

Reduction of Brass Corrosion Layers Using Hydrogen Plasma

Effects of various mean powers of plasma discharge

Lucie Řádková, Petra Fojtíková, Věra Sázavská, František Krčma

*Brno University of Technology, Faculty of Chemistry, Institute of Physical Chemistry
Purkyňova 464/118, 612 00, Brno, Czech Republic
xcradkova@fch.vutbr.cz*

1 Introduction

Reduction of corrosion layers using hydrogen plasma is a relatively new method, which should be used for conservation and restoration of archaeological artifacts. The conservation of artifacts represents a serious problem because of post-corrosion which occurs after excavation¹. Firstly, Daniels used a glow discharge in hydrogen to reduce silver tarnish back to silver². He used it for Daguerreotypes too, and his process was successful². The method of plasma treatment for metallic artifacts was developed at 80's of the 20th century at Institute of Inorganic Chemistry, University of Zürich. The method was successfully applied to the treatment of more than 13 000 historical objects from various periods (400 B.C. until 19th Century) and places of excavation³. This technology is used mainly for iron objects because optimal conditions for the corrosion removal from other metals are not fully known yet³.

2 Experimental

2.1 Sample preparation

The model corroded samples were prepared for this study because original objects have unevaluable historical value as well as their corrosion layers are non-identical. Two sets of corrosion layers were prepared; the first one was in ammonia atmosphere and the second one was in hydrochloric acid vapor. At first, the samples were grinded and subsequently put into desiccator. There was a Petri dish with ammonia solution or hydrochloric acid solution at the bottom of the desiccator. The corrosion process took four weeks. Samples were dried and stored in polyethylene ziplock bags before plasma application.

2.2 Experimental setup

The treatment was carried out in a Quartz cylindrical reactor (Figure 1) which was 90 cm long and 9.5 cm in the inner diameter. Radio-frequency electric field (13.56 MHz) was applied by two external copper electrodes using an automatic matching network, and capacitive coupled RF discharge was generated in pure hydrogen gas (99.9%).

The reactive atomic hydrogen was formed by the plasma discharge. This atomic hydrogen reacted with the corrosive layer containing oxygen. This reaction can lead to the sputtering of the corrosion layer and forms an unstable OH radical, which emitted light in the region of 305–320 nm. This radiation was detected by the optical emission spectroscopy, and it was applied as a process monitoring quantity⁴. Rotational temperatures and integral intensity of OH radicals were determined from the obtained data. The sample temperature was measured by a thermocouple installed inside the sample volume. Temperature was read out when the discharge was stopped for 5 s to eliminate RF field influence on this measurement.

