

Diagnostic of plasmachemical treatment of archaeological artifacts

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Plasmachemical treatment of archaeological artifacts is a relatively new technique. Up to now, it has been used more or less intuitively in practice, but for a widespread application an exact characterization of the process is necessary. The process is based on using low-pressure hydrogen plasma in which the artifacts (in this case silver coins and some pieces of iron) are treated for several hours, usually in more steps. The problem is how long period of the plasmatic treatment is optimal and how to characterize its efficiency. From the kinetic point of view, the oxide and chloride molecules reduction is the main process. Significant, but not very intense radiation of the $\cdot\text{OH}$ radical was observed in the optical emission spectra. Due to the fact that in pure hydrogen plasma the $\cdot\text{OH}$ emission spectra is not overlapped by any radiation, we use its integral intensity in the range of 300 - 330 nm as an indicator of the oxides reduction effectiveness. The $\cdot\text{OH}$ radiation shows specific dependence on time. Initially a fast increase, later a slower non-exponential decrease. The duration of the $\cdot\text{OH}$ integral intensity decrease to the value of 10% of its maximum can be taken as the end of the reduction. It was found out that during the first two hours the reduction is completed. Besides, during the plasmachemical treatment of artifacts in ammonia-water vapour the intensities of the spectral lines of atomic hydrogen (H^α and H^β) were measured as a function of plasmachemical treatment time. But in this case the end of reduction processes was difficult to estimate. The measuring device used for our experiments could be used in practice for plasmachemical treatment monitoring.

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Key words: optical spectroscopy, archaeology, plasmachemical reduction, ancient metal conservation

1 Introduction

Plasmachemical treatment of archaeological artifacts is a relatively new technique developed during the 1980s [1, 2]. Although this technique was used for conservation of artifacts whose components are mainly metals, the plasmachemical process as such was used more or less intuitively [4]. The process is based on using low-pressure hydrogen plasma in which the artifacts are treated for several hours, usually in more steps [4, 5, 6]. The problem is how long period of the plasmatic treatment is optimal and how to characterize its efficiency. The ancient artifacts always contain some corrosion layers on their surface. The studies focused on the

composition of the layers show that various oxide and chloride complexes, usually containing crystalline water too, are the dominant compounds of the layer [6, 7]. Bulk corrosion contains especially chlorides and sulphides while surface corrosion is caused by oxygen and water.

2 Experimental setup

The principle of plasmachemical treatment is based on the removal of the oxide and chloride molecules from the corroded surface in low-temperature, low-pressure hydrogen plasma. The scheme of our experimental device is given in Fig. 1. The experiment usually takes place at the total gas pressure of 100–110 Pa and at the hydrogen flow rate of 100 Sccm. The capacitively coupled RF power supply gives the total power of 400–450 W. Details concerning the experimental device as well as the operating conditions can be found in [7].

