

Effect of plasmachemical treatment on corrosion layers of iron

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Application of plasmas is a new way of effective and fast treatment leading to conservation of metallic corroded objects. Removal of corrosion products is based on plasmachemical reduction of corrosion layers by radio-frequency (RF) low pressure hydrogen plasma. Influence of this process on corroded iron samples was investigated. OH radicals formed during this process were measured by optical emission spectroscopy; simultaneously, sample temperature was measured by a thermocouple placed inside the objects. The value of OH radical integral intensity represented quantitative ablation of oxygen from a corrosion layer. Sample temperature was an important indicator of sample protection against metallographic changes. It was proved that both hydrogen atom reduction and thermal decomposition were employed in the removal process. The XRD and SEM/EDX analyses of corroded and treated samples were done.

1. Introduction

The application of hydrogen plasma in the conservation and restoration of metallic objects has been investigated for the last twenty years in order to determine its potentials and limits for culture heritage objects treatment. Although many thousands original objects were conserved using this method [1], the process is still under development. As original objects are unique, the model samples under various experimental conditions were tested. The application of RF discharge plasma for a removal of corrosion layers mainly from iron objects was developed by Veprek during the 1980s [1, 2].

The method is based on a reduction of corrosion products on the metal object (model samples or excavated archeological artifacts) by reactive hydrogen atoms in low pressure radio-frequency (RF) hydrogen glow discharge plasma at low temperature. The corrosion layers become brittle after the plasma application and thus they can be removed easily by conservators.

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 of size (10x10x5) mm used in our experiments were made of low doped construction steel (98.9% Fe). They were let corroded in vapor of concentrated hydrochlorid acid for five weeks (see Fig. 1) in dessicator. After this corrosion process, the samples were kept for 24 hours in a vacuum

dryer and then the plasmachemical treatment was applied.

A simplified schematic drawing of our experimental device is in Fig. 2. A cylindrical quartz plasma reactor had its inner diameter of 95 mm and a length of 900 mm. Outside copper electrodes were placed on the opposite sides (top and bottom) of the reactor wall.

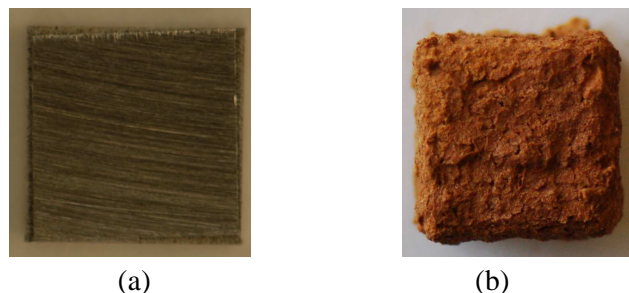


Fig. 1: a-before corrosion, b-corroded sample.

A capacitive coupled RF (13.56 MHz) power supply was operated in a continuous or pulsed regime with a duty cycle of 75 %, 50 % and 25 % at repetition frequency of 1000 Hz. The flowing 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. Optical emission spectra were measured in the range of 250–350 nm 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. Thus OH spectrum reflects the efficiency of the corrosion removal process. The plasma treatment was stopped when the value of

relative intensity of OH radicals reached one tenth of the maximum OH radical intensity [4].

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

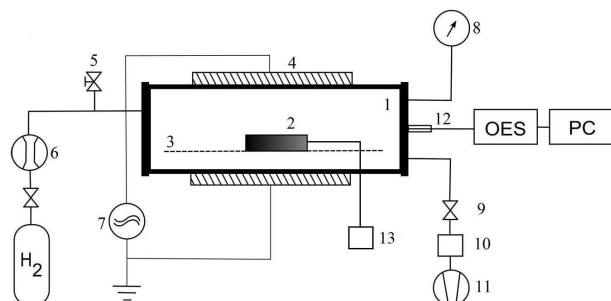


Fig. 2: Experimental set-up: 1 – Quartz discharge reactor (90 cm long, i.d. 95 mm); 2 – corroded sample; 3 – glass sample holder; 4 – outer copper electrodes; 5 – air-inlet valve; 6 – mass flow controller; 7 – RF power supply and matching network; 8 – pressure gauge; 9, 10 – valves; 11 – rotary oil pump;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

3. Results and discussion

The model samples were treated under different experimental conditions for 90 minutes. Temperature of the sample initially increased, but it was nearly constant after about 30 minutes of the treatment (this time was independent on the applied mean power). 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 4.

