

Zeitschrift: Zeitschrift für schweizerische Archäologie und Kunstgeschichte =
Revue suisse d'art et d'archéologie = Rivista svizzera d'arte e
d'archeologia = Journal of Swiss archeology and art history

Herausgeber: Schweizerisches Nationalmuseum

Band: 54 (1997)

Heft: 1: Unser Umgang mit dem Kulturgut : Gegenwart und Zukunft ;
Conservation of metal objects in low-pressure hydrogen plasma = Die
Niederdruck-Wasserstoffplasma-Methode zur Konservierung von
Metallobjekten : Möglichkeiten ihrer Anwendung und Verbesserung

Artikel: The perspectives of plasmachemical treatment on ancient artifacts

Autor: Klíma, Miloš / Zajíková, Lenka / Jana, Jan

DOI: <https://doi.org/10.5169/seals-169507>

Nutzungsbedingungen

Die ETH-Bibliothek ist die Anbieterin der digitalisierten Zeitschriften auf E-Periodica. Sie besitzt keine Urheberrechte an den Zeitschriften und ist nicht verantwortlich für deren Inhalte. Die Rechte liegen in der Regel bei den Herausgebern beziehungsweise den externen Rechteinhabern. Das Veröffentlichen von Bildern in Print- und Online-Publikationen sowie auf Social Media-Kanälen oder Webseiten ist nur mit vorheriger Genehmigung der Rechteinhaber erlaubt. [Mehr erfahren](#)

Conditions d'utilisation

L'ETH Library est le fournisseur des revues numérisées. Elle ne détient aucun droit d'auteur sur les revues et n'est pas responsable de leur contenu. En règle générale, les droits sont détenus par les éditeurs ou les détenteurs de droits externes. La reproduction d'images dans des publications imprimées ou en ligne ainsi que sur des canaux de médias sociaux ou des sites web n'est autorisée qu'avec l'accord préalable des détenteurs des droits. [En savoir plus](#)

Terms of use

The ETH Library is the provider of the digitised journals. It does not own any copyrights to the journals and is not responsible for their content. The rights usually lie with the publishers or the external rights holders. Publishing images in print and online publications, as well as on social media channels or websites, is only permitted with the prior consent of the rights holders. [Find out more](#)

Download PDF: 31.07.2025

ETH-Bibliothek Zürich, E-Periodica, <https://www.e-periodica.ch>

The Perspectives of Plasmachemical Treatment on Ancient Artifacts

by MILOŠ KLÍMA, LENKA ZAJÍČKOVÁ, JAN JANČA and coworkers

Abstract

In this paper some perspective technologies concerning the plasma treatment of ancient artefacts are briefly described. One of them is the treatment by a radio plasma jet (RPJ) or a *supersonic* RPJ. The RPJ reactor operates with a nozzle connected to the radio-frequency (rf) power that is flowed through by gas. The advantages of RPJ are local treatment, accelerate surface modification and the possibility to ignite the RPJ at atmospheric pressure. We presented also a new plasma method consisting in plasma-treatment of objects immersed in solution. Phenomena arising from the interaction between the RPJ and the liquid state make the application useful for archaeological glasses, metals and even tissues. In the second part of the paper the problems of a brocade regeneration and conservation is described using a plasma treatment by low pressure rf discharges with hydrogen or hydrogen-argon (H_2/Ar) mixtures. The artifact under treatment was immersed in a solution of Complexon III (Ethylene Diamine Tetra Acetate = EDTA). We have suggested new procedures for the brocade regeneration expecting to achieve better results.

Introduction

In museum collections there is a huge amount of historical objects consisting of different materials (*composites*). The combination of inseparable materials in the same object requires special conservation technologies. With the method described each particular material is treated individually in regard to the basic requirements of conservation technologies. Our present research investigates local surface plasmachemical treatments of historical composite objects.

Summary of the plasma methods

We study perspective plasmachