

# Plasma Treatment of Corrosion Layers from Brass

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## Abstract

New efficacious way of restoration and preservation of metal archaeological artifacts is described. This method is based on generation of reactive atomic hydrogen in low pressure RF hydrogen plasma discharge. Atomic hydrogen reacts with oxygen from corrosion layers of sample and forms OH radical. The value of integral intensity of OH radicals represents quantitative ablation of oxygen from corrosion layer. Another monitored magnitude was temperature of samples. Sample temperature sample is very significant indicator for protection sample against metallographic changes of metal bulk material and therefore damage of samples. We proved that the corroded sample became much less warm in pulsed than in continuous regime. Thus there is no risk of metallographic changes or damage of sample in pulsed regime.

**Keywords:** corroded brass, radio-frequency plasma, corrosion, electron microscopy, OES.

## Introduction

The plasma treatment of archaeological objects is based on a partial reduction of the incrustation and corrosion layers by RF low pressure hydrogen plasma [1, 2]. The corrosion removal process is very complex. It is not fully known up to now if reducing effect with atomic hydrogen or corrosion sputtering induced by heavy particles plays the main role.

The method is based on using RF low-pressure hydrogen plasma. It was evolved as a by-product of plasmachemical deposition research. This method is a relatively new technique developed by Veprek mainly for iron objects during the 1980s [3, 4]. Compared to conventional techniques, this method provides several significant advantages, as such the possibility of appearance of tiny details of the object shape and of its original surface [5]. The reduced corrosion layer of objects becomes brittle. It can be removed easily by conservators and thus mechanical stress applied to the objects decreases [6].

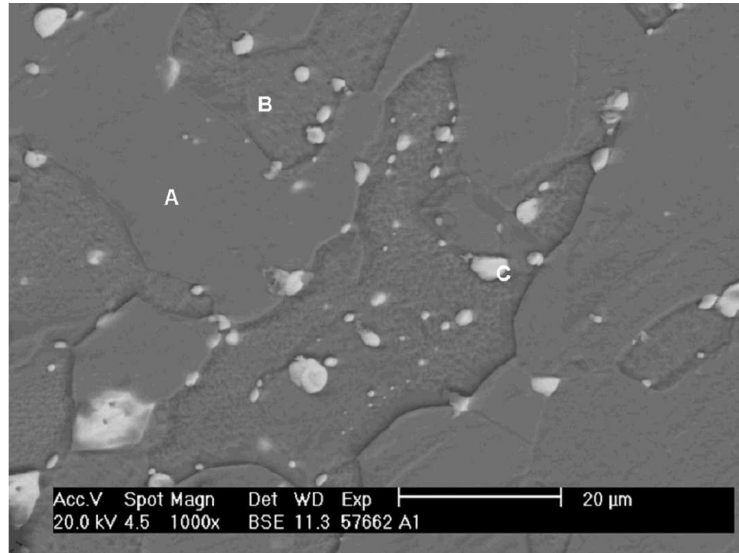
The technology is used mainly for iron or silver based materials, but even for them, the optimal conditions for the corrosion removal are not fully known yet. Knowledge of other metallic materials is more or less completely missing.

The optical emission spectroscopy of OH radical was used for the process monitoring [7]. Obtained spectrum was also used for the rotational temperature calculation. Sample temperature was measured during plasma treatment by thermocouple. The application of pulsed discharge regime can also conserve the corrosion removal process at lower mean power and thus the treated samples are affected by lower heating stress [7].

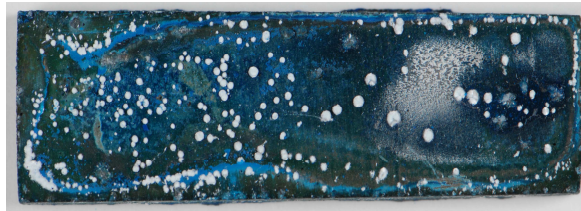
## Experimental

Brass is an alloy of copper and zinc, but EDS analysis shows that the used brass has three components. The real atomic composition of brass is 38,1% Zn; 5,2% Pb and 56,8% Cu. Detailed structure from electron microscopy is shown in Figure 1. Structure formed by solid solution of zinc in copper (location A), intermetallic compound CuZn (location B), and lead patterns (location C).

Each archaeological object is an original, and it has its “corrosion history”. Due to this fact, any 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 to results in the dependence on treatment conditions. Brass samples were prepared using ammonium solution, the samples were stored in this atmosphere for two weeks. Picture of the sample is shown in Ffigure 2 and composition of corrosion is 24,52% C; 46,69% O; 24,13% Cu and 4,65% Zn (Figure 8).