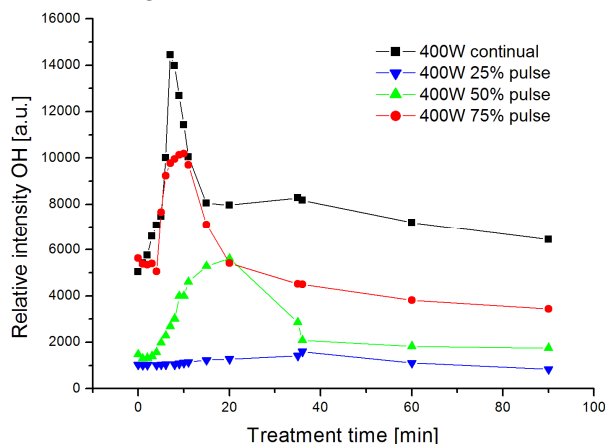


Fig. 3: Dependencies of relative OH radical intensity on treatment time.

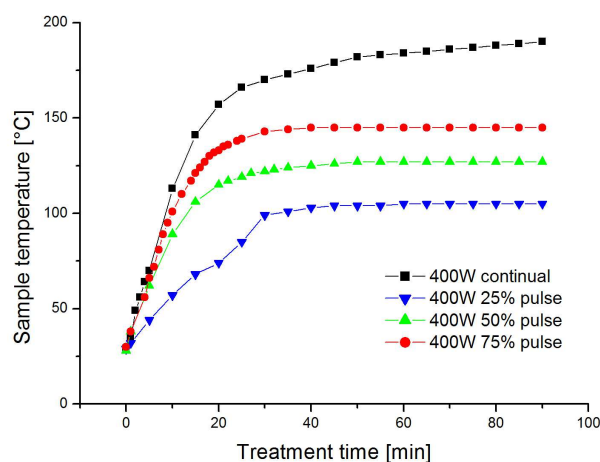


Fig. 4: Dependencies of sample temperature on treatment time.

It is evident that both maximal intensity of OH radicals emission 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 the continual regime; in pulsed regime, the $I_{rel}OH$ maximum was shifted to later treatment times with decreasing the effective power. This indicates a slower reduction process of the corroded layer. The value of $I_{rel}OH$ also decreased with decreasing effective power which it reflects smaller amount of removed corrosion products (respectively slower corrosion removal). It is clear that higher used power is better for the reduction process as it demonstrate in Fig. 5. Application of the continual regime and duty cycle of 75% caused a total remove of the corrosion layer from the sample surface. When shorter duty cycles were applied, a visible crust remained on the surface. On the other hand, the higher used power induced the higher sample temperature. Sample temperature did not exceed 200°C during all these experiments. This temperature was found as a limit temperature for the protection of metallographic changes in archaeological iron [5].

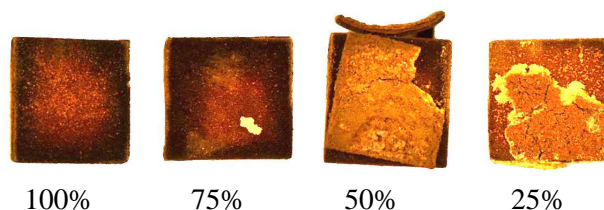


Fig. 5: The images of treated samples at 400 W using different duty cycles.

The corroded samples XRD spectra show presence of rookhite ($FeCl_2 \cdot 2H_2O$) and akaganeite ($Fe^{3+}O(OH,Cl)$). These compounds are typical

products of HCl corrosion and correspond to corroded archaeological objects.

The corrosion layers were analysed before the plasma treatment by electron microscopy with elementary X-ray spectroscopy. This analysis was repeated on the same samples after the plasma treatment. A microphotography of the corroded sample showed relatively complex surface structures (see Fig. 6) and also demonstrated non-homogeneity of the corrosion layer. There is the example of microphotography of treated sample (400 W, 50% pulse) in Fig. 7. It demonstrates a significant difference in structure and homogeneity of corrosion layers before and after the treatment.