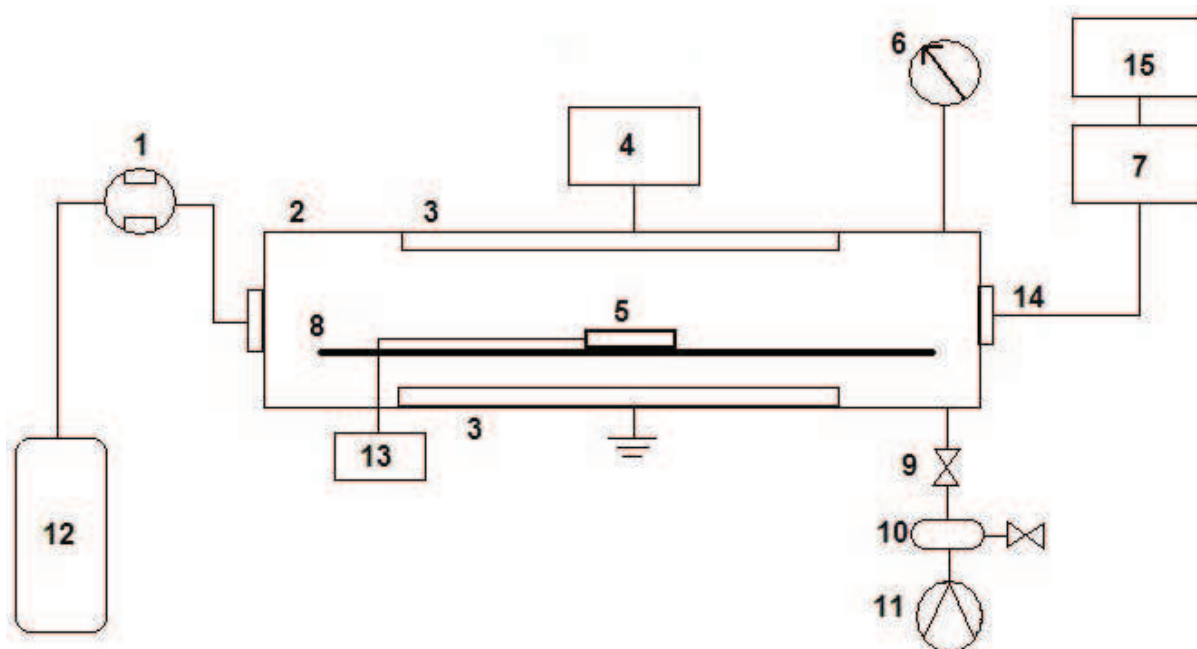


Figure 1: Schematic drawing of the experimental set-up: 1-mass flow controller; 2-Quartz discharge reactor; 3-outer copper electrodes; 4-RF power supply and matching network; 5-sample; 6-capacitance pressure gauge; 7-OES-spectromete;r 8-sample glass grid holder; 9, 10-valves; 11-rotary oil pump; 12-hydrogen; 13-thermocouple; 14-optical fibre; 15-PC

Corroded samples were treated by low pressure low temperature hydrogen plasma. Samples were treated at different conditions overviewed in Table 1. The pressure was 150 Pa at hydrogen flow rate of 50 sccm; treatment time was 90 minutes at all conditions.

Table 1: The total power vs. the effective power

Discharge power	Mode	Duty cycle	Effective power
100 W	continual	100%	100 W
200 W	pulse	50%	100 W
300 W	pulse	33%	100 W
400 W	pulse	25%	100 W

The effective power was calculated using equation

$$P_{eff} = P_{total} \cdot \frac{t_{on}}{t_{on} + t_{off}} \quad (1)$$

Plasma discharge was switched on for the whole time in the continual regime. The discharge was switched on and switched off ($t_{on/off}$) in the order of milliseconds in the pulsed regime. For example, 25% pulsed regime means that the discharge is switched on for 0.25 ms (t_{on}) and it is switched off for 0.75 ms (t_{off}) with the frequency of 1000 Hz. However, the mean energy in the pulsed regime is significantly lower, the process kinetics is different in each regime. Of course, the reactive particles generated by the discharge can react with the surface during the post-discharge period, too.

3 Results and discussion

3.1 Corroded samples composition

XRD pattern has shown that the corrosion layer was formed by zinc chloride hydroxide (ZnOHCl), ammonium chloride (NH₄Cl) and zinc hydroxyl chloride hydrate (Zn₅(OH)₈Cl₂·H₂O) in the case of ammonia atmosphere. The corrosion layer was redish brown with black crystals on the surface. In the other corrosion atmosphere, the corrosion layer was formed by zinc oxide chloride hydrate (Zn₂OCl₂·2H₂O) and lead chloride (PbCl₂). The corrosion layer was brown in this case.

3.2 Plasmachemical reduction

The temperature measured inside the samples was the highest in case of power of 100 W in the continuous mode and the lowest in case of power of 400 W in pulsed mode with duty cycle of 25% (Tab.2). Usually, the temperature was increasing during the first 35 minutes and then it was almost constant. The highest temperature during the treatment was between 80 and 140 °C independently on the corrosion layer kind.

Table 2: Maximal temperature of samples during the treatment

	100 W 100%	200 W 50%	300 W 33%	400 W 25%
Acid atmosphere	131 °C	103 °C	94 °C	89 °C
Ammonia atmosphere	139 °C	109 °C	94 °C	91 °C

Reduction process is characterized by OH radicals generated in the plasma discharge. Relative intensity of OH radicals was calculated from the spectrum obtained by optical emission spectroscopy. Figures 2 and 3, respectively show a time-dependence of the relative intensity of OH radicals during the plasma treatment. The effective power is the same, but the relative intensity is different. The highest intensity is in the continuous mode, and with the lower value of the pulse mode the relative intensity of OH radicals decreases. The OH radical intensity is not significantly dependent on the duty cycle if the pulsed regime is used.

