

Plasmachemical Removal of Corrosion Layers from Iron in RF Low Pressure Hydrogen Plasma

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Abstract. An effective and fast way of restoration and preservation of archaeological artifacts is described. The process is based on using RF low-pressure hydrogen plasma in which the artifacts are treated for several tens of minutes, usually in more steps. The value of integral intensity of OH radicals monitors the reduction process in plasma. Temperature depending on selected regime (continual or pulsed) plays an important role during the process. Our results show that pulsed regime can be effectively used in the corrosion removal process.

Introduction

Plasmachemical treatment of archaeological artifacts is a relatively new technique developed during the 1980s [1, 2]. It is an effective and fast way of restoration and preservation of archaeological artifacts. The method is based on a partial reduction of the incrustation and corrosion layers by hydrogen glow discharge plasma comparing to the conventional restoration techniques. This method offers significant advantages such as preservation of the quality of the object surface and time savings [3]. Finer surface details can be preserved. The corrosion removal process is a very complex procedure. It has been proved that both hydrogen atom reduction and heavy particles sputtering are important in this process but it is not fully known which of them plays the main role. Financial expenses represent the second problem. Plasmachemical reduction of corrosion layers is a very expensive method and the area of archaeology is not funded satisfactorily. This fact blocks distribution of this method to museums. That is why we have been investigating both the new technological procedure and the optimal conditions.

Observations

We prepared three sets of iron samples in different corrosive environments. The model corroded iron samples were prepared from iron with defined roughness (the samples were ground by the abrasive P 600 paper, which means 600 solids per square inch) using HCl vapour (for one week) and HNO₃ and H₂SO₄ acids (by dipping for 3 seconds and one week storage in desiccators). This allows us to study the influence of discharge under analogous corrosive conditions and therefore the results were found comparable. The samples were being covered by sufficient and uniform corrosion for one week. (This process was used by Cihlar, [4]). This procedure of corrosion simulates atmospheric corrosion, where main corrosive agents are chlorides, NO_x, SO_x. Each created corrosive layer was degraded in a different way. Accordingly, we used different corrosive environments. Corrosive layers were analyzed by electron microscopy giving the approximate constitution as well as surface relief. A ray microsonde for the determination of surface elementary conservation was used.

The experiment was done in Quartz reactor (i.d. 10 cm, length of 90 cm) with outer copper electrodes (Figure 1.). The capacitively coupled RF power supply gave the total power up to 600 W in continuous or pulsed regime. We used only pulses with duty cycle of 50% and 25%. Flowing plasma was created in pure hydrogen at pressure of 170 Pa. The applied discharge power was 200–500 W depending on the duty cycle.

The optical emission spectroscopy focused on OH radical was used for the process monitoring. Atomic hydrogen reacts with oxygen from corrosion layers and forms OH radical (in excited state). This OH radical emits energy in UV area of light spectrum (305–325 nm). Its integral intensity was used for the quantitative analysis of oxygen removal from the corrosion layer. Plasma treatment stopped when value of relative intensity of OH radicals reached one tenth of maximum of OH radicals [4]. Simultaneously the rotational temperature was calculated. The plasma treatment duration was 40–120 minutes depending on the duty cycle and corrosion layer kind.

