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Plasmachemical Removal of Corrosion Layers from Iron in Pulsed RF Discharge

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Abstract. Plasmachemical treatment of archaeological artefacts by RF hydrogen low pressure plasma is a relatively new technique developed during the 1980s. The corrosion removal process is very complex and its mechanism is not fully understood up to now and also optimal conditions are not known well. To study the process condition influence, the model corroded samples were prepared on iron with defined roughness using HCl, HNO₃ and H₂SO₄ corrosion agents. The corrosion layers before and after plasma treatment were analyzed by electron microscopy including the study of corrosion layer profile. The experiment was done in Quartz reactor with outer electrodes creating capacitive coupled RF discharge in pure hydrogen at pressure of 170 Pa. The duty cycle was varied from continuous regime up to 1:25. The plasma treatment duration was 40–120 minutes depending on the duty cycle. The results showed that the application of pulsed discharge regime could maintain the corrosion removal process at lower mean power as well and thus the treated samples were affected by lower heating stress. On the other hand, the process was significantly longer.

1. Introduction

Plasmachemical treatment of archaeological artefacts is a relatively new technique developed during the 1980s [1,2]. Although this technique was used for conservation of artefacts which components are mainly metals, the plasmachemical process in itself was used more or less intuitively [3]. The process is based on using low-pressure hydrogen plasma in which the artefacts are treated for several hours, usually in more steps. The problem is how long period of the plasmatic treatment is optimal and how to characterize its efficiency. The ancient artefacts always contain some corrosion layers on their surface. The studies focused on the composition of the layers show that various oxide and chloride complexes, usually containing crystalline water, too, are the dominant compounds of the layer. Bulk corrosion contains especially chlorides and sulphides while surface corrosion is caused by oxygen and water. Each original archaeological object is unique with specific composition of corrosion layers and thus these objects are not ideal for the detail research of the plasma treatment process. The main problem of plasma chemical removal of corrosion layers is the elevation of object temperature. The treatment above 200 °C caused irreversible changes in the metallographic structure of many metals. This could result in serious mistakes when interpreting the original processing of such metal [4]. The sample temperature is proportional to the plasma applied power. So the best choice should be to keep the power as low as possible. On the other hand, too low power is not sufficient for the creation of reactive particles in plasma in needed concentration. The application of pulsed plasma systems could be a possible solution of these antagonistic tasks. This paper gives our first results obtained during the removal of various corrosion structures artificially prepared on iron.

2. Experimental

The flowing RF capacitively coupled discharge in pure hydrogen was used for our study. Its schematic drawn is showed in figure 1 with more details. The pressure was kept at 170 Pa during all the treatment at hydrogen flow rate of 10.2 Sccm. The integral spectrum of OH radical in the range of 305–315 nm was used as the process monitor according to our previous works [5]. The plasma treatment was stopped at the moment when OH integral intensity decreased down to 10% of its maximal value according to [5]. This spectrum was also used for the rotational temperature calculation. The model corroded samples were prepared on iron with defined roughness using HCl vapour (for one week) and HNO₃ and H₂SO₄ acids (by dipping for 5 seconds and one week storage in desiccator). This allowed study of the influence of discharge conditions on the more or less same corroded samples and thus the results were comparable. The corrosion layers were analyzed by electron microscopy including the study of corrosion layer profile.

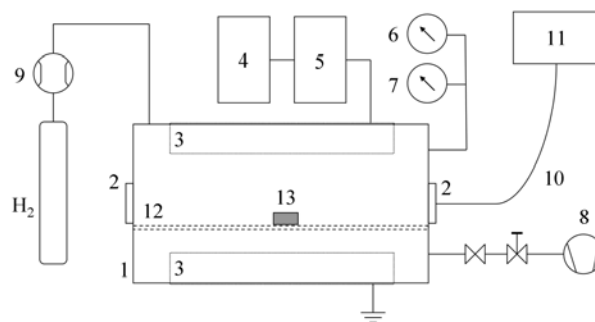


Figure 1. Experimental set-up. 1 – Quartz reactor (i.d. 96 mm, length 900 mm); Quartz windows; 3 – outer copper electrodes; 4 – RF power supply Cesar 136; 5 – automatic matching network; 6 – capacitance gauge; 7 – Pirani gauge; 8 – rotary oil pump; 9 – MFC; 10 – Quartz optical cable; 11 – spectrometer Jobin Yvon TRIAX 550 with CCD; 12 – glass sample holder; 13 – treated sample.

