

INFLUENCE OF THE SANDY INCRUSTATIONS ON THE PLASMA CHEMICAL CORROSION REMOVAL FROM BRONZE

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Treatment of bronze samples by low-temperature, low-pressure hydrogen plasma was performed. This process is called plasmachemical reduction. The bronze blocks of dimension $50 \times 15 \times 5 \text{ mm}^3$ were used for this study because there is impossible to use original objects for the comparative studies due to their uniqueness. A creation of model corrosion layer on the surface of each sample was the next step. Model corrosion layers were created in the vapours of concentrated hydrochloric acid. The prepared model corrosion layers were exposed to the effect of hydrogen plasma at pressure of 150–170 Pa. It was chosen different experimental conditions for each sample. Plasma treatment monitoring was provided by optical emission spectroscopy (OES). Rotational temperature was calculated from OES, the temperature of the sample that is a critical process parameter was measured by thermocouple placed inside the apparatus.

1. Introduction

Application of low-temperature, low-pressure hydrogen plasma for conservation of archaeological artifacts is a new technique. Principle is based on the removal of the corrosion molecules from the corroded surface [1]. Full optimization for gentle and sufficient treatment was not performed yet [2]. The method has relatively short history. First successful research was performed by professor Stanislav Vepřek, around the year 1980 in Zürich. More than 14,000 historical metallic objects were treated by low-pressure, high-frequency hydrogen plasma [3, 4]. Before the year 1980, the basic research was performed by the group around Daniels. Their work was based on treatment of tarnish silver objects and Daguerreotypes by low-pressure, low-frequency glow discharge in gas mixtures [5]. There are three major advantages of using plasma treatment for historical artifacts. The first advantage is the reduction of oxides in the conglomerate layer and a subsequent facilitating of mechanical removal of disfiguring corrosion layers [6]. Secondly, there is no contact of conserved object with aggressive chemicals. Non-destructivity of the surface is the third main advantage. Nothing is ideal, so this technique has also some disadvantages. The main problem is heating of the sample during the plasma treatment. Thus it is necessary to control the temperature of each sample; in our case a thermocouple installed into the treated model sample was used for this purpose. The presented contribution brings results obtained during plasma treatment of bronze samples. Model corrosion layers were prepared on these samples with and without incrustations of sand and then followed their treatment by hydrogen plasma. Temperature and optical emission spectrum of each sample were measured. Rotational temperature and relative intensity of OH radicals were calculated from measured values.

2. Preparation of samples and creation of model corrosion layers

Six samples were prepared for the presented experiment. Bronze blocks with size of $50 \times 15 \times 5 \text{ mm}^3$ were grinded by an electrical metallographic grinder MTH Kompakt 1031 using the sandpaper P600 (sandpaper with roughness of 600 grains per square inch) because of unification of surface roughness. The sample surface was washed by ethanol and finally dried by flow of hot air. The exposure of the corrosion environment followed immediately. Hydrochloric acid was chosen as a model corrosive environment because chlorine compounds play a typical role as bronze corrosion accelerators. Two dessicators were prepared. A Petri dish with 20 ml of concentrated hydrochloric acid was installed at the bottom of dessicator; a ceramic holder with 3 pretreated samples was placed above it. The samples were surrounded by sand in the first dessicator; air environment was used in the second one. Both dessicators were closed and put to a dark place in order to create two sets of model

corrosion layers (Figure 1). After 30 days, the corrosion process was stopped and samples were extracted and put into lockable bags. Plasmachemical reduction of model corrosion layers followed.



Fig. 1. Sample (No. 3) with model corrosion layer created in hydrochloric acid (left) and sample (No. 6) with corrosion layer created in hydrochloric acid with addition of sand (right).

3. Apparatus and conditions during experiment

Our experimental equipment was constructed according to the design of prof. Vepřek [2,3], and was further improved.