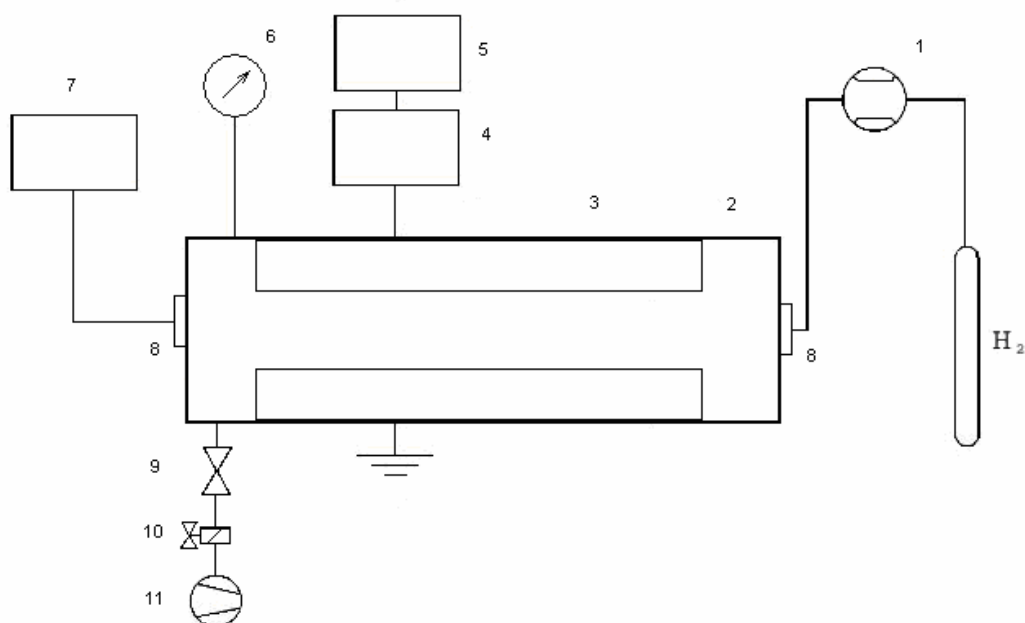


Figure 1. Experimental set-up: 1 – mass flow controller; 2 – Quartz discharge reactor (90 cm long, internal diameter 95 mm); 3 – outer copper electrodes; 4 – matching network; 5 – RF power supply; 6 – capacitance gauge; 7 – spectrometer TRIAX 550; 8 – quartz window; 9, 10 – valves; 11 – rotary oil pump.

A very good corrosion removal was observed at samples treated in continual regime plasma at RF power of 300 W, but significant heating of samples was observed, too. Treatment in pulsed regimes required higher powers applied during the pulse but the average energy was lower and thus the sample temperature did not increase so much. Rotational temperature was around (600 ± 100) K. The treatment using 25% duty cycle was not sufficient for the corrosion removal because the total energy was too low or the sample temperature was not, up to now, high enough for corrosion reduction.

Discussion

It is obvious that the maximum of OH integral intensity shifts according to the power regime. This is related to the sample temperature. In my opinion, temperature is not as high in the pulsed as in the continual regime because the sample was exposed to less influence of plasma in the pulsed than in the continual regime. Thus, we can assume that temperature plays an important role in the reduction process.

The course of reduction was very quick in continual regime that is why we did not register maximum of OH radicals intensity (Fig. 2 and 6). A maximum was evident at sample which was corroded in H_2SO_4 (Fig. 4) because sulphate corrosion layer was more compact and worse degradable than other corrosion layers.

The formed chloride corrosion layer (Fig. 2, 3) and nitric corrosion layer (Fig. 6, 7) were reduced successfully in continual regime and 50% pulsed duty cycle with higher power. This statement is confirmed by electron microscopy analysis (Fig. 8, 9). Figure 8 shows the analysis of the sample corroded in HCl and it is evident that chlorides were almost reduced. Quantity of oxygen increased, which was caused by oxidation of the sample exposed to air. In the case of sample which was corroded in HNO_3 (Fig. 9), amount of oxygen and nitrogen decreased followed by decrease of quantity of nitric molecules.

The worst experimental results were obtained during the treatment of corrosive layers created by submersion into the H_2SO_4 (Fig. 4, 5) probably because they had very homogeneous structure. Electron microscopy showed (Fig. 10) low decrease of quantity of oxygen and sulphur. The sulphate molecules were also very heavy in comparison with chlorides and nitrides, which indicated an important role of sputtering in the corrosion removal.

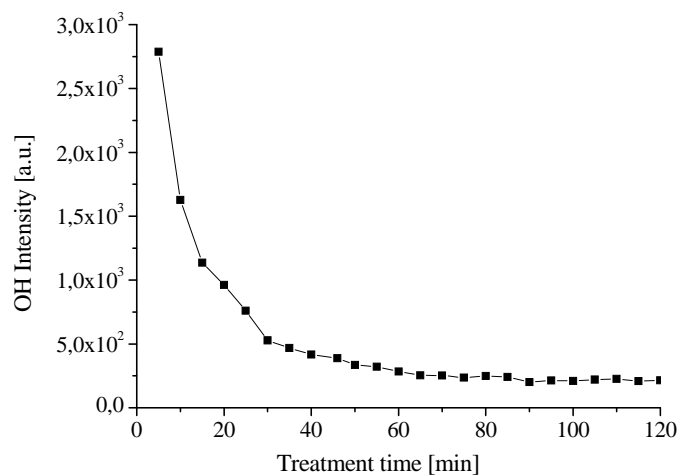


Figure 2. Relative intensity of OH radicals in dependence on treatment time, chloride corrosion layers, power of 300 W in continual regime.

