

Study of hydrogen/argon RF plasma used for brass corrosion removal

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Application of plasmas is a new way of effective and fast treatment leading to conservation of metallic corroded objects. Removal of corrosion products is based on plasmachemical reduction of corrosion layers by radio-frequency (RF) low pressure hydrogen/argon plasma. The influence of this process on corroded brass samples was investigated. OH radicals formed during this process were measured by optical emission spectroscopy (OES); simultaneously, sample temperature was measured by a thermocouple placed inside the objects. The integral intensity of OH radicals represented quantitative measure of oxygen ablation from a corrosion layer. Sample temperature was chosen as important indicator of sample protection against metallographic changes. The SEM/EDS analyses of corroded and treated samples were performed. The applied plasma was monitored by OES and electron concentrations were estimated from H β spectral line profiles.

1. Introduction

The application of hydrogen and hydrogen /argon plasma in the conservation and restoration of metallic objects has been investigated for the last thirty years in order to determine its potentials and limits for culture heritage objects surface treatment [1, 2]. Scientists from different research branches have directed their attention to the application of this unconventional cleaning method of the metal artefacts [3-5]. Although many thousands original objects were already treated using this method [6], the process is still under the development. As original objects are unique, the model samples under various experimental conditions were used in the presented study.

The method is based on a reduction of corrosion products on the metal object (model samples or excavated archaeological artefacts) by reactive hydrogen atoms in low pressure radio-frequency (RF) hydrogen glow discharge plasma at low temperature [7]. The corrosion layers become brittle after the plasma application and thus they can be removed easily by conservators.

This work extends our recent experiments with plasmachemical treatment of metal objects [8, 9]. The presented contribution describes new experiments with model brass samples and results of analyses by Scanning Electron Microscopy (SEM) / Energy Dispersive X-ray Spectroscopy (EDS). The electron concentration of plasma was estimated from the H β line profiles measured by optical emission spectroscopy (OES).

2. Experimental set-up

Two sets of experiments were realized. The first one was the OES measurement of generated plasma

without corroded sample for different mixtures of Ar/H $_2$ and different applied discharge powers (100 W – 300 W). The optical emission spectra were recorded by Jobin-Yvon monochromator TRIAX 550 with CCD detector. The 3600 gr/mm grating was used for the measurement of hydrogen spectral line H β at 486 nm. The electron concentration was determined from H β line profile according to standard procedure described in [10].

The second set of experiments was performed with corroded brass samples, (10x10x5) mm³. They were let to corrode in vapours of concentrated ammonia solution for four weeks in desiccator. After this corrosion process, the samples were kept for 12 hours in a vacuum dryer (at temperature of 60°C) and kept in special bags containing oxygen and humidity absorbers. Then the plasmachemical treatment was applied.

A schematic drawing of our experimental device is shown in Fig. 1. The cylindrical quartz plasma reactor had an inner diameter of 95 mm and a length of 900 mm. External copper electrodes were placed on the opposite sides (top and bottom) of the reactor wall.

A capacitive coupled RF (13.56 MHz) power supply was operated in a continuous regime at power up to 300 W. The plasma was generated in various mixtures of hydrogen and argon with total gas flow of 50 sccm at pressure of 200 Pa.

The real temperature of sample during the plasma processing was measured by a K-type thermocouple installed inside the sample. Overall optical emission spectra were measured in the range of 250–350 nm by Ocean Optics HR 4000 spectrometer with 2400 gr/mm grating. For the process monitoring, the integral spectra of OH

radicals in the spectral region of 305–325 nm were used as the atomic hydrogen reacts with oxygen atoms originated from corrosion layers and OH radicals in excited states are created. Thus, the OH spectrum reflects the efficiency of the corrosion removal process. The plasma treatment was always stopped when the intensity of OH radicals significantly decreased [8]. The samples were treated from 75 minutes up to 100 minutes.

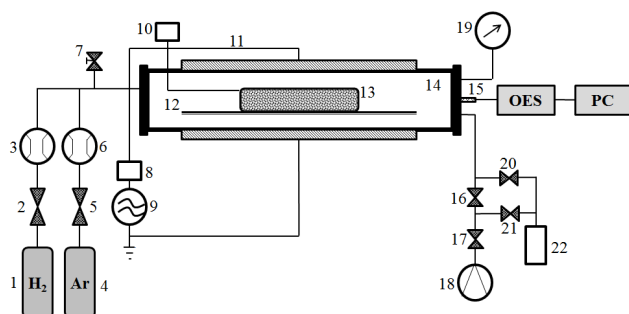


Fig. 1: Schematic drawing of the experimental set-up: 1, 4 - hydrogen/argon bottles; 2, 5 - valves; 3, 6 - mass flow controllers; 7 - air valve; 8 - matching unit; 9 - RF power supply; 10 - thermocouple; 11 - outer copper electrodes; 12 - sample glass grid holder; 13 - treated sample; 14 - Quartz discharge reactor; 15 - optical fibre; 16, 17, 20, 21 - valves; 18 - rotary oil pump; 19 - capacitance pressure gauge; 22 - liquid nitrogen trap.

