

Heating of Metal Archaeological Artefacts during Low-Pressure Plasma Treatment

Vera Sazavska, Radek Prikryl, Frantisek Krcma, Adam Kujawa, Brno University of Technology, Faculty of Chemistry

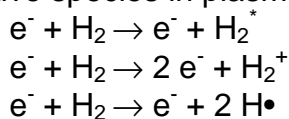
Summary

Plasmachemical treatment is an effective and fast way of restoration and preservation of archeological artefacts. The method is based on a partial reduction of the incrustation and corrosion layers by hydrogen discharge plasma. Compared to the conventional restoration techniques, it offers significant advantages like the quality of the object surface and time savings [1]. On the contrary, the heating stress of the treated object can cause metallographic changes which could lead even to the damage of the archaeological artefact. Temperature of the treated artefact is a very important indicator for the object protection against metallographic changes of metal bulk material.

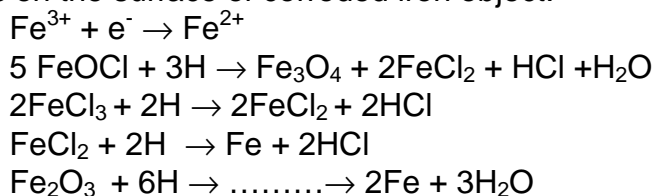
1 Introduction

Plasmachemical treatment of archaeological artefacts is a relatively new technique developed during the 1980s [2, 3]. This process is still under development for conservation of archeological artefacts made of various materials, and it is used in several technical musea [4]. The process is based on using RF low-pressure hydrogen plasma in which the artefacts are treated for several hours, usually in more steps [5, 6]. The hydrogen molecule is dissociated to very reactive species like radicals, ions, and excited hydrogen in plasma discharge. These species react with compounds from corrosion layers. Corrosion products (like oxides, chlorides, etc.) can be reduced to the pure metal due to the reduction effect of hydrogen (for example, reaction on the surface of corroded iron object is demonstrated below).

Production of the active species in plasma discharge:



Example of reactions on the surface of corroded iron object:



2 Experimental part

The experiment was done in the Quartz cylindrical reactor (i.d. 95 mm, length of 90 cm) with outer copper electrodes (Figure 1). The capacitive coupled RF power supply (frequency of 13.56 MHz) gave the total power up to 600 W in a continuous or pulsed regime. We used pulses with a duty cycle of 75 %, 50 % and 25 %, and frequency was 1000 Hz (25% pulse means 0.25 ms discharge on and 0.75 ms off). Flowing plasma was created in pure hydrogen (gas flow of 50 sccm) at pressure of 200 Pa. The real temperature of samples was measured continuously by thermocouple installed inside the model sample.

The optical emission spectroscopy (OES) of OH radical was used for the process monitoring. Atomic hydrogen reacts with oxygen from corrosion layers and forms OH radical (in excited state) [7]. OH radical emits in the spectral region of 305–325 nm, and the integral intensity of this region was used for the quantitative analysis of oxygen removal from the corrosion layer [6, 8]. Simultaneously, rotational temperature was calculated from emission spectra.

Plasma treatment was stopped when a value of relative intensity of OH radicals reached one tenth of maximum OH radical intensity [8]. The plasma treatment duration was 60–120 minutes depending on the duty cycle.