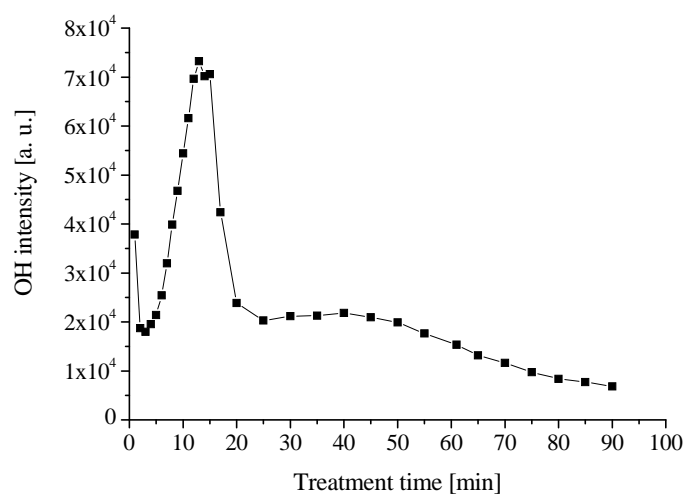


Figure 3. Relative intensity of OH radicals in dependence on treatment time, chloride corrosion layers, power of 400 W in pulsed regime with 50% pulse duty cycle.

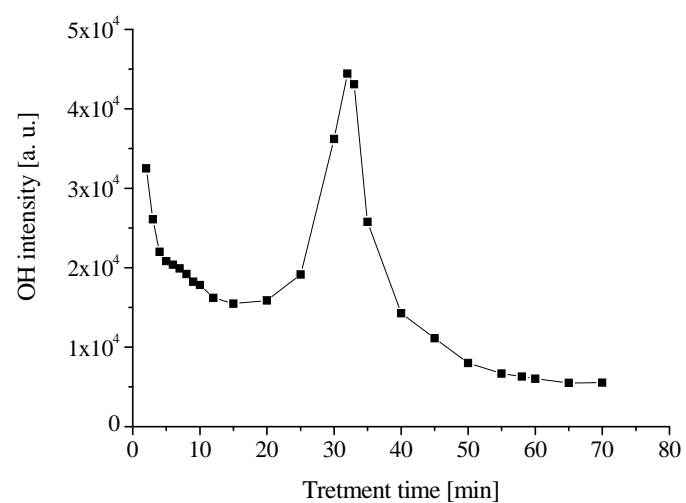


Figure 4. Relative intensity of OH radicals in dependence on treatment time, sulphate corrosion layers, power of 300 W in continual regime.

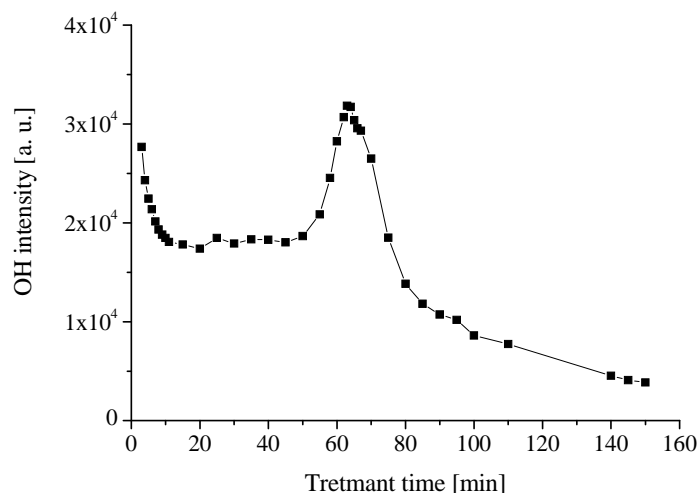


Figure 5. Relative intensity of OH radicals in dependence on treatment time, sulphate corrosion layers, power of 400 W in pulsed regime with 50% pulse duty cycle.

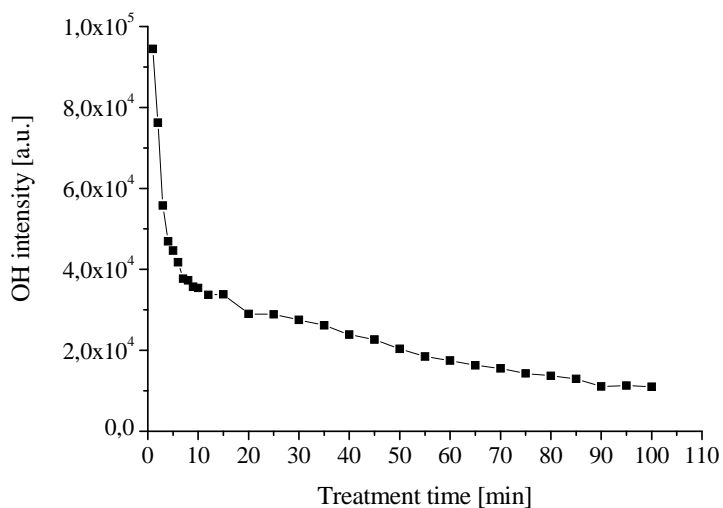


Figure 6. Relative intensity of OH radicals in dependence on treatment time, nitric corrosion layers, power of 300 W in continual regime.