Corroded and treated samples were analysed by SEM-EDS in order to determine changes in their surface appearance as well as elemental composition changes caused by hydrogen plasma.

3. Results and discussion

3.1 Sample temperature and relative intensity of OH radical spectra

The corroded samples before and after treatment are shown in Fig. 2. Originally blue corrosion layer converted into the brown one. The temperature of the sample initially increased as it is shown in Fig. 3 but it was nearly constant after about 30 minutes of the treatment (this time was independent on the applied mean power and gas mixture composition). The OH integral intensity and sample temperature vs treatment time were evaluated for all treated samples. The results for discharge power of 200 W are shown in Figs. 3 and 4. It is evident that both maximal intensity of OH radicals emission and measured sample temperature depend on the gas composition. The maximal sample temperature was

observed during the samples treatment in gas mixture of 10 sccm H₂/40 sccm Ar and of 20 sccm H₂/30 sccm Ar. The lowest sample temperature was observed at 30 sccm H₂/20 sccm Ar. At these conditions, the sample was not significantly heated in contrary to the treatment at other conditions; the maximal sample temperature reached about 175 °C.

The maximal intensity of OH radical spectra was reached at the treatment time of 10 minutes for all gas mixtures. The intensity of OH spectra decreases with increasing hydrogen content; this could be caused by decreasing of the electron mean energy. Namely, at higher hydrogen concentration, the electrons lose their energy in more frequent inelastic collisions with hydrogen molecules.

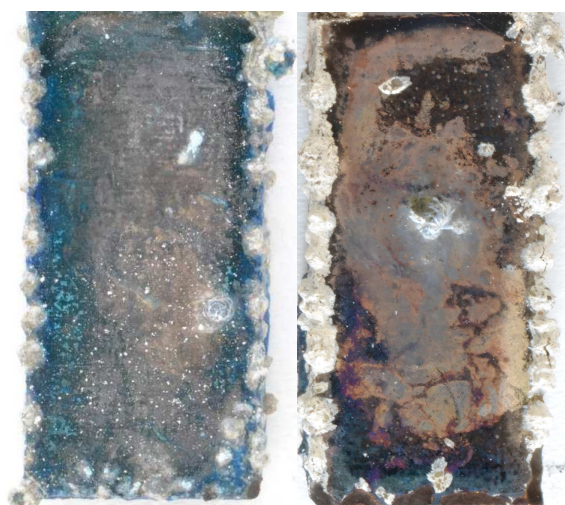


Fig. 2: The corroded sample before (left) and after (right) treatment in 30 sccm H₂/20 sccm Ar plasma at 200 W.

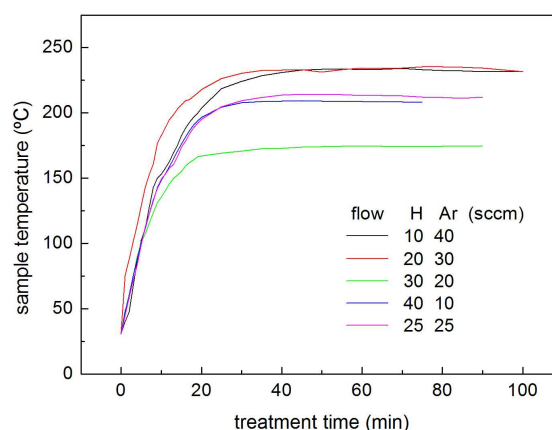


Fig. 3: Time evolution of sample temperature during the plasma treatment at 200 W in selected hydrogen/argon mixtures.

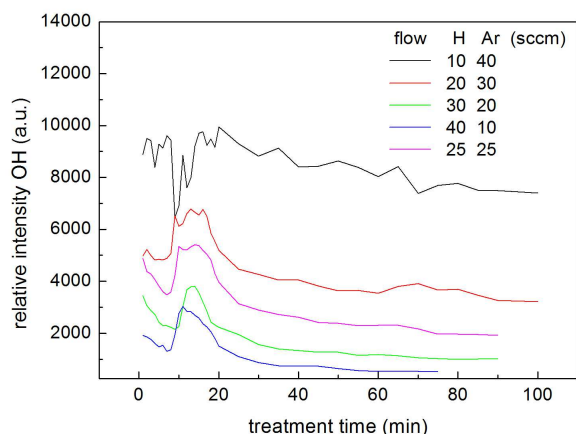


Fig. 4: OH radical intensities during the plasma treatment at 200 W for various hydrogen/argon mixtures.

3.2 SEM-EDS analyses

Studied samples were analysed by SEM-EDS before and after the plasma chemical treatment. Every sample was analysed integrally over two areas of $3.45 \times 4.45 \mu\text{m}^2$. The results are summarized in Tab. 1 for the weight percentages of elements (wt%) while the atomic percentages of elements (at%) for treated samples are presented in Tab. 2. Before treatment, the corrosion layer contained about 20.9 wt% and 49.7 at% of oxygen and 1.6 wt% and 1.7 at% of chlorine.