3. Results

The time evolution of OH radical integral intensity during the removal of chlorine based corrosion at different discharge conditions is shown in figure 2. In the case of pulsed discharge at 400 W, a peak at about 13 min after the process beginning is well visible at duty cycle of 1:50 and at 23 min at duty cycle of 1:25. No such peak is visible in the continuous regime. At 500 W this peak has higher intensity and moves to the shorter treatment times (at duty cycle 1:25) and disappears at duty cycle of 1:50. These experimental results show that the corrosion removal is dependent on the total energy supplied into the plasma. The corrosion removal is faster with the energy increase.

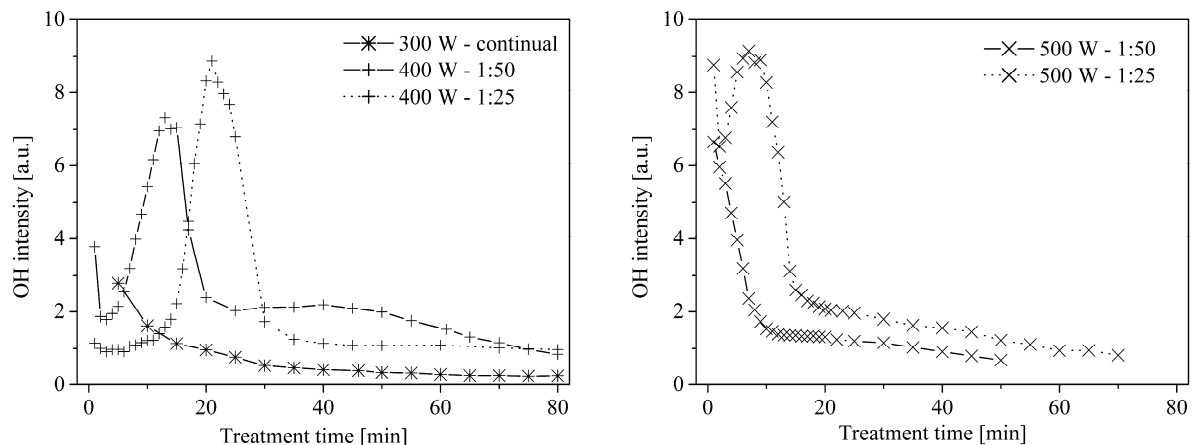


Figure 2. Time evolution of OH integral intensity during the treatment of samples corroded in HCl vapour at different discharge conditions.

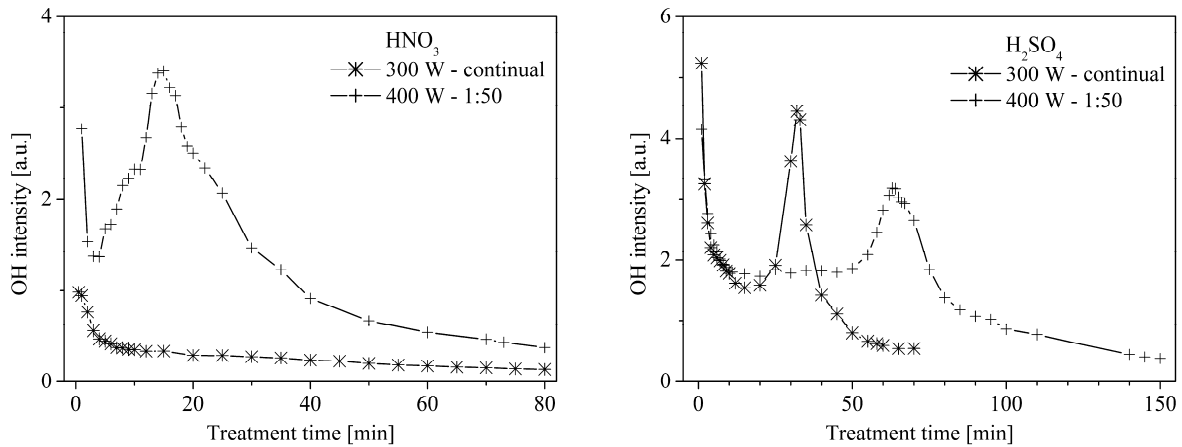


Figure 3. Time evolution of OH integral intensity during the treatment of samples corroded in HNO_3 (left) and H_2SO_4 (right) at different discharge conditions.