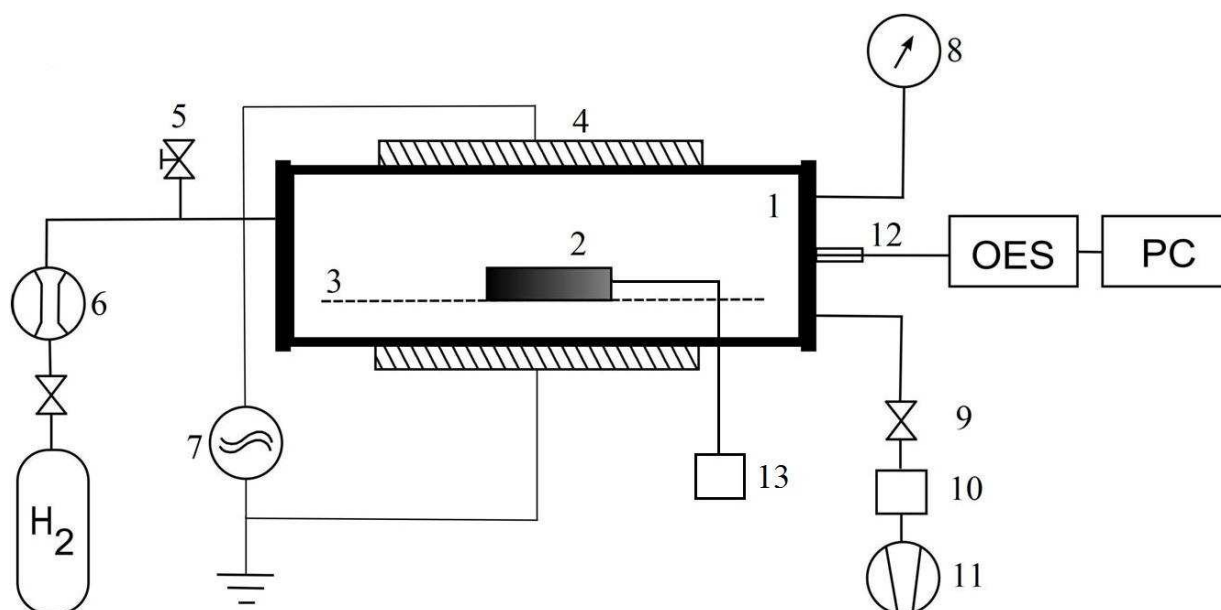


Figure 1: Experimental set-up: 1 – Quartz discharge reactor (90 cm long, i.d. 95 mm); 2 – corroded sample; 3 – glass sample holder; 4 – outer copper electrodes; 5 – gas-inlet valve; 6 – mass flow controller; 7 – RF power supply and matching network; 8 – pressure gauge; 9, 10 – valves; 11 – rotary oil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

3 Results and discussion

The metal objects warm up due to electromagnetic induction in plasma discharge. Therefore, temperature monitoring of the treated object is necessary. Some kinds of metals are sensitive to the heating stress, for example copper and copper alloys. Strong heating of the sample can cause metallographic changes which could lead even to a damage of the metal archaeological artefact. Also the information about the object manufacture could be lost. On the contrary, the chemical process of reduction by hydrogen needs a starting temperature.

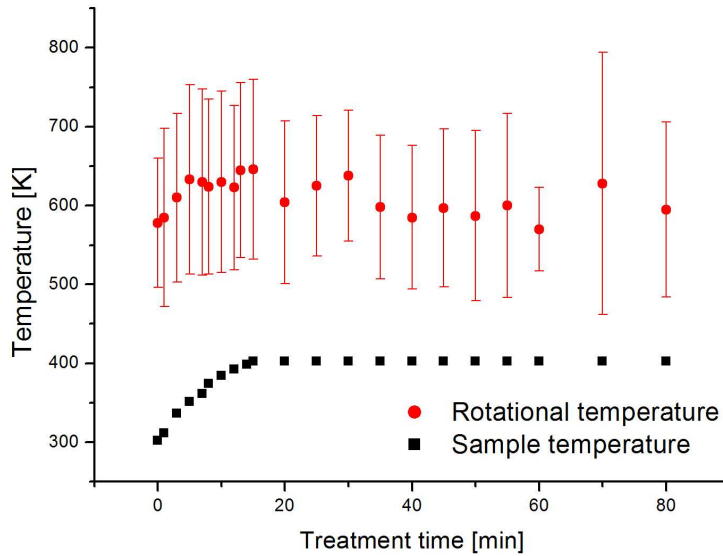


Figure 2: Comparison of rotational temperature with sample temperature during the plasma treatment at 300 W and a 50% pulse

The first plasma parameter studied by this work was rotational temperature. Rotational temperature corresponded to the temperature of neutral gas in plasma. It was different from the sample temperature (Figure 2). Rotation temperature has a predictive value only in the active continuous plasma discharge. In the pulsed regime, plasma discharge occurs discontinuously (although periodically). Therefore, rotational temperature cannot be equal to the real temperature of the sample. Sample temperature reach always lower values with respect to rotational temperature. On the contrary, sample temperature can reach up to the rotational temperature in the continuous regime. The rotational temperature was more or less constant during the plasma treatment (600 K).

Table 1: Maximal sample temperature for each used power and duty cycle

Duty cycle	Sample temperature [°C]			
	100 W	200 W	300 W	400 W
Continual regime	120	150	180	200
75% pulse	100	130	140	150
50% pulse	90	100	115	130
25% pulse	60	70	100	110