A quartz cylindrical reactor (length of 90 cm, inner diameter of 9.5 cm) is a base of the plasmachemical apparatus (Figures 2 and 3). The chamber was continuously pumped by rotary oil pump allowing based pressure of 5 Pa. An electromagnetic butterfly valve was used for the control of pumping speed during the experiment. Pure hydrogen (99.9%) was fed into the reactor through a mass flow controller. The RF generator Cesar (13.56 MHz) supplied through automatic matching network two copper electrodes placed out of the cylindrical reactor. The plasmachemical process of corrosion layers removal was continuously monitored by optical emission spectroscopy (Ocean Optics HR 4000 spectrometer) collecting emitted light at the reactor axis. The sample temperature, that is one of the most critical experimental parameters, was controlled by K-type thermocouple mounted inside the treated sample. Due to the strong influence of electromagnetic field on the readed values, temperature was measures every minute at the end of discharge switch-off for 5 seconds. Whole experimental system was fully PC controlled.

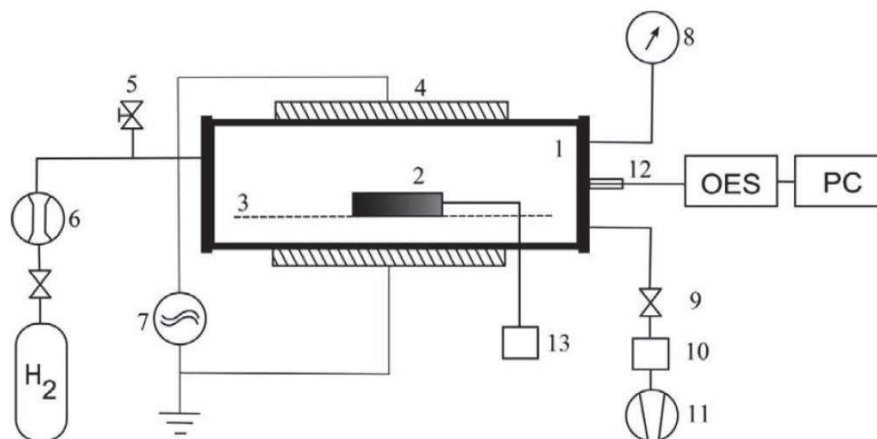


Fig. 2. Schematic drawing of apparatus: 1 – quartz cylindrical reactor, 2 – corroded sample, 3 – glass holder, 4 – two outside copper electrodes, 5 – aeration valve, 6 – mass flow controller, 7 – RF generator and matching network, 8 – pressure gauge, 9 – ball valve, 10 – electromagnetic valve, 11 – rotary oil pump, 12 – optical fiber, 13 – thermocouple.



Fig. 3. Photo of apparatus during the experiment.

Each corroded sample was put on the glass holder at the middle of the reactor. The samples were treated for 90 minutes at the pressure ranged between 150–170 Pa at the fixed hydrogen flow rate of 50 sccm. The applied power was parameter for the presented study and it is reviewed in Table 1.

Tab. 1. Review of experimental conditions.

Sample	Corrosion condition	Supplied power [W]
1	hydrochloric acid	100
2		200
3		300
4	hydrochloric acid + sand	100
5		200
6		300

4. Results and discussion

The OH radical is created in an active discharge by reactions of atomic hydrogen with the corrosion layers at the model corrosion layer on the sample surface. Due to this fact, the OH radical spectrum can be used as a monitor for the reduction in plasma [7].

Results from OES (time dependences of relative intensity of OH radicals) are shown in Figure 4. The intensities shows one maximum between 5–10 minutes for samples corroded only in the hydrochloric acid vapours. Nearly exponential decreasing of relative intensity followed immediately. In the case of samples corroded in sandy environment, two maxima of relative intensity were observed for all samples. First maximum probably corresponds to the reduction of outer layer composed mainly of sand itself and the second maximum reflects the reduction of inner corrosion layers in the touch of original surface. Thus the exponential decreasing of relative intensity is much slower and two times longer plasma treatment is needed to reach the constant state.

