

Effect of Hydrogen Plasma on Model Corrosion Layers of Bronze

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Abstract. Our work is about plasmachemical reduction of model corrosion layers. The model corrosion layers were produced on bronze samples with size of 10 x 10 x 5 mm³, containing Cu and Sn. Concentrated hydrochloric acid was used as a corrosive environment. The application of reduction process in low-pressure low-temperature hydrogen plasma followed. A quartz cylindrical reactor with two outer copper electrodes was used. Plasma discharge was generated in pure hydrogen by a RF generator. Each corroded sample was treated in different conditions (supplied power and a continual or pulsed regime with a variable duty cycle mode). Process monitoring was ensured by optical emission spectroscopy. After treatment, samples were analyzed by SEM and EDX.

1. Introduction

Beginning of plasma treatment of various subjects is dated on eighties of the twentieth century when group around Daniels used low-pressure hydrogen plasma for the promising treatment of Daguerreotypes and tarnished silver objects [1]. The first success for iron artifacts was achieved by prof. Vepřek around year 1980. He used RF excited hydrogen plasma. Our experimental equipment was constructed according to the design of prof. Vepřek [2], and was further improved.

Together with mechanical cleaning, desalination and surface treatment, hydrogen plasma treatment is a part of conservation process leading to protection of archeological artifacts. Advantages of the method are non-destructivity and no contact with aggressive chemicals. The conservation process has to be performed very specifically because of uniqueness of every archeological artifact. It is not possible to perform research on real artifacts therefore the model samples are necessary. Nowadays, hydrogen plasma treatment is commonly used for iron artifacts. For copper alloys, especially bronze, the optimized conditions during the treatment have not been determined yet. The aim of this study is to determine save conditions of plasma treatment on bronze model samples.



2. Experiment

2.1. Preparation of model corrosion layers

Bronze blocs with the size of $10 \times 10 \times 5 \text{ mm}^3$ were grinded by an electric grinder because of the unification of roughness of all samples. Sandpaper with roughness of 600 grains per inch square was used. Immediately, the exposure of the corrosion environment followed. Hydrochloric acid was chosen as a model corrosive environment because chlorine compounds play a typical role as bronze corrosion accelerators.

Grinded samples were exposed to vapor of hydrochloric acid in a dessicator. The Petri dish was placed to the bottom of the dessicator, and 20 ml of concentrated hydrochloric acid were infused into it. The perforated ceramic holder with samples was above the Petri dish. Closed dessicator 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.

2.2. The experimental setup

The experimental setup is shown in the Figure 1. The quartz cylindrical reactor (length of 90 cm, inner diameter of 9.5 cm) is a base of the plasmachemical apparatus. Other parts are connected to the reactor: vacuum system, source of working gas, source of energy, system of monitoring process (optical emission spectroscopy) and a pressure gauge. The vacuum system is used to product vacuum of about 10 Pa, and it is composed of a rotary oil pump, an electromagnetic and a ball valve. Pure hydrogen was chosen as working gas, and it was fed into the reactor through a mass flow controller. The RF generator supplies energy needed for the plasma discharge creation (it works on the technical frequency of 13.56 MHz). The generator is connected to two grounding copper electrodes placed out of the cylindrical reactor by a fiberglass. Plasmachemical process of corrosion layers removal is monitored by optical emission spectroscopy. Signal from the reactor is routed through the quartz slot to the optical fiber. The optical fiber is connected with a spectrometer Ocean Optics HR 4000. The experiment is PC controlled.

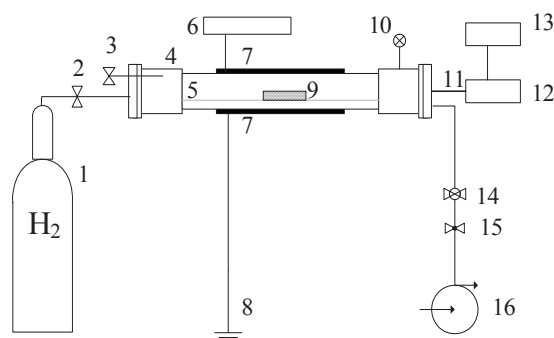


Figure 4. Experimental setup: 1 – hydrogen, 2 – mass flow controller, 3 – aeration valve, 4 – reactor, 5 – holder, 6 – RF generator, 7 – 2 copper electrodes, 8 – grounding, 9 – sample, 10 – pressure gauge, 11 – optical fiber, 12 – spectrometer, 13 – computer, 14 – ball valve, 15 – electromagnetic valve, 16 – rotary oil pump.

2.3. Analysis

The plasma treated samples were analyzed by a scanning electron microscope (SEM) Magellan 400L in order to obtain ultra high resolution surface morphology and chemical composition by energy dispersive x-ray analysis (EDX). SEM pictures were taken at the energy of 5 keV and 15 keV with the magnification of 1000–1200. EDX analysis was performed from the area of $5 \times 5 \mu\text{m}^2$.

2.4. The course of experiment

For each sample, different conditions of supplied power (from 50 to 400 W) and the duty cycle mode (Table 1) were chosen. During the experiment, the pressure in the reactor ranged about 150–170 Pa

and the flow rate of hydrogen was 50 sccm. The corroded sample was put on the glass holder in the middle of the reactor between two electrodes.

The active time of discharge was adjustable in the pulsed mode, expressed as a percentage

$$DUTY\ CYCLE = \frac{t_{on}}{t_{on} + t_{off}} \cdot 100 [\%], \quad (1)$$

where t_{on} / t_{off} is time when the discharge was switched on/off [ms]. Time of 1 pulse was 1 ms because the frequency of repetition of 1 pulse was chosen as 1000 Hz. Because of pulse mode, the power (supplied by RF generator) is reduced to effective power which is calculating using the equation

$$P_{eff} = P \cdot DUTY\ CYCLE [W] \quad (2)$$

In continual mode, the power is the same as an effective power because the discharge is switched on all time [3].

