

## PULSED RF LOW PRESSURE HYDROGEN PLASMA FOR PLASMACHEMICAL CORROSION REMOVAL

V. SAZAVSKA, F. KRCMA, N. ZEMANEK, L. RADKOVA, P. FOJTIKOVA,  
R. PRIKRYL, M. ZMRZLY, D. JANOVA

<sup>1</sup>*Faculty of Chemistry, Faculty of Mechanical Engineering  
Brno University of Technology*

<sup>2</sup>*Purkynova 464/118, 612 00 Brno, Czech republic  
E-mail: xcsazavska@fch.vutbr.cz*

**Abstract.** An effective and fast way of restoration and preservation of archeological artifacts is described. The process is based on using RF low-pressure hydrogen plasma in which the artifacts are treated for several tens of minutes. It proves that both hydrogen atom reduction and thermal decomposition are important. Temperature depends on used regime (continual or pulsed). Our results show that pulsed regime can be effectively applied in the corrosion removal process. The value of integral intensity of OH radicals measured by OES monitors the reduction process in plasma.

### 1. INTRODUCTION

Plasmachemical reduction of corroded samples was discovered as a by-product of research of plasmachemical deposition. Plasmachemical treatment of archaeological artifacts is a relatively new technique developed by Veprek mainly for iron objects during the 1980s (Veprek et al. 1985, 1987). The method is based on a partial reduction of the incrustation and corrosion layers by RF low pressure hydrogen plasma. It induces changes of structure and constitution of corrosive layers of metal objects. The reduced layer of objects becomes brittle and can be removed easily by conservators and thus decreases mechanical stress to the objects (Kotzamanidi et al. 2002).

Corrosion of samples buried in soil or in seawater is a complex electrochemical process which chlorides penetrate from the environment through the corrosion layers toward the metallic surface (Neff et al. 2005, Réguer et al. 2007, Wang et al. 2008). Because of the low oxygen content in the soil and because of the formation of various protecting layers which inhibit corrosion, the object often survives two thousand years buried in the soil with relatively little corrosion. However, after excavation, when it is exposed to air of humidity, a fast postcorrosion is initiated which usually leads to a complete corrosion damage (Veprek et al. 1985, 1987).

## 2. THE SAMPLE

Each of archaeological objects is original and has its “corrosion history. Universal way of corroded object treatment is difficult or even impossible to propose. This problem was solved by means of model samples (identical material and corrosion) which were compared with results in dependence on treatment conditions.

We used the most often materials of archaeological artefacts: iron and bronze (Cu-Sn). We prepared three sets of metal samples in different corrosive environments. The model corroded metal samples were prepared on iron and bronze with defined roughness (samples were grinded by abrasive paper P 280, it means 280 solids per square inch) using HCl vapor (for one week) and HNO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub> acids (by dipping for 3 seconds and one week storage in desiccators). The main corrosive agents acting in corrosion process were chlorides, NO<sub>x</sub>, SO<sub>x</sub>. Corrosive layers were analyzed by EDX-SEM (Energy Dispersive X-ray analysis - Scanning Electron Microscope) that determined surface elementary constitution.

The experiment was done in Quartz reactor (i.d. 10 cm, length of 90 cm) with outer copper electrodes. The capacitive coupled RF power supply (frequency of 13.56 MHz) gave the total power up to 600 W in continuous or pulsed regime. We used only pulses with duty cycle of 50% and 25%. Flowing plasma was created in pure hydrogen at pressure of 100 Pa. The applied discharge power was 100–500 W depending on the duty cycle. Temperature of samples was measured by means of thermocouple installed inside the sample.

The optical emission spectroscopy of OH radical was used for the process monitoring. Atomic hydrogen reacts with oxygen from corrosion layers and forms OH radical. This OH radical emits in UV area of spectrum (305–325 nm). Its integral intensity was used for the quantitative analysis of oxygen removal from the corrosion layer. Plasma treatment was stopped when the value of relative intensity of OH radicals reached one tenth of its maximum (Cihlár 2005). Simultaneously the rotational temperature was calculated. The plasma treatment duration was 40–120 minutes depending on the duty cycle and corrosion layer kind.

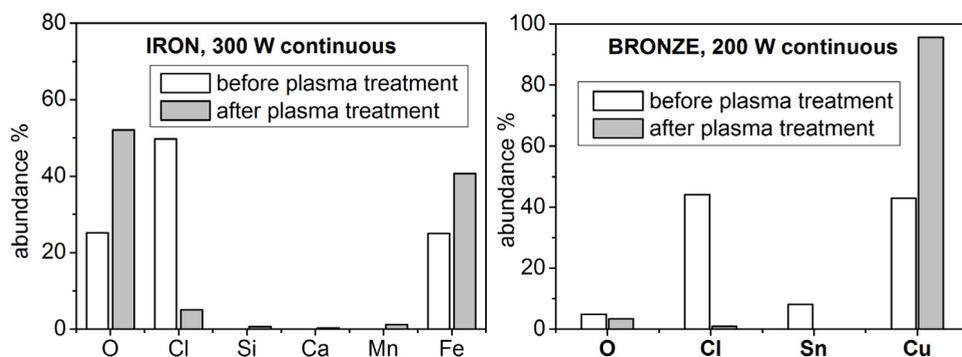
## 3. PRELIMINARY RESULTS

Very good corrosion removal was observed at samples treated in continual regime plasma but significant heating of samples was observed, too. Treatment in pulsed regimes required higher powers applied during the pulse but the average energy was lower and thus the sample temperature was not such elevated. Rotational temperature was in both regimes around (600±100) K.