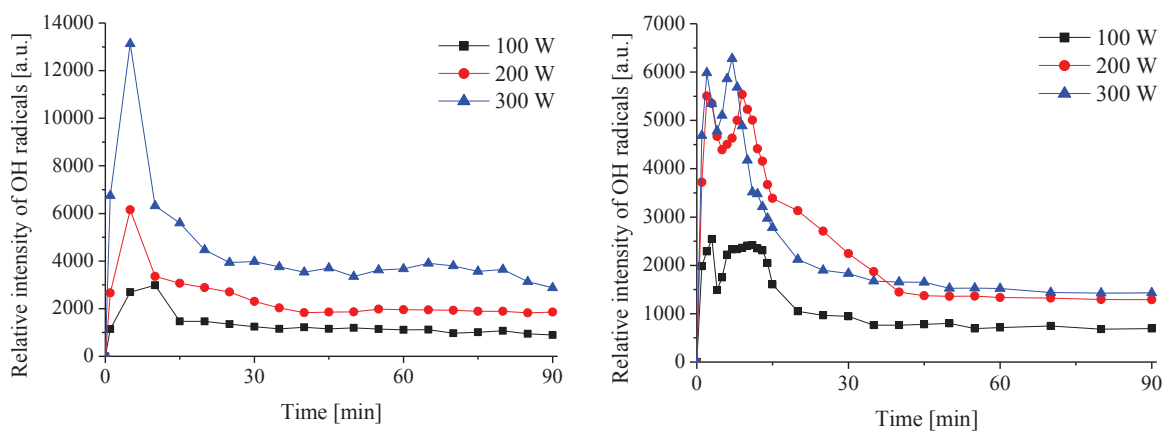


Fig. 4. Time dependence of relative intensity of OH radicals: samples No. 1, 2 and 3 are on the left side and samples No. 4, 5 and 6 are on the right side.

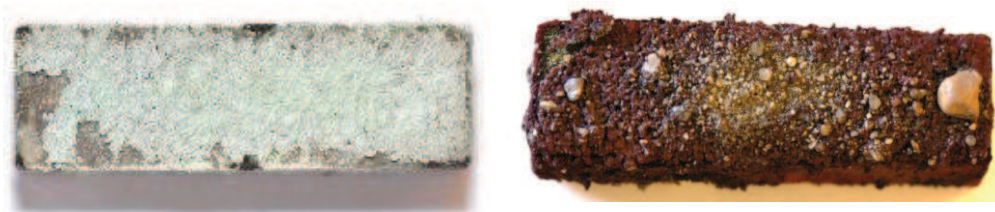


Fig. 5. Samples after plasmachemical reduction (applied power of 300 W): sample No. 3 (left) and sample No. 6 (right).

A visual pattern of treated samples No. 3 and No. 6 are shown in Figure 5 (compare with Figure 1).

Temperature plays an important role at process of reduction of corrosion layers. Thus, a thermocouple was connected to the apparatus. Results are demonstrated at time dependences in Figure 6. The lowest values, as should be expected, are observed for samples treated at the lowest used power of 100 W; on the other hand, the highest temperatures are at power of 300 W. The temperatures show steady state after about 40 minutes in both cases. The maximal temperatures are higher in the case of samples without sandy incrustations because there is no shielding effect of sandy grains and the sample surface is directly exposed to the plasma.