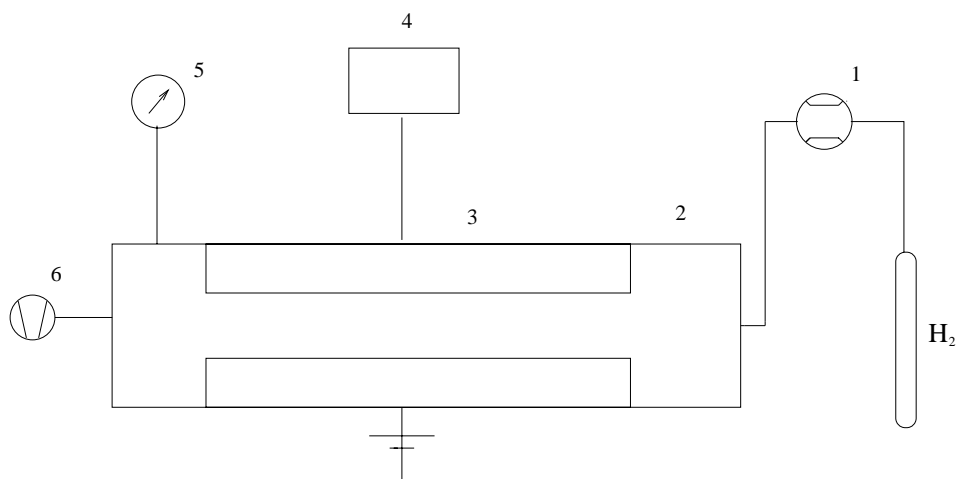


Fig. 1. Experimental setup: 1 - mass flow controller; 2 - Pyrex glass reactor (length 88 cm, inner diameter 10 cm); 3 - outer cylindrical copper electrodes (length 50 cm); 4 - RF power supply; 5 - baratron gauge; 6 - rotary oil pump.

3 Principle of process monitoring

The optical spectrum emitted from the discharge in the part behind the treated artifact was measured by a spectrometer Jobin Yvon HR 640 coupled with a multi-channel UV CCD detector. To minimize the disturbing effects we used a relatively long integration time of 10 s. An example of the experimental spectrum emitted from the hydrogen discharge is given in Fig. 2.

In the hydrogen discharge, electron collisions with various particles are the most important ones as demonstrated in [3], for example:

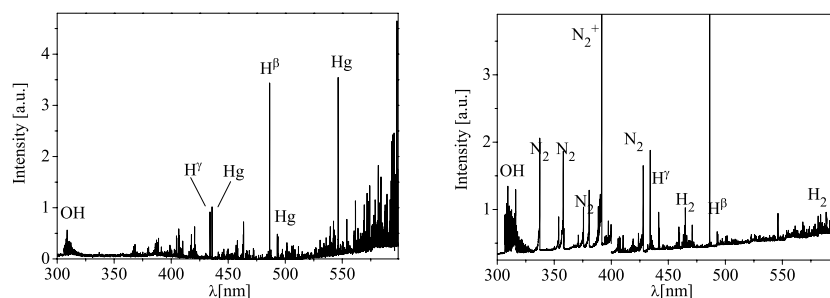
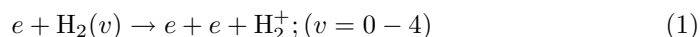
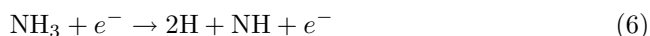
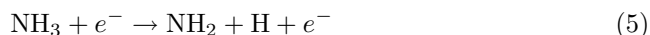
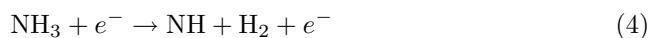


Fig. 2. An experimental spectrum obtained during the plasma treatment of an ancient iron hook in hydrogen plasma and of a silver coin in the ammonia–water vapour 10 minutes after the beginning of the treatment.

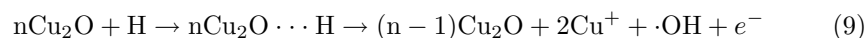
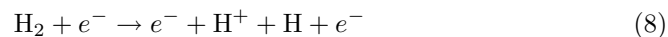


In other set of experiments the solution of ammonia was used as a cheap supply of hydrogen. For ammonia–water vapour treatment the experimental device is identical with the device mentioned above. In the ammonia–water discharge, the supposed reactions are as follows:



3.1 Spectral lines

In the spectrum emitted from the hydrogen discharge, various spectral lines of atomic hydrogen as well as molecular spectra of $\cdot\text{OH}$ radical can be observed. The $\cdot\text{OH}$ radical is created in an active discharge by reactions of atomic hydrogen with oxygen in the corrosion layers at the artifact surface. Reduction of oxides (in the case of coin made of copper) probably follows this schema:



Due to this fact, the $\cdot\text{OH}$ radical spectrum in Fig. 3 can be used as an indicator of the oxide reduction in plasma. Our numerous experimental data show the most intense radiation of the $\Delta\nu = 0$ sequence of $\cdot\text{OH}$ ($A^2\Sigma^+ \rightarrow X^2\Pi^-$) spectral system. This system is well known, because the rotational structure of this system is used in many cases for the determination of neutral gas temperature. The overlap of the $\cdot\text{OH}$ spectrum with the nitrogen second positive bands is not observed in our case. Thus the integral spectral intensity over the whole $\Delta\nu = 0$ sequence range can be used for monitoring of the oxides reduction.

