Plasmachemical Removal of Corrosion Layers from Brass

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Influence of RF low-pressure hydrogen plasma on corroded brass samples was investigated. OH radicals formed during this process were measured by optical emission spectroscopy; simultaneously, sample temperature was measured by a thermocouple. The value of integral intensity of OH radicals 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.

Plasmachemical removal of corrosion layers from metal samples was developed by Prof. Veprek during the 1980s [1,2]. This process is still under development for conservation of archeological artefacts made of various materials, and it is used in several technical musea [3]. The method is based on a partial reduction of the incrustation and corrosion layers by RF low pressure hydrogen plasma. It induces changes in structure and constitution of corrosion layers on metal objects.

This work extends our recent experiments with plasmachemical treatment of metal objects [4]. The presented contribution describes new experiments with model brass samples which were corroded in HCl solution for two weeks. The plasma treatment was carried out in the Quartz cylindrical reactor (i.d. 95 mm, 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. Flowing plasma was created in pure hydrogen (gas flow of 50 sccm) at pressure of 150 Pa. The real temperature of samples was monitored by a thermocouple installed inside the sample.

Optical emission spectra of OH radicals were measured by an Ocean Optics HR 4000 spectrometer with 2400 gr/mm grating. Atomic hydrogen reacts with oxygen from corrosion layers and forms OH radicals in excited states. OH radicals emit in the spectral region of 305–325 nm, and integral intensity over this region was used for the quantitative analysis of oxygen removal from the corrosion layer. The plasma treatment was stopped when a value of relative intensity of OH radicals reached one tenth of the maximum OH radical intensity [5]. The plasma treatment duration was 60–120 minutes depending on the duty cycle. The plasma temperature was calculated from lower OH rotational levels.

It is well known that brass is an alloy of copper and zinc. The detailed EDS analysis of used samples showed the presence of 56.8% Cu, 38.1% Zn and 5.2% Pb and [4]. Due to this fact the treatment temperature must not exceed 450 K. Based on our previous experimental results [4], conditions (i.e. the mean applied discharge power and the duty cycle) providing this temperature limitation were selected. Temperature of the sample was nearly constant after about 30 minutes, and this time was independent on the applied power. The rotational temperature was stabilized within about first 15 minutes of the discharge operation. It is an important parameter of plasma, and in this case it corresponded to temperature of neutral gas. Rotational temperature was more or less independent on the discharge regime, and it was significantly higher than temperature of the sample (uncertainty of calculated rotational temperature was estimated on 20 %).

The experimental conditions, maximal measured sample temperatures as well as calculated rotational temperatures are summarized in Tab. 1. The frequency of pulses was 100 Hz and thus for example, the duty cycle of 25 % means the discharge on for 2.5 ms and off for 7.5 ms. The duty cycle of 100 % means a continual regime of the discharge. The dependencies of OH radical integral intensity and sample temperature on treatment time were evaluated for all treatment samples. A typical example is given in Fig. 1 where two cases are demonstrated. Results of the sample treated under the 75 % pulsed regime and the mean discharge power of 400 W showed that the maximal intensity of OH radicals was reached at treatment time of 20 min. At this time, sample temperature was high enough to allow plasmachemical reactions leading to corrosion reduction because the OH radical intensity was decreasing from this moment. However, results of the sample treated under the 25 % pulsed regime

and the mean discharge power of 500 W showed that intensity of OH radicals was more or less constant during the whole treatment time. Sample temperature did not exceed 400 K in this case.

Tab. 1: Experimental conditions, measured sample temperature and calculated rotational temperature.

Discharge power	200 W	300 W	300 W	400 W	500 W	500 W
Duty cycle	100 %	50 %	75 %	75 %	25 %	50 %
Sample temperature	430 K	400 K	360 K	450K	390 K	430 K
Rotational temperature	650 K	650 K	630 K	670 K	670 K	660 K

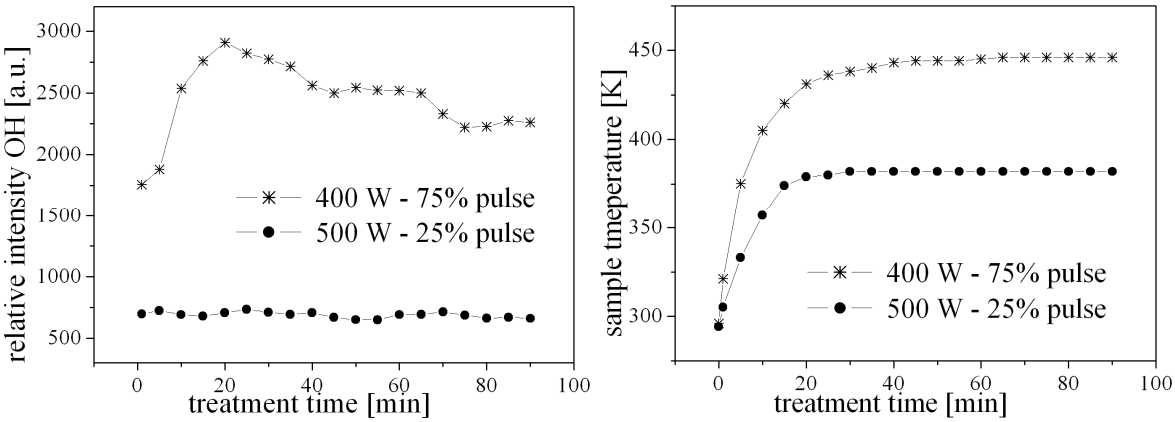

Fig. 1: Dependencies of relative OH radical intensity and sample temperature on treatment time.

From demonstrated results follow that there is only a very slow corrosion removal at sample temperature lower than 400 K. A decrease of intensity of OH radicals was observed at sample temperatures higher than 400 K. However, changes of corrosion layers composition were observed by a thermogravimetric and element analysis in all cases. The presented results clearly demonstrated that there was a relatively narrow sample temperature interval in which the corrosion removal was effective. The presented results are valid for the brass samples and pure hydrogen plasma, only. The detailed study for the other materials as well as different gas mixtures will be a subject of our further research.

The most significant advantages of the presented method, as compared to conventional ones, are the efficient removal of chlorides and significant reduction of treatment time [1-3]. For archeological practice it is important that finer surface details and a memory of instruments which were used for object creation can be preserved.

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