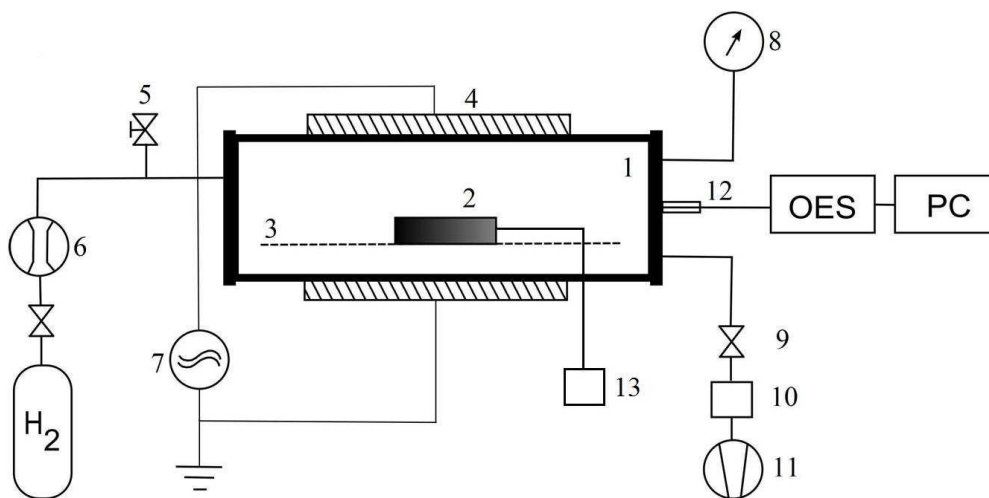


**Figure 1.** Metallographic cut of brass. Location A is solid solution of zinc in copper, location B is intermetallic compound CuZn, and white areas in locations C represent lead.



**Figure 2.** Corroded sample of brass.

The plasma treatment was carried out in the Quartz cylindrical reactor (i.d. 95 mm, length of 90 cm) with outer copper electrodes (Figure 3). 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 pulses with duty cycle of 75 %, 50 %, 25 % and frequency was 100 Hz (25 % pulse means 2,5 ms on and 7,5 ms off). Flowing plasma was created in pure hydrogen (gas flow of 50 sccm) at pressure of 150 Pa. The mean applied discharge power was 100–400 W depending on the duty cycle. The real temperature of samples was measured continuously by means of thermocouple installed inside the sample.



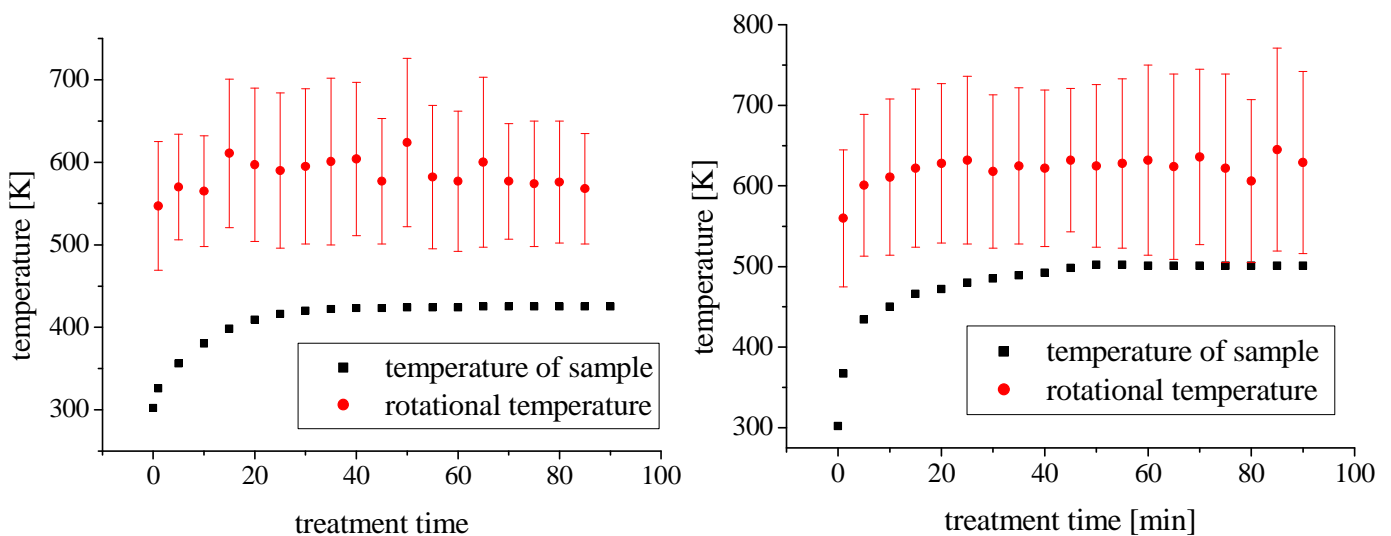
**Figure 3.** Experimental set-up: 1 – quartz discharge reactor (90 cm long, i.d. 95 mm); 2 – corroded sample; 3 – glass sample holder; 4 – outer copper electrodes; 5 – air-inlet valve; 6 – mass flow controller; 7 – RF power supply and matching network; 8 – pressure gauge; 9, 10 – valves; 11 – rotary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

The optical emission spectroscopy of OH radical was used for the process monitoring using Ocean Optics HR 4000 spectrometer with 2400 gr/mm grating. Atomic hydrogen reacts with oxygen from corrosion layers and forms OH radical (in excited state) [8]. OH radical emits in the spectral region of 305–325 nm, and its integral intensity area this region was used for the quantitative analysis of oxygen removal from the corrosion layer [6]. Plasma treatment was stopped when value of relative intensity of OH radicals reached one tenth of maximum OH radical intensity [7]. The plasma treatment duration was 60–120 minutes depending on the duty cycle. Simultaneously, the rotational temperature from lower rotation levels of OH radical spectrum was calculated.

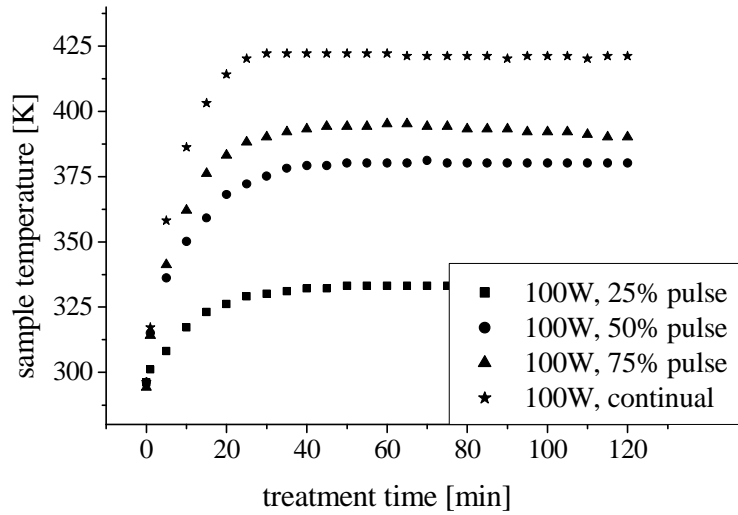
## Results and discussion

Reduction process is characterized by generated OH radicals in plasma discharge. We calculated rotation temperature from spectrum obtained by means of optical emission spectroscopy. Rotation temperature has predicative value only in the active continuous plasma discharge. In pulsed regime, plasma discharge occurs periodically therefore rotational temperature cannot be equal to temperature of sample. Sample temperature must reach always lower values with respect to rotational temperature. On the contrary, sample temperature can reach up to the rotational temperature in continuous regime. In Figure 4, rotational temperature is shown in both regimes around  $(600 \pm 100)$  K. Sample temperature reach its maximum at 425 K for power of 300 W in 50% pulse, and 500 K for power of 300 W in continuous regime.

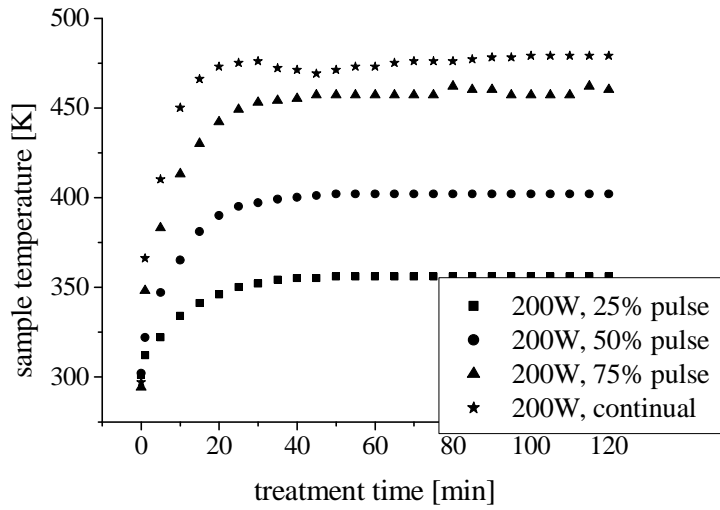
It is obvious that the sample temperature shifts according to the used power regime. Measured temperatures of samples are presented in Figures 5, 6, 7 for three applied power. Sample temperature is not such high in the pulsed regime as in the continual regime because the sample was exposed to lower plasma influence in the pulsed regime than in the continual regime.