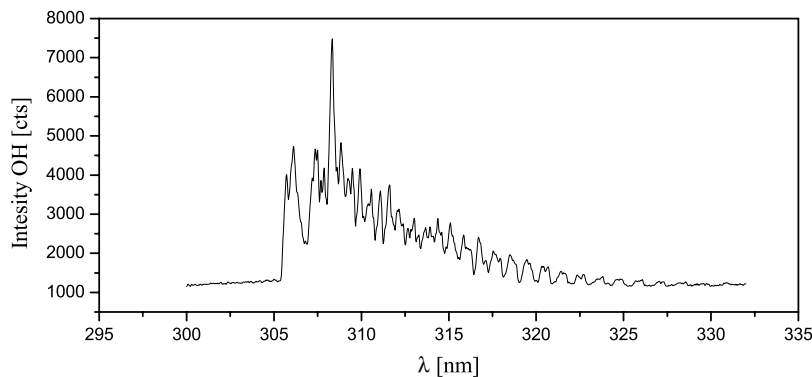


Fig. 3. An experimental unresolved spectrum of $\cdot\text{OH}$ radicals obtained during the plasma treatment of the artifact.

Apart from this measurement, the intensity of spectral lines H^α and H^β was measured as a function of treatment time during the treatment of artifacts in ammonia-water vapour discharges. In the spectrum besides spectral lines of H^α and H^β , low intensive spectral band of OH^- , $\cdot\text{OH}$, O_2 , H_2O , N_2 , $\cdot\text{NH}$ and $\cdot\text{NO}$ also appeared.

4 Results

The integral intensity of $\cdot\text{OH}$ in the spectral range of 305-330 nm as a function of the treatment duration is given in Fig. 4 showing plasmachemical treatment of an ancient iron hook. Among the plasmachemical processes, the artifact was treated by classical conservation methods, both mechanical and chemical. The intensity dependencies in all four stages show initial strong enhancement of $\cdot\text{OH}$ intensity (during the first 10 - 15 minutes) resulting from the increase in the artifact temperature [6]. Later on, a slower decrease in the intensity can be observed. During the first stage the main reduction was completed in the first two hours, then the oxides reduction was much slower and it has an approximately constant rate. After the layers reduced in the first stage are reduced further on, the plasmachemical reduction increases and then slowly decreases. Finally, the plasmachemical reduction

ends after approximately 3 hours of the fourth stage.

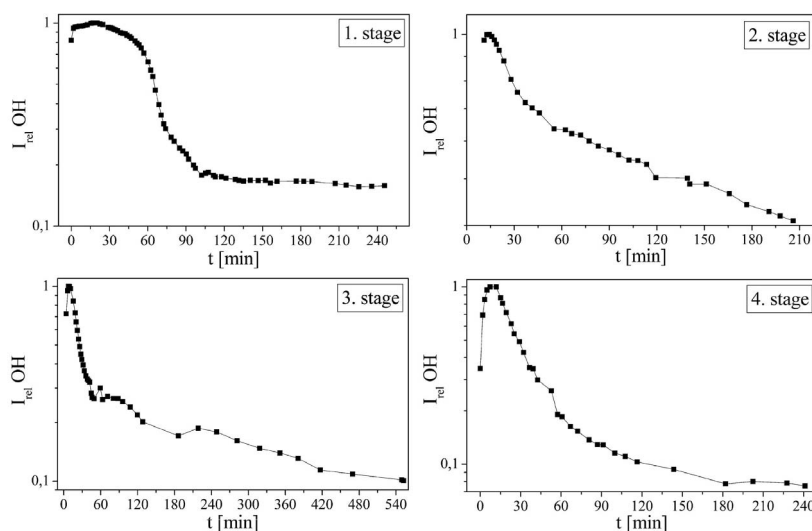


Fig. 4. The integral intensity of $\cdot\text{OH}$ in the spectral range of 305 – 330 nm as a function of the iron hook treatment. All graphs are normalized to their maximal values.

