

Effect of Plasma Treatment on Corrosion Layers of Bronze

Mazankova V.¹, Krcma F.¹, Fojtikova P.¹, Mika F.²

¹Brno University of Technology, Faculty of Chemistry, Department of Physical and Applied Chemistry, Purkynova 118, 612 00 Brno, Czech Republic, mazankova@fch.vutbr.cz

²Institute of Scientific Instruments of the Academy of Sciences Czech Republic, v.v.i., Kralovopolska 147, Brno 612 00, Czech Republic

Plasma chemical process for conservation of metallic objects is a relatively new way of effective and fast treatment of corroded objects. Removal of corrosion products is based on plasma chemical reduction of corrosion layers by radio-frequency (RF) low pressure hydrogen plasma. Model corrosion layers on bronze were studied. SEM/EDX analyses on corroded and treated samples were performed.

Keywords: corrosion layer removal, RF hydrogen plasma, bronze, SEM/EDX

1 INTRODUCTION

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

The application of RF discharge plasma for removal of corrosion layers mainly from iron objects was developed by Prof. Veprek during the 1980s [1,2]. 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 corrosion layer becomes brittle and can be removed easily by the conservators.

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

2 EXPERIMENT

Uniform corroded bronze (87% Cu and 13% Sn) samples were cut to the size of $(10 \times 10 \times 5) \text{ mm}^3$ and were grinded by an electric grinder because of the unification of roughness of all samples. A sandpaper with roughness of 600 grains per inch square was used. Immediately, the exposition of the

corrosion environment followed. Hydrochloric acid was chosen as a model corrosive environment because chlorine compounds play a typical role as corrosion accelerators.

Grinded samples were exposed to vapor of hydrochloric acid in a desiccator. The Petri dish containing 20 ml of concentrated hydrochloric acid was placed to the bottom of the desiccator. The perforated ceramic holder with samples was placed above the Petri dish. The closed desiccator was placed in a dark place, and the development of corrosion was observed. After 14 days, surfaces of all samples were covered with corrosion products, and the corrosion process was stopped.

The simplified schematic drawing of our plasma experimental device is in Fig. 1.

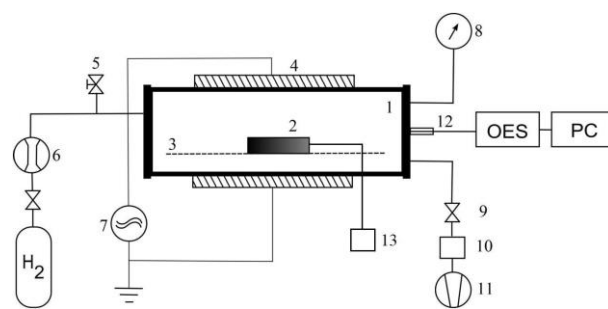


Fig. 1: Experimental set-up: 1 – Quartz discharge reactor (90 cm long, i.d. 95 mm); 2 – corroded sample; 3 – glass sample holder; 4 – outer copper electrodes; 5 – gas-inlet valve; 6 – mass flow controller; 7 – RF power supply and matching network; 8 – pressure gauge; 9, 10 – valves; 11 – rotary oil pump;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

The quartz plasma reactor was cylindrical with inner diameter of 95 mm and length of 900 mm. Copper electrodes were placed out of the reactor on the reactor wall opposite each other. A capacitive coupled RF power supply working at frequency of 13.56 MHz gave the total power up to 600 W in a continuous or pulsed regime. We used pulses with a duty cycle of 50 % and 66 % with repetition frequency of 1000 Hz. Flowing plasma was created in pure hydrogen with gas flow of 50 sccm at pressure of 200 Pa.

The sample temperature was measured by a thermocouple installed inside the model sample during the plasma treatment. The optical emission spectroscopy (OES) of OH radical was used for process monitoring. Optical emission spectra of OH radicals were measured by an Ocean Optics HR 4000 spectrometer with a 2400 gr/mm grating, and resolution of 0.02 nm. Atomic hydrogen reacts with oxygen from corrosion layers and forms OH radicals in excited states. OH radicals emit in the spectral region of 305–315 nm, and integral intensity over this region was used for the quantitative analysis of oxygen removal from the corrosion layer. The plasma treatment duration was 90 minutes. Corroded and treated samples were analyzed by the SEM-EDX method in order to determine changes of their surface elemental composition caused by hydrogen plasma.

3 RESULTS AND DISCUSSION

The integral intensity of OH radicals was calculated from measured spectra (see Fig. 2).