As low as possible contents of oxygen and chlorine in treated surfaces are important. The best result was obtained if sample was treated in the plasma created in 30 sccm of hydrogen, 20 sccm of argon gas mixture. In the case of oxygen, a significant decrease of this element was not observed. However, the decrease of chlorine is more important than the decrease of oxygen because of the secondary electrolytic corrosion in which chlorine plays catalytic role.

Tab. 1: EDS analysis – weight percentages of selected elements

elem.	flow H ₂ / Ar (sccm)				
	10/40	20/30	30/20	40/10	25/25
O	13.9	15.8	16.8	15.5	19.6
Pb	7.3	7.2	12.5	12.1	15.2
Cl	0.6	0.1	0.0	0.5	0.4
Cu	64.5	42.7	47.0	39.8	49.4
Zn	13.7	34.2	23.6	32.1	15.4
Total	100.0	100.0	100.0	100.0	100.0

Tab. 2: EDS analysis – atomic percentages of selected elements

elem.	flow H ₂ / Ar (sccm)				
	10/40	20/30	30/20	40/10	25/25
O	40.1	42.8	47.9	44.9	52.4
Pb	2.0	1.9	3.6	4.2	5.2
Cl	0.8	0.1	0.0	0.6	0.5
Cu	47.6	31.8	32.7	28.4	32.3
Zn	9.6	23.4	15.8	21.9	9.6
Total	100.0	100.0	100.0	100.0	100.0

3.3 Calculation of electron concentration

The OES was performed for plasma diagnostic. The electron concentration in plasma was estimated from H_β spectral line profiles which were recorded for sets of several parameters such as power, hydrogen and argon flows. The typical set of profiles corresponding to the best experimental conditions in case of corroded sample treatment (30 sccm H₂/20 sccm Ar) is shown in Fig. 5.

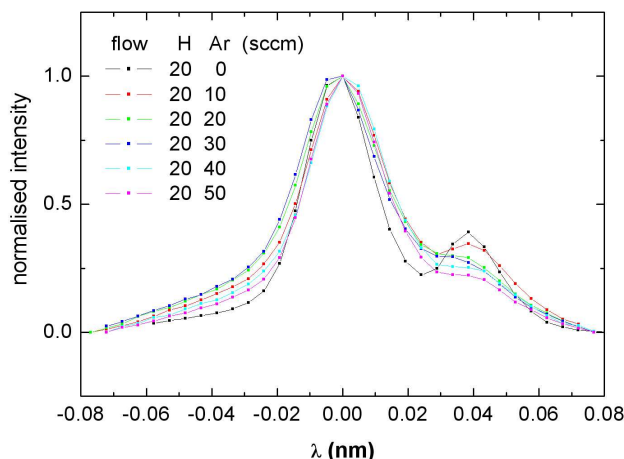


Fig. 5: Spectral line profile of H_β for the set of measurements: 200 W, 30 sccm H₂/0-50 sccm Ar. The rotational line of hydrogen molecule is presented in the right side of profiles.

The electron number density n_e was estimated from the full total halfwidth of H_β line profiles. It was assumed that the broadening of H_β line is caused only by the Stark effect. This assumption is nearly correct because OH rotational temperature is independent on the experimental conditions (applied power, hydrogen/argon ratio) and it is around 600K. Then the electron density n_e can be estimated by the simple formula given in [10]. This formula was used with respect to the presence of the rotational line in the full profile which prevents in this moment to the determination of electron concentration with higher

precision. However, the complete solution of this inversion problem, i.e. the deconvolution of H_{β} line profile and the rotational component as well as the apparatus function which makes possible to use full profile for the calculation, is under development.

The apparatus function was taken into consideration and it had to be subtracted as the ratio of total linewidth to the width of apparatus function was about 5:1. The results for gas mixture 30 sccm H_2 /20 sccm Ar and different power are shown in Tab. 3. It has been proved that electron concentration increases when the discharge power increases. Achieved maximum of concentration is relevant with respect to the estimation of uncertainty.

Tab. 3: Calculated electron concentration for different discharge power.

30 sccm H_2 / 20 sccm Ar	
discharge power (W)	electron concentration (cm^{-3})
100	3.5×10^{13}
200	6.4×10^{13}
300	7.5×10^{13}

The results for other used gas mixtures H_2 /Ar at 200 W discharge power are summarized in Tab. 4.

Tab. 4: Calculated electron concentration for different gas mixtures.

discharge power 200 W	
discharge power (W)	electron concentration (cm^{-3})
10 / 40	4.10×10^{13}
20 / 40	6.16×10^{13}
30 / 20	6.35×10^{13}
40 / 10	3.78×10^{13}

4. Conclusion

The corroded brass samples were treated in H_2 /Ar RF plasma at low pressure at different gas compositions and different RF powers. The plasma parameters were monitored by OES and the electron concentration was estimated from the measured hydrogen line profiles. The chlorine content in corroded surface layers was reduced significantly; the oxygen content was reduced only slightly.

5. Acknowledgement

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6. References

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