Of course, the time dependencies of the plasmachemical treatment necessary for each stage strongly depend on the treated artifact and on the mechanical and chemical operations taking place among the individual stages. It could be concluded from the example given above that there is some optimal treatment duration for each stage of the plasmachemical treatment.

The results of our spectroscopic observations show that the optimal moment for interruption of the plasmatic stage comes when more or less constant $\cdot\text{OH}$ intensity is reached and the duration of the $\cdot\text{OH}$ intensity decrease to the value of 10 % of its maximum during the particular stage.

In the case of the second experiment, due to the presence of hydrogen and nitrogen compounds and due to their reactions (nitridation) and sorption of hydrogen on the surface of the artifact, the monitoring of the treatment processes was not too effective. By means of this method it is difficult to determine the end of reduction processes as it can be seen in Fig. 5.

Conclusions and prospects

Our experimental spectroscopic observations of the plasmachemical treatment of archaeological artifacts clearly demonstrate that the measurement of integral $\cdot\text{OH}$ radical spectral intensity in the range of 305 - 330 nm can be used as an indicator for the plasmatic treatment processes. The time dependence of the $\cdot\text{OH}$ intensity

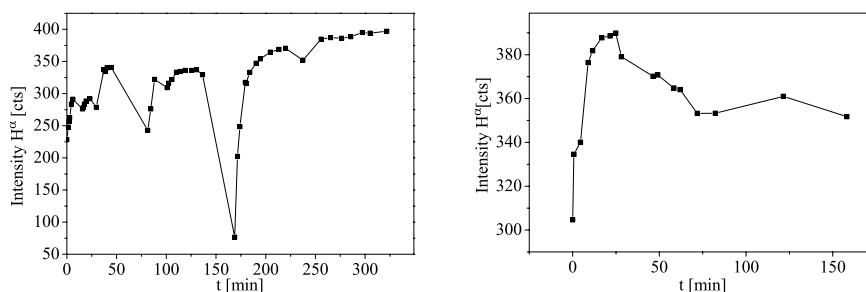


Fig. 5. The intensity of H^{α} (at 656,279 nm) as a function of the copper and silver coins treatment time in ammonia vapour.

can provide important information about the number of plasmatic stages needed for successful removal of oxides as well as information about the optimal duration of each stage. On this basis the simplified monitoring device can be proposed for wide use in practice. This device uses the appropriate interference filter passing the light in the range mentioned above. Due to the fact that the plasma reactor is made of Pyrex glass and the maximum $\cdot OH$ intensity is 307 nm, the optimal filter has a maximum transitivity of about 306 nm and band width of about 20 nm. The photodiode with UV increased sensitivity can be used as a detector. The strong RF disturbing radiation for the discharge must be eliminated by sufficient electrical shielding including the input orifice of the detecting device. We have constructed this device for common use in practice.

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References

- [1] S. Veprek, J. Patscheider, J. Elmer: *Plasma Chem. Plasma Process.* **5** (1985) 201
- [2] S. Veprek, J. Elmer, Ch. Eckmann, M. Jurcik-Rajman: *J. Electrochem. Soc.* **134** (1987) 2398
- [3] M. Lieberman, A. Lichtenberg: *Principles of plasma discharges and materials processing*, John Wiley & Sons, New York 1994
- [4] M. Klíma: *Archeologické Rozhledy* **50** (1998) 255 - in Czech
- [5] M. Klíma, L. Zajíčková, J. Janča et al.: *Zeitschrift für Schweizerische Archäologie und Kunstgeschichte* **54** (1997) 2398
- [6] M. Klíma, L. Zajíčková, J. Janča: *Zeitschrift für Schweizerische Archäologie und Kunstgeschichte* **54** (1997) 29
- [7] M. Klíma: *Plasmachemical Regeneration of Degraded Ancient Artifacts*, PhD Thesis, Masaryk University Brno, 2000