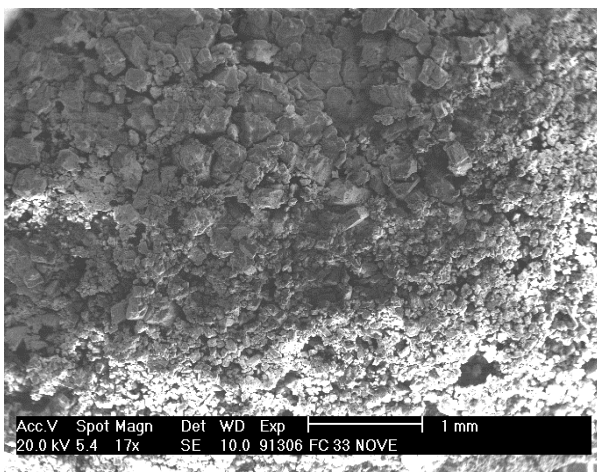


Fig. 6: The SEM image of the surface of corroded sample.

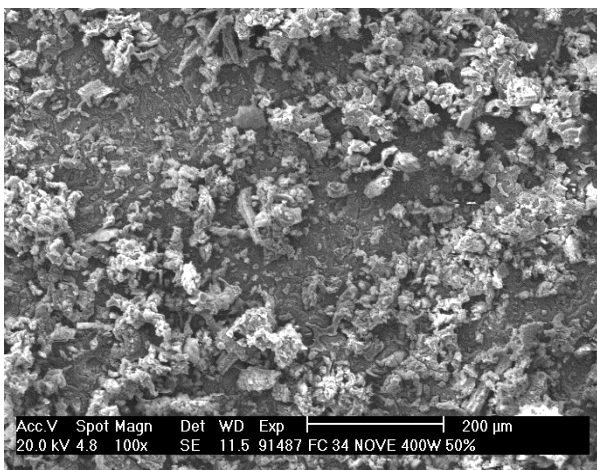


Fig. 7: The SEM image of the surface of treated sample.

The elementary analysis of surface layers showed a significant difference of corrosive elements abundance depending on treatment conditions as it is shown in Fig. 8 and 9. Comparison of the pulsed and the continual regime of plasma treatment is given, too. 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. On the other hand, content of iron on the surface significantly increases with increasing power.

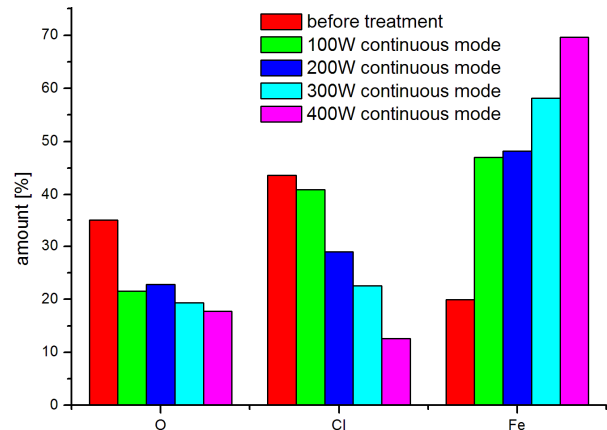


Fig. 8: Comparison of sample surface composition – effect of applied power.

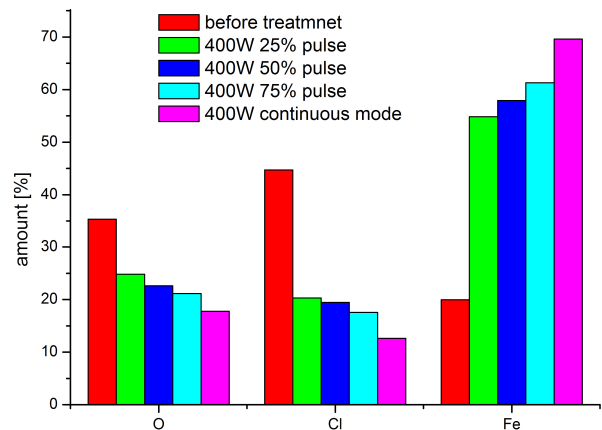


Fig. 9: Comparison of sample surface composition – effect of the duty cycle.

4. Conclusion

Corrosions as well as their removal are a very complex problem. Plasma chemical treatment of prepared model corroded iron samples was performed by the 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 analyses XRD and SEM/EDX on corroded and treatment samples were

performed. The analyses show that the decrease of the main corrosion agents as chlorine and oxygen was achieved by the hydrogen plasma treatment. So our experiments have shown that the best conditions for the treatment of corrosion layers on iron are power supply of 400 W at pulsed regime of 75%. The sample temperature did not exceed limit of 200°C and the corrosion layer was removed from the sample surface under these conditions.

5. Acknowledgement

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6. References

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