Figure 3 shows the similar situation for the other kinds of corrosion. The nitrate corrosion layer removal shows the same behaviour as chlorine ones but the peak of OH intensity is not such sharp and the removal process is slower. Unfortunately, the strong emission of molecular nitrogen second positive system was observed during the treatment in short time interval at the OH radical maximal intensity. The sulphuric corrosion layers are the hardest removable as it is shown in figure 3 – right. Also in this case there is a well visible characteristic peak of OH radical emission but it is observed at significantly later treatment time.

The rotational temperature of plasma was monitored. An example of its time dependence during the treatment is shown in figure 4. Nearly the same results were obtained during treatment of all samples more or less independently on the discharge conditions. It must be noted at this place that this temperature is not the temperature of sample which we have not been able to measure correctly up to now.

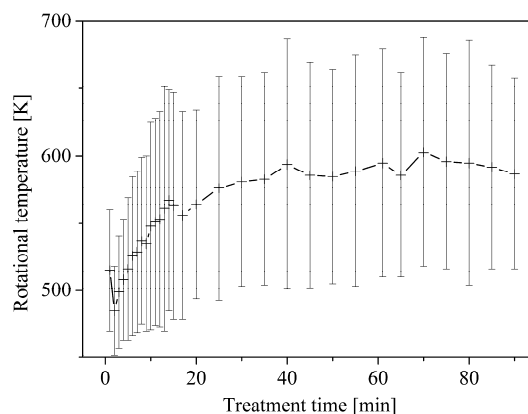


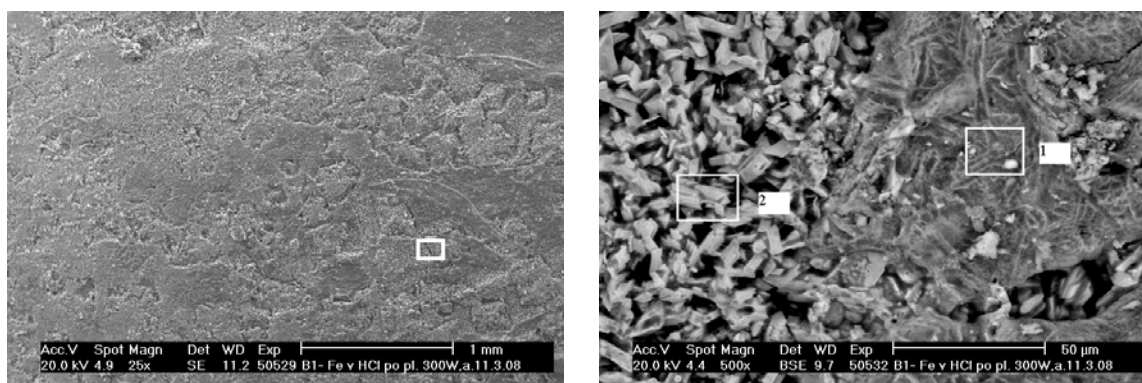
Figure 4. Rotational temperature of hydrogen plasma at 400 W with duty cycle 1:50 during the treatment of sample corroded in HCl vapour.

Finally, figure 5 shows the corrosion layer structure after the plasma treatment and its elementary composition. It is well visible that the chlorine content in the sample surface layers was strongly decreased although it was not removed completely yet.

4. Conclusion

The experimental results show the presence of the characteristic peak in OH radical emission during the plasma treatment of model corrosion layers. Its position during the treatment depends on the

corrosion layer kind as well as on the total applied energy into the plasma. Its dependence on the corrosion composition can be dependent on the chemical boundary or on the anion weight. The detail study of this effect is a subject of the contemporary study. The rotational temperature of plasma is slightly increasing during the treatment in the interval 500–600K and it is not dependent on the plasma conditions and corrosion kind. The contents of the corrosion salts in the surface layers of the samples is significantly decreased but not fully removed.



Element	Non-treated		Treated – position 1		Treated – position 2	
	weight %	atomic %	weight %	atomic %	weight %	atomic %
O	11.45	25.70	24.65	52.10	29.78	56.89
Si	0.40	0.51	0.55	0.66	6.71	7.30
Cl	46.39	46.96	5.29	5.05	2.98	2.57
Ca	–	–	0.34	0.28	0.42	0.32
Mn	–	–	1.95	1.20	1.39	0.77
Fe	41.75	26.83	67.22	40.70	50.73	32.15

Figure 5. A result of material analyzes of HCl vapour corroded sample after plasma treatment at 300 W in continuous regime and its comparison with non-treated sample. The sample after treatment was stored for 1 month at ambient laboratory conditions where sample oxidation was not protected.

Acknowledgments

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