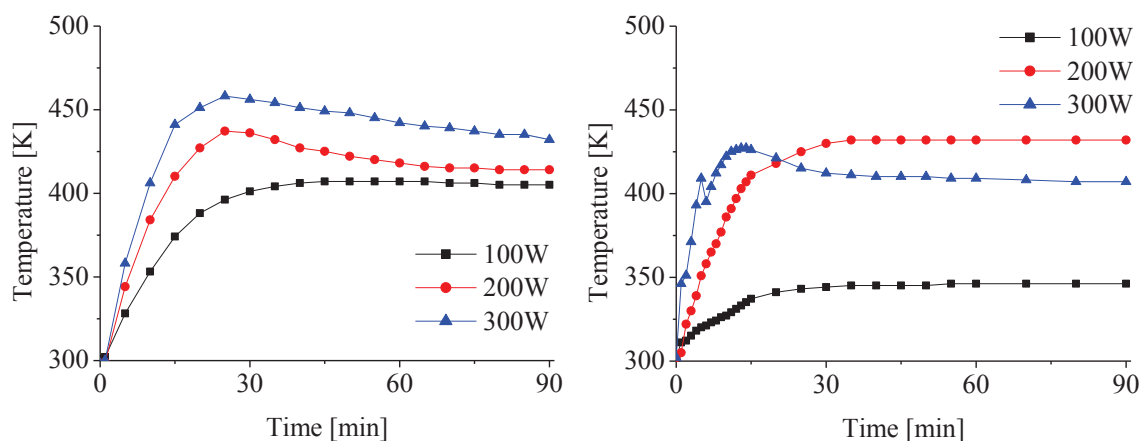


Fig. 6. Temperature time dependence of samples: samples No. 1, 2 and 3 are on the left side and samples No. 4, 5 and 6 are on the right side.

Rotational temperature, as a plasma parameter, was calculated from OH radical A-X 0-0 band. It is more or less independent on the treatment conditions and there is also no influence on the treated sample character, as it is shown on Fig. 7.

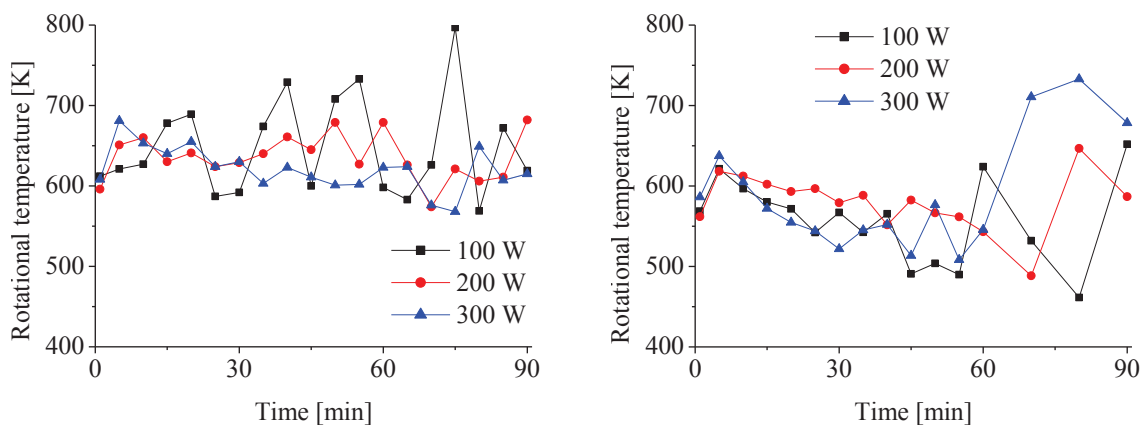


Fig. 7. Dependence of rotational temperature during experiment: samples No. 1, 2 and 3 are on the left side and samples No. 4, 5 and 6 are on the right side.

5. Conclusions

Plasmachemical reduction of model corrosion layers on the bronze samples with and without sandy incrustations was performed. Both sets of samples corroded in the vapour of concentrated hydrochloric acid during 30 days, sand was added to one set. Some differences were observed between created corrosion layers. Two maxima of relative intensity of OH radicals were recognized at the treatment of samples with corrosion layers with sand. The first one corresponds probably to reduction of outer layer composed of sand grains. The second one corresponds to reduction of inner layer on the original

surface of bronze. The temperatures of samples with sandy incrustation were lower which corresponds with the higher thickness of created corrosion layer. Rotational temperatures were calculated from measured optical emission spectra and they were nearly independent on the applied power.

6. References

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