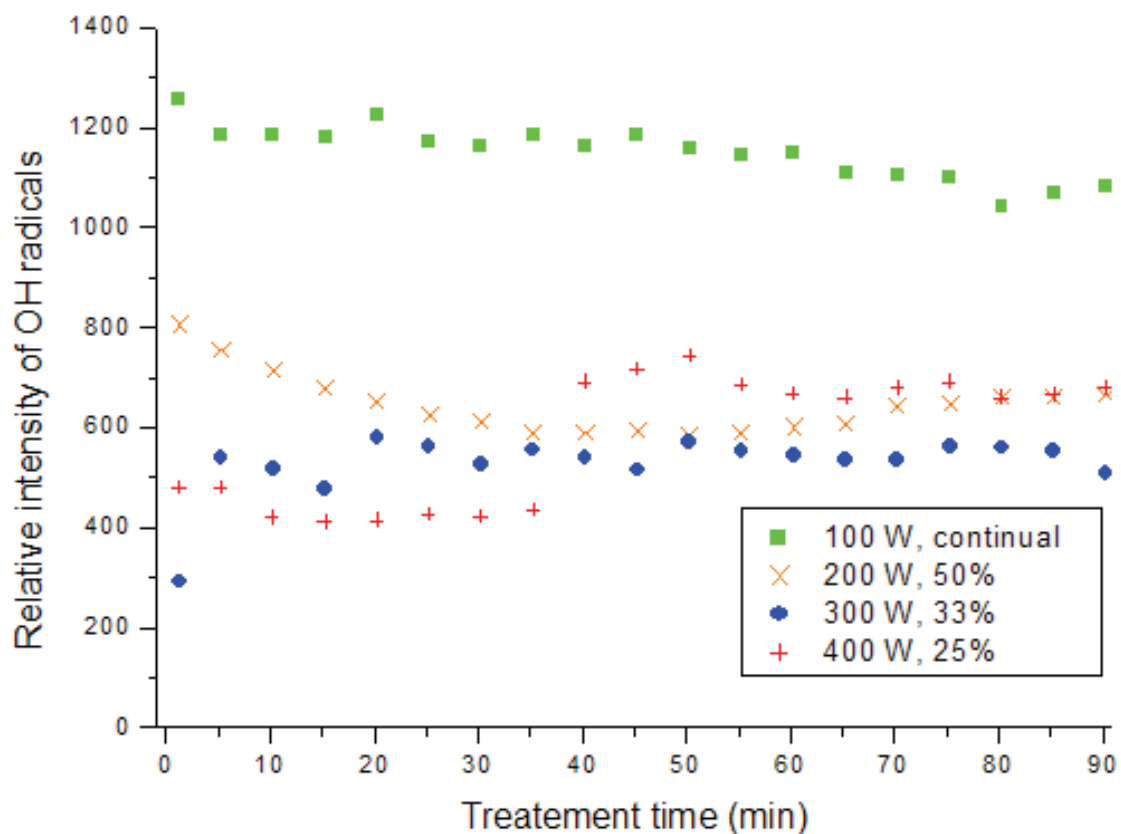


Figure 2: Relative intensity of OH radicals (ammonia atmosphere)