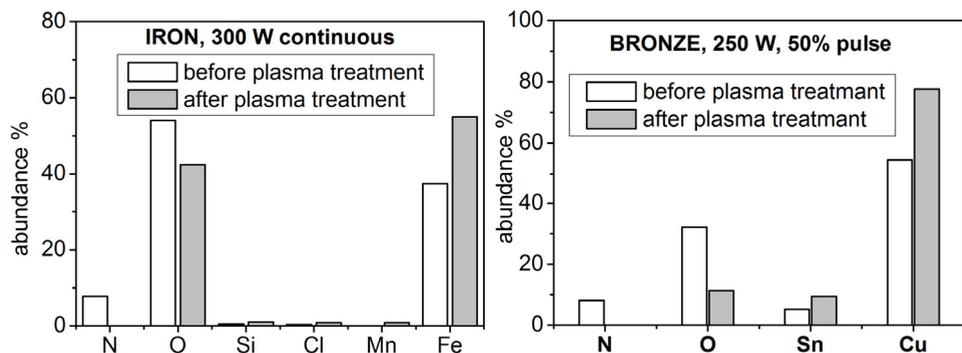
High temperature can induce metallographic changes of metal bulk material and therefore damage of samples. For example temperature of metallographic changes of iron artifact is over 520 K that was proved by D. Perlik from Central-bohemian museum (Perlík 2001). Measured temperature of samples was around 430 K in continuous regime and around 370 K in pulsed regime. Temperature was not such high in the pulsed regime as in the continual regime because the sample

was exposed to plasma with lower mean power in the pulsed regime than in the continual regime.

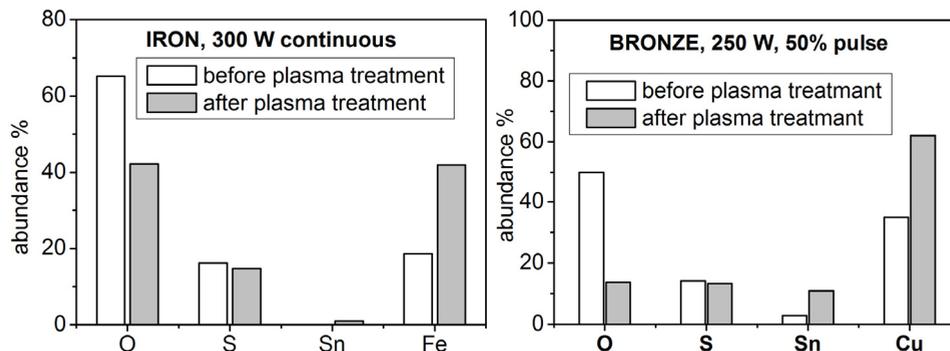
Analysis by EDX-SEM showed a substantial removal of chlorides (Fig. 1). Fig. 1-left shows increase of oxygen quantity. This fact was evoked because the sample was secondary oxidized on air between plasma treatment and analyzis. In the case of sample which was corroded in  $\text{HNO}_3$  (Fig. 2) decrease of oxygen and nitrogen amount was followed by degrease of nitric molecule quantity. The worst experimental results were obtained for corrosive layers created by submersion into  $\text{H}_2\text{SO}_4$  (Fig. 3) probably because they had very homogeneous structure (Sazavska et al. 2010). The sulphate molecules were also very heavy in comparison to chlorides and nitrides, which indicated an important role of sputtering in the corrosion removal.



**Figure 1:** EDX-SEM analysis on surface of sample which was corroded in HCl (left - iron, right - bronze).



**Figure 2:** EDX-SEM analysis on surface of sample which was corroded in  $\text{HNO}_3$  (left - iron, right - bronze).



**Figure 3:** EDX-SEM analysis on surface of sample which was corroded in  $H_2SO_4$  (left - iron, right - bronze).

Problem of this method is a removal of patinas of bronze. Patina has historical and aesthetic valuation for historians and conservators. Next problem is expensiveness of this method and sphere of archeology suffers from the lack of money. This fact blocks distribution of this method to museums.

The most significant advantages of this method as compared to conventional ones are the efficient removal of chlorides and significant reduction of treatment time (Veprek *et al.* 1985, 1987, de Graaf *et al.* 1995). Finer surface details and memory of instruments (used for object production) can be preserved.

### Acknowledgements

This work has been supported by the Czech Science Foundation, project No. 104/09/H080.

### References

- Cihlář, M.: 2005, Diploma thesis, Brno.
- de Graaf, M. J. *et al.*: 1995, *Surface and Coatings Technology*, 351-354.
- Kotzamanidi, I. *et al.*: 2002, *Anti-Corr. Methods and Materials*, **49**, 256-263.
- Neff, D. *et al.*: 2005, *Corrosion Science*, **47**, 515-535.
- Perlík, D.: 2001, Brno.
- Réguer, S. *et al.*: 2007, *Corrosion Science*, **49**, 2726-2744.
- Sazavska, V. *et al.*: 2010, *J. Phys.: Conf. Ser.*, **207**, 10.1088/1742-6596/207/1/012011.
- Veprek, S., Elmer, J., Eckmann, Ch., Jurcik-Rajman, M.: 1987, *J. Electrochem. Soc.*, 134.
- Veprek, S., Patscheider, J., Elmer, J.: 1985, *Plasma Chem. Plasma Process.*, **5**, 201.
- Wang, Z. *et al.*: 2008, *Chinese Journal of Chemical Engineering*, **16** (2), 299-305.