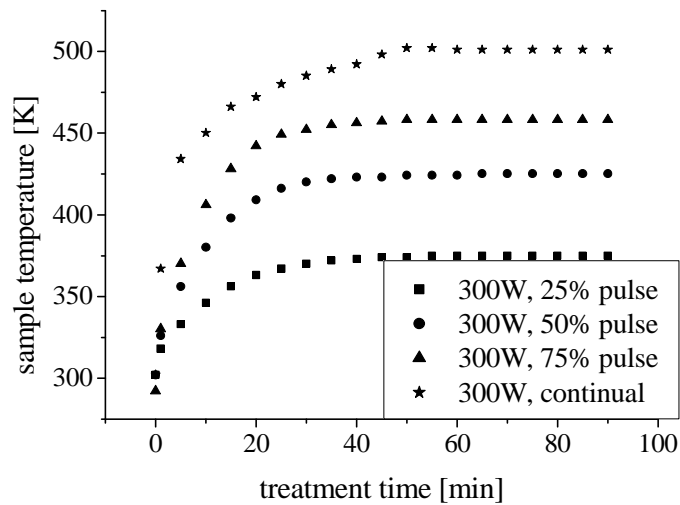
**Figure 4.** Comparison of rotation temperature and sample temperature during plasma treatment at 300 W, 50% pulse (left), and 300 W in continual regime (right).



**Figure 5.** Temporal evaluation on the sample temperature during the plasma treatment at 100 W.



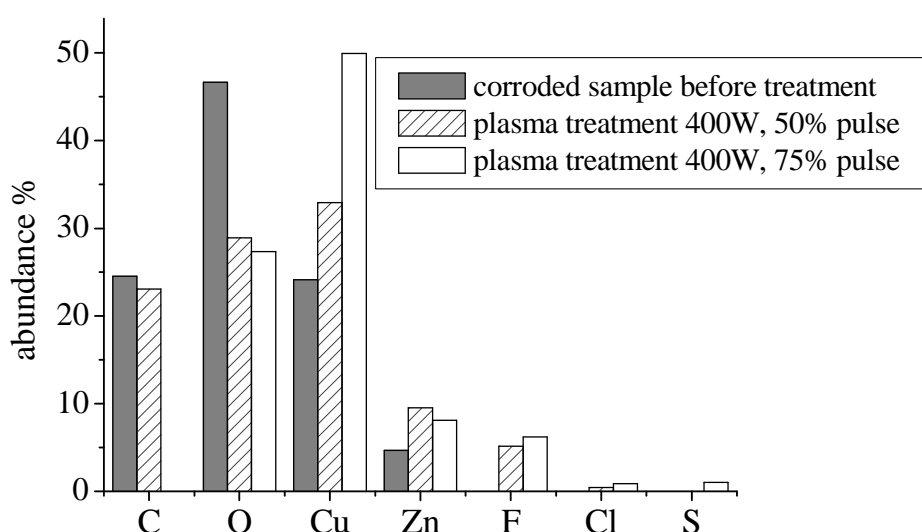
**Figure 6.** Temporal evaluation on the sample temperature during the plasma treatment at 200 W.



**Figure 7.** Temporal evaluation of the sample temperature during the plasma treatment at 300 W.

Very good corrosion removal was observed if samples were treated in continuous plasma regime, 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. EDS analysis (Figure 8) showed the decrease of atomic oxygen abundance, and the increase of copper and zinc abundance after plasma treatment. Accordingly, the corrosion layer was treated only in part. Nevertheless, relatively high atomic oxygen abundance after plasma treatment indicated that reoxidation occurred prior to treated sample analysis. In future, we are going to solve this problem. Treated sample will be put in a box with a protective argon atmosphere promptly after plasma treatment.

Figure 8 shows that power regime significantly influence final treatment of corroded samples. Corrosion removal is nearly directly proportional to the applied power. Unfortunately, the higher power induces sample temperature elevation. The high temperature of sample can induce metallographic changes of metal bulk material and therefore damage of samples [9]. Thus an optimal applied power inducing good corrosion removal without temperature enhancement over critical value is needed.



**Figure 8.** EDS analysis before (grey column) and after plasma treatment (striped and white column).

## Conclusion

The presented results showed that the corrosion removal process can be effective in the pulsed discharge regime. The main advantage of the pulsed regime is lower heating of sample. The pulse regime disadvantage is that treatment time is longer than in continual regime. We can assume that temperature plays an important role in the kinetics of reduction process. When we used low power of 100 W at 25% pulse, the corroded sample was untreated. On the other side, high power can evocate considerable sample heating that can result in the damage of the sample. The detailed analysis of the sample composition after treatment is the main goal of our contemporary research.

## Acknowledgements

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

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