Table 1: Conditions during plasmachemical reduction for all 10 samples.

SAMPLE	POWER [W]	MODE*	DUTY CYCLE [%]	EFFECTIVE POWER [W]
1	50	C	100	50 (Group A)
2	100	P	50	
3	200	P	25	
4	100	C	100	100 (Group B)
5	200	P	50	
6	300	P	33	
7	400	P	25	
8	200	C	100	200 (Group C)
9	300	P	66	
10	400	P	50	

*Note: C – continual, P – pulsed.

3. Results and discussion

3.1. Time dependence of OH radical emission

Atomic hydrogen is one of the products created by plasma. If atomic hydrogen reacts with oxygen in the corrosion layer, OH radicals are produced. This running process was monitored by the optical emission spectroscopy.

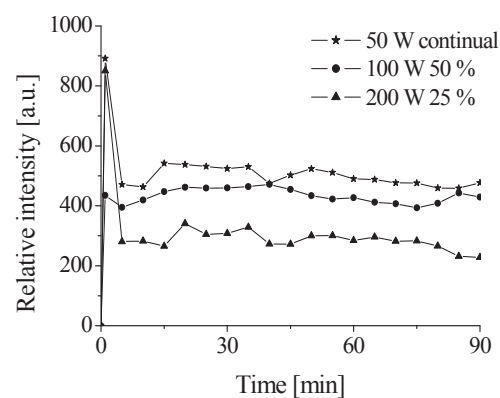


Figure 2. Time dependence of relative intensity of OH radicals for Group A samples.

Figure 2 shows the dependences of the relative intensity of OH radicals on time at different conditions. We can see an increase of the intensity in the first 5 minutes. When the intensity maximum is reached, the decrease followed. The process was stopped after 90 minutes because of a steady tendency of the relative intensity of OH radicals.

3.2. SEM and EDX analyses

All ten samples were analyzed by SEM. For illustration, sample 8 was chosen (Group C) and the picture of its surface as well as the result of the EDX analysis is shown below.

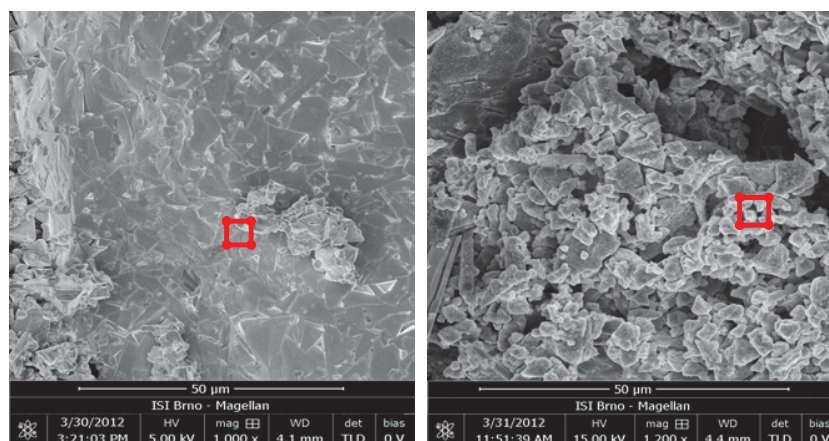


Figure 3. Corroded bronze sample 8 before (left) and after (right) the treatment, recorded by SEM. The red square is an area $5 \times 5 \mu\text{m}^2$ from which the EDX analysis was done (Figure 4, Table 2).

From the EDX results (Table 2), we can see that the mass of oxygen and chlorine is decreasing. This effect is desirable because due to the decrease of oxygen (formation of OH radicals by the reaction with atomic hydrogen), it is possible to monitor the experiment. Reduced mass of chlorine is also a benefit because chlorine is the main agent of the soil corrosion.

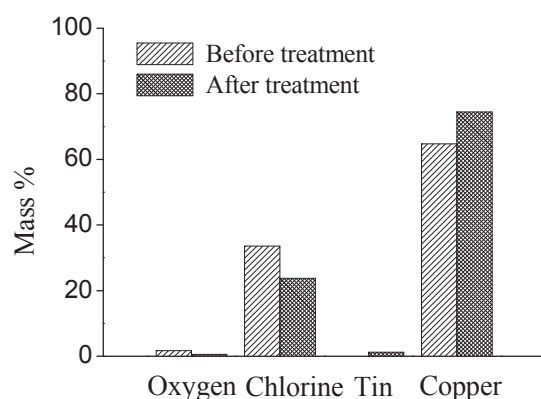


Figure 4. Mass % of the sample 8 (EDX).

Before treatment		
	Mass %	Atomic %
Oxygen	1.67	5.04
Chlorine	33.55	45.71
Tin	---	---
Copper	64.78	49.25
After treatment		
	Mass %	Atomic %
Oxygen	0.56	1.87
Chlorine	23.76	35.5
Tin	1.22	0.54
Copper	74.46	62.09

Table 2. Results of EDX analysis of sample 8.

4. Conclusion

The plasmachemical reduction of bronze samples with model corrosion layers was performed. The results of OES show that the process of reduction began in the first two minutes of treatment. From EDX analysis results, it is evident that there was a decrease of oxygen and chlorine. Decrease of chlorine is eligible because chloride ions are the main agents of the soil corrosion. This method is a part of an archeological approach at conservation of artifacts. The main advantage is its non-destructivity and no contact with aggressive chemicals.

Acknowledgements

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References

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