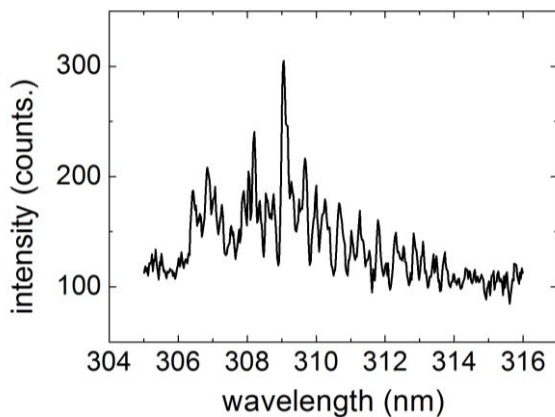


Fig. 2: Spectrum of OH radical during the plasma treatment

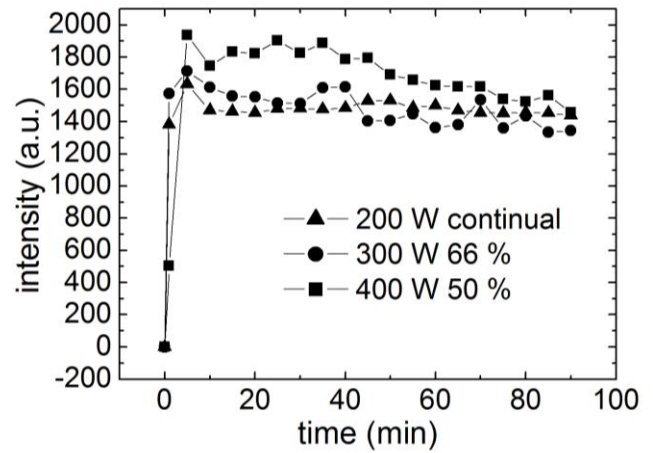


Fig. 3: Time evolution of relative OH radical intensity for three plasma regimes

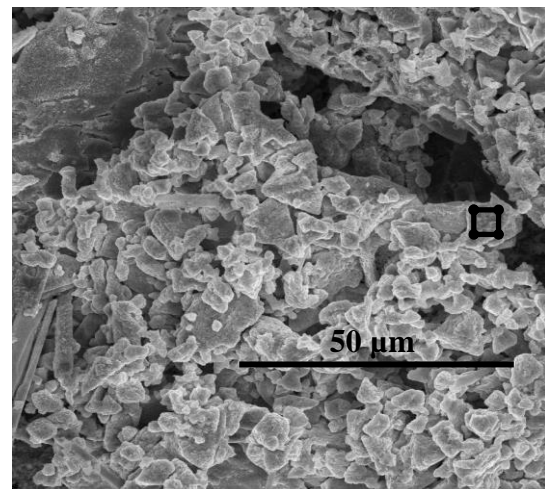
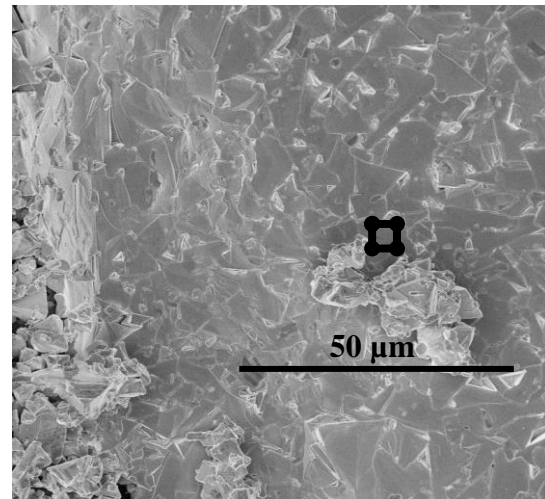


Fig. 4: SEM images of the surface of the corroded sample (top) and the treated sample (bottom)

Time evolution of OH radical integral intensity was evaluated for all treated samples. A typical example for samples treated at the

same effective power of 200 W is given in Fig. 3. Three cases are demonstrated: continual regime (200 W) and two different pulsed regimes 50% (400 W) and 66% (300 W). Fig. 3 shows that the maximal intensity of OH radicals was reached at treatment time of 5 min and the OH radical intensity was decreasing from this moment for about next 5 min. For the remaining treatment time, the OH radicals intensity was nearly constant.

Tab. 1: Results of EDX analysis of the sample before the treatment (200 W, continual regime)

	Mass %	Atomic %
Oxygen	2.0	5.0
Chlorine	34.0	46.0
Tin	-	-
Copper	64.0	49.0

Tab. 2: Results of EDX analysis of the sample after the treatment (200 W, continual regime)

	Mass %	Atomic %
Oxygen	1.0	2.0
Chlorine	24.0	36.0
Tin	1.0	1.0
Copper	74.0	61.0

The corrosion layers were analyzed before the plasma treatment by SEM/EDX. The same analysis was repeated after the plasma treatment. The microphotography of the treated sample (200 W, continual regime) showed relatively complicated surface structures (see Fig. 4), and also demonstrated non-homogeneity of the corrosion layer. The hydrogen plasma led to a removal of oxygen and chlorine from corrosion layers. Thus, the layers become more brittle and fragmented. The red square represents an area of $5 \times 5 \mu\text{m}^2$ over which the EDX analysis was performed.

The elementary analysis of surface layers showed a significant difference of corrosive elements abundance depending on the treatment conditions. Results for the selected sample are in Tab. 1, 2.

It can be seen that the amount of oxygen and chlorine decreases. This effect is due to the reaction of oxygen forming the OH radicals. Thanks to this process, it is possible to monitor the experiment. Reduced amount of chlorine is also a benefit because chlorine is the main agent of the soil corrosion.

4 CONCLUSION

The corruptions as well as their removal are really complex problem. Plasma chemical treatment of model corroded bronze samples was arranged by RF hydrogen low pressure plasma. Our experiment was realized in different power regimes. The duty cycle was varied from continuous to 66% pulsed. The SEM/EDX analyses on corroded and treated samples were performed. The analyses showed that the decrease of chlorine and oxygen was achieved by hydrogen plasma. This method is a part of a plasmachemical approach to conservation of original artifacts. The main advantage is its non-destructivity and no contact with aggressive chemicals.

Acknowledgement

This research has been supported by the Czech Ministry of Culture under research project No. DF11P01OVV004.

REFERENCES

- [1] Veprek S, Patscheider J, Elmer J, Plasma Chem Plasma Process 5 (1985) 201.
- [2] Veprek S, Elmer J, Eckmann Ch, Jurcik-Rajman M, J Electrochem Soc (1985) 134.
- [3] Mazankova V, Sazavska V, Radkova L, Krcma F proc. XXI ESCAMPIG 2012.