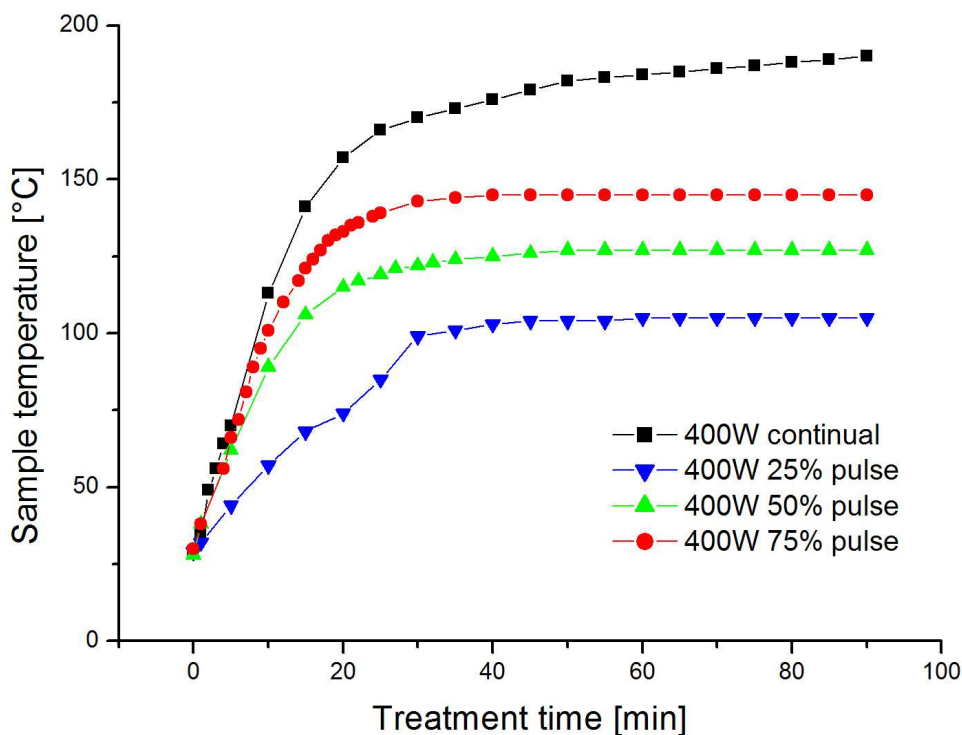
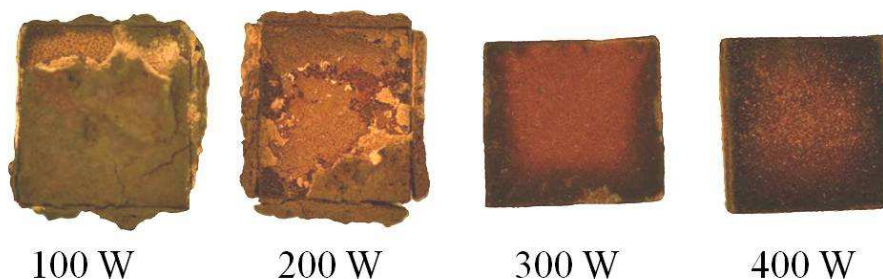
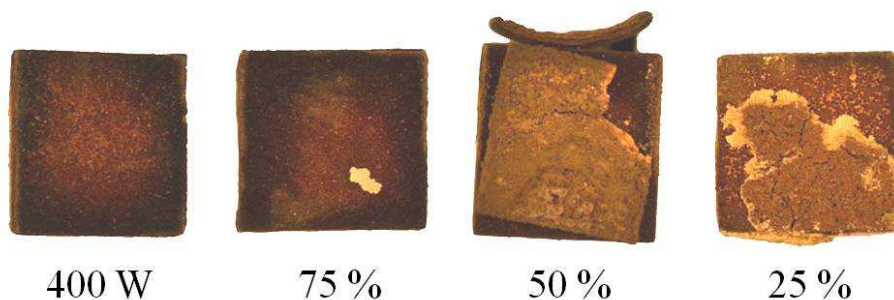


Figure 4: Dependencies of sample temperature on treatment time.

It is visible that maximal intensity of OH radicals and measured sample temperature depend on discharge regime. The maximal intensity of OH radicals ( $I_{rel}OH$ ) was reached at treatment time of 10 minutes for continual regime; in pulsed regime, the  $I_{rel}OH$  maximum shifts to the later treatment times with decreasing the effective power. This indicates slower reduction process of corroded layer. Also the value of  $I_{rel}OH$  decreases with decreasing effective power and it reflects smaller amount of removed corrosion products (respectively slower corrosion removal). It is clear that higher used power (see Figures 5 and 6) is the best for reduction process but it induces the higher sample temperature. Maximal measured sample temperature was 195°C (400 W in continual regime).



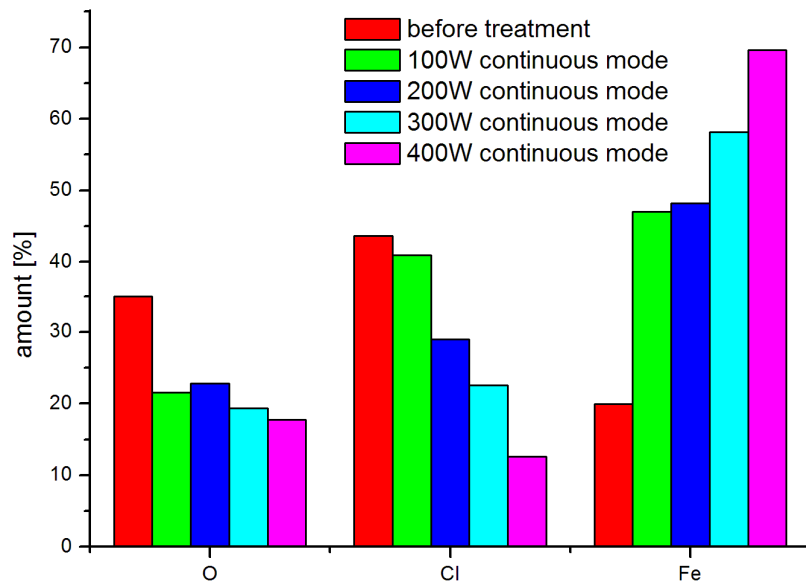
**Figure 5:** The images of samples treated in continual regime.



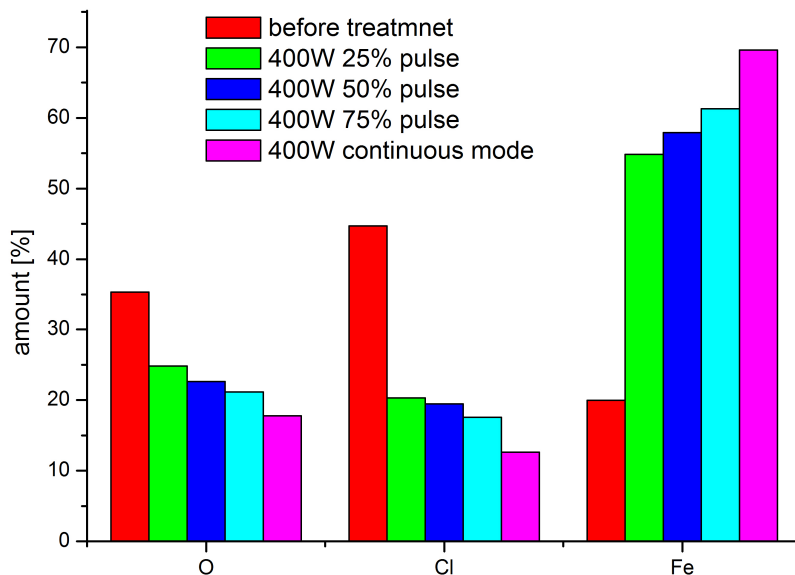
**Figure 6:** The images of samples treated at 400 W using different duty cycle.

The corroded samples XRD spectra show presence of rookhite ( $FeCl_2 \cdot 2H_2O$ ) and akaganeite ( $Fe^{3+} O(OH,Cl)$ ). The corrosion layers were analysed before the plasma treatment by electron microscopy with elementary X-ray spectroscopy (SEM-EDX). The same analysis was repeated after the plasma treatment.

The elementary analysis of surface layers showed a significant difference of corrosive elements abundance depending on treatment conditions as it is shown in Figures 7 and 8. 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.



**Figure 7:** Comparison of sample surface composition – effect of applied power.



**Figure 8:** Comparison of sample surface composition – effect of duty cycle.

#### 4. Conclusion

The corrosions as well as their removal are a very complex problem. Plasma chemical treatment of prepared model corroded iron samples was performed by RF hydrogen low pressure plasma. Our experiment was realized at different plasma operation regimes. The duty cycle was varied from continuous to 25% pulse. The sample temperature and intensity of OH radicals were measured during the sample treatment. The metal objects warm up due to electromagnetic induction in plasma discharge. Therefore, temperature monitoring of the treated object is necessary. Strong heating of the sample can cause metallographic changes which could lead even to a damage of the metal archaeological artefact. On the contrary, the chemical process of reduction by hydrogen needs a starting temperature. Sample temperatures were from 55°C to 195 °C in different conditions.

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 treatment.

## 5 Acknowledgements

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## 6 References

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