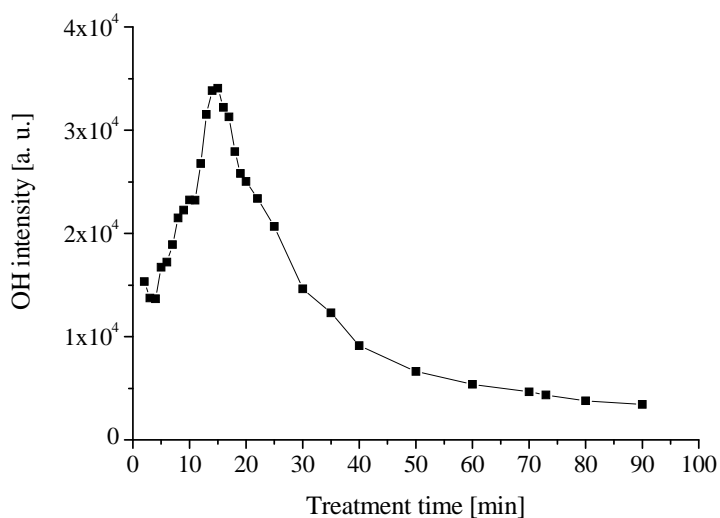


Figure 7. Relative intensity of OH radicals in dependence on treatment time, nitric corrosion layers, power of 400 W in pulsed regime with 50% pulse duty cycle.

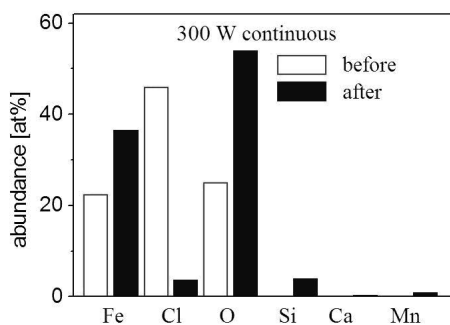


Figure 8. Electron microscopy analysis of surface of sample which was corroded in HCl (white column: corroded sample, black column: sample after treatment, power of 300 W in continuous regime).

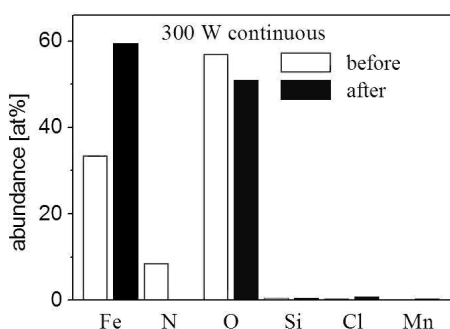


Figure 9. Electron microscopy analysis of surface of sample which was corroded in HNO₃ (white column: corroded sample, black column: sample after treatment, power of 300 W in continuous regime).

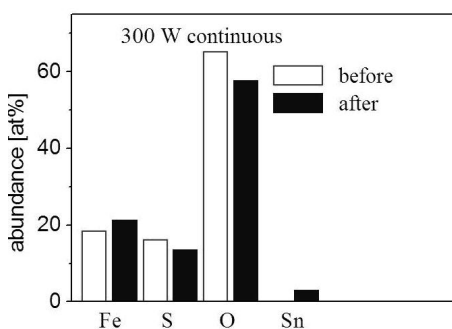


Figure 10. Electron microscopy analysis of surface of sample which was corroded in H₂SO₄ (white column: corroded sample, black column: sample after treatment, power of 300 W in continuous regime).

Conclusion

Our results show that the application of pulsed discharge regime can support the corrosion removal process also at lower mean power and thus the treated samples were affected by lower heating stress. However, the process ran longer. In the future we are going to measure thermal changes of samples by a simple probe. This will help us to understand processes which run on sample surface at plasmachemical reduction better. Then we will be able to optimize the conditions and combine hydrogen plasma effects with methods of classical conservation.

Acknowledgments. This work has been supported by the Czech Science Foundation, project No. 104/09/H080.

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