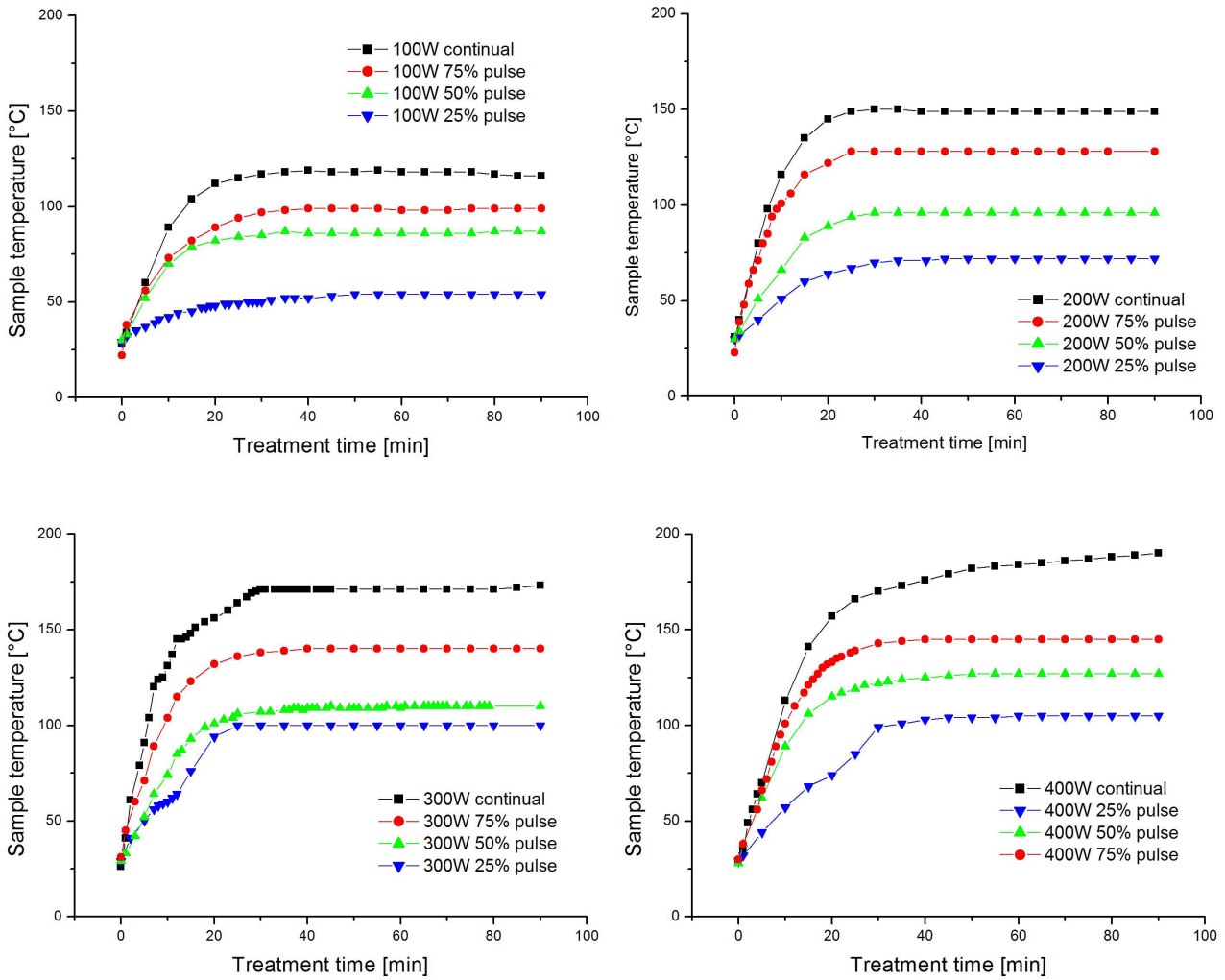


Figure 3: Sample temperature during the plasma treatment at different conditions

Measured temperatures of samples are presented in Figure 3. The sample temperature slowly increased until its stabilization. The temperature of the sample depended on the duty cycle, and it increased with increasing applied power. Further, it was higher in the continual regime than in the pulsed regime (Table 1). Sample temperature is not such high in the pulsed regime as in the continual regime because the sample was exposed to the lower plasma operation in the pulsed regime than in the continual regime.

4 Conclusion

We proved that the corroded sample became less warm in the pulsed regime than in the continual regime of the treatment in the RF low-pressure hydrogen plasma. Thus, there is no risk of metallographic changes or damage of the sample in the pulsed regime.

5 Acknowledgements

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

6 References

- [1] M.J. de Graaf, R.J. Severens, L.J. van IJendoorn, F. Munnik, H.J.M. Meijers, H. Kars, M.C.M. van de Sanden, D.C. Shram, *Surface and Coatings Technology*, 74-75 (1995) 351
- [2] S. Veprek, J. Patscheider, J. Elmer, *Plasma Chem. Plasma Process.* **5** (1985) 201
- [3] S. Veprek, J. Elmer, Ch. Eckmann, M. Jurcik-Rajman, *J. Electrochem. Soc.* **134** (1987) 2398
- [4] K. Schmidt-Ott, *Proceedings Archaeological Iron Conservation Colloquium* (2010)
- [5] M. Klima, L. Zajickova, J. Janca, *Zeitschrift für Schweizerische Archäologie und Kunstgeschichte* **54** (1997) 29
- [6] Z. Raskova, F. Krcma, M. Klima, J. Kousal, *Czech. J. Phys.* **52** (2002) D927.
- [7] V. Sázkavská, L. Řádková, F. Krčma, M. Zmrzlý, R. Příklad, M. Zahoran., *Proceedings of 18th Symposium on Application of Plasma Processes*, 266-271 (2011)
- [8] V. Sazavská, F. Krcma, T. Simsova, N. Zemanek, *Journal of Physics: Conference Series* **207**, Article No. 012011, 4 pages (2010), ISSN: 1742-6596