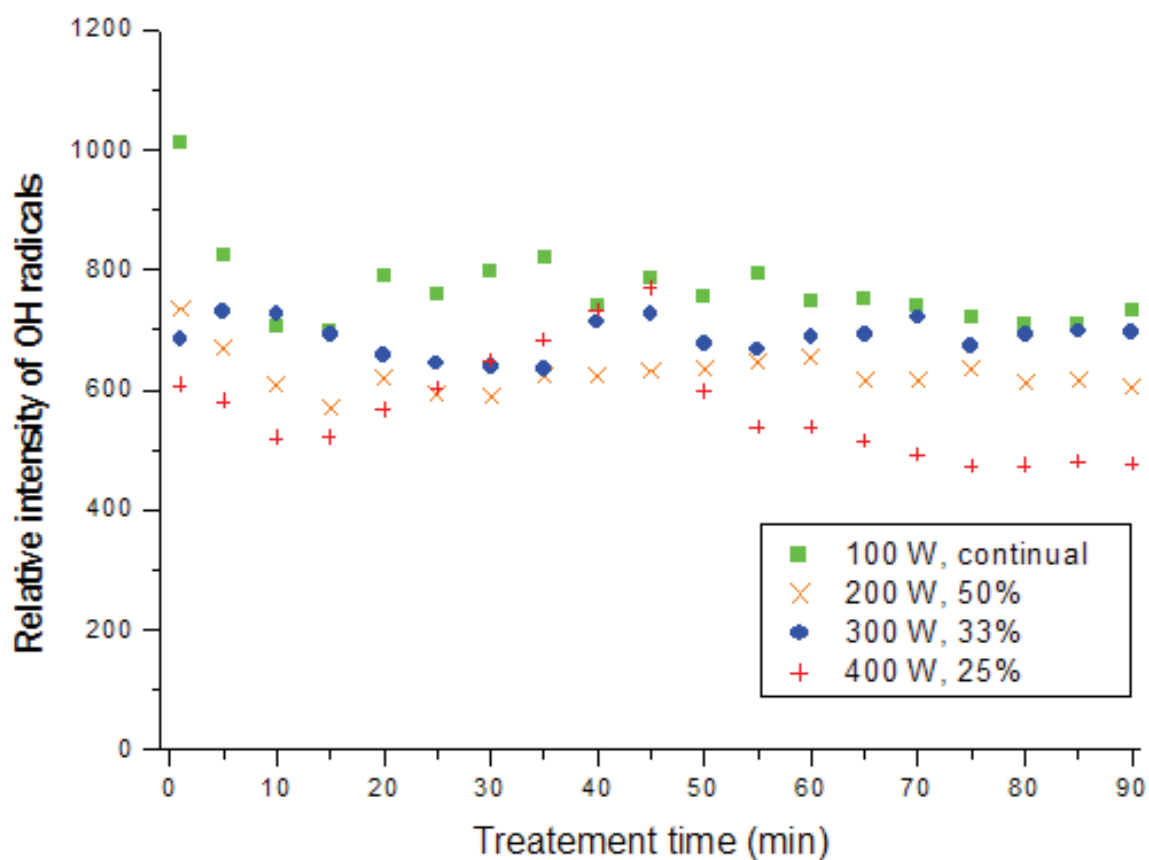


Figure 3: Relative intensity of OH radicals (acid atmosphere)

Rotational temperature was calculated from the OH radical spectrum, too. Table 3 shows maximal rotation temperatures during the plasma treatment. It can be seen this temperature was not depend on plasma power, it was about 700 K.

Table 3: Maximal rotation temperature of samples during the treatment

	100 W 100%	200 W 50%	300 W 33%	400 W 25%
Acid atmosphere	790±50 K	780±50 K	750±50 K	770±50 K
Ammonia atmosphere	720±50 K	720±60 K	760±50 K	670±40 K

3.3 Composition of the plasma treated samples

XRD pattern after plasmachemical treatment has shown that layers of the treated samples were formed by copper zinc (CuZn), zinc chloride hydroxide (ZnOHCl), ammonium chloride (NH₄Cl) and zinc hydroxyl chloride hydrate (Zn₅(OH)₈Cl₂·H₂O) in case of the ammonia atmosphere. Amount of all these compounds changed by the plasmachemical treatment, as it is shown in Table 2. The same compounds like in case of corroded samples were observed, but their quantity was different (see Table 4). The treated layers were brown with a white cover on the surface.

Table 4: Composition of layers in ammonia atmosphere

	Corroded sample	100 W 100%	200 W 50%	300 W 33%	400 W 25%
CuZn	77%	0%*	37%	50%	57%
ZnOHCl	19%	0%*	62%	42%	39%
NH ₄ Cl	1%	0%*	2%	2%	2%
Zn ₅ (OH) ₈ Cl ₂ ·H ₂ O	3%	0%*	-	6%	2%

* non-measurable amount

XRD pattern after the plasmachemical treatment has shown that the corrosion layer was formed by copper zinc (CuZn), zinc oxide chloride hydrate (Zn₂OCl₂·2H₂O) and lead chloride (PbCl₂) in case of the acid atmosphere. The same compounds like in case of the corroded samples were observed, but in non-measurable amount, only. The treated layers were dark brown or even black with white cover on the surface.

4 Conclusion

Corroded brass samples were treated by low pressure low temperature hydrogen plasma. The effect of RF discharge operation mode and applied power was studied on samples prepared in two different corrosion atmospheres. The effective power was the same, but the relative intensities of OH radicals, that reflect the corrosion removal, were different. The corroded samples were usually less warm in the pulsed mode than in the continuous mode. Temperature of samples during the treatment decreased with the decreasing duty cycle parameter at constant mean power. Amount of corrosion products

on the surface of samples decreased after plasma treatment. Composition of plasma treated samples depended on the operation mode.

5 References

1. Patscheider J., Vepřek S.: Application of Low-Pressure Hydrogen Plasma to the Conservation of Ancient Iron Artifacts, *Studies in Conservation* 31, 29 (1986)
2. Daniels V. D., Holland L., Pascoe M. W.: *Studies in Conservation* 24, 85 (1979)
3. Vepřek S, Patscheider J, Elmer J.: Recent progress in the restoration of archeological metallic artifacts by means of low-pressure plasma treatment, *Plasma Chemistry and Plasma Processing* 8, 445 (1988)
4. Rašková Z., Krčma F., Klíma M., Kousal J.: Characterisation of Plasmachemical Treatment of Archaeological Artifacts, *Czechoslovak Journal of Physics* 52, D927 (2002)

Acknowledgements

This work has been supported by the Ministry of Culture of the Czech Republic, project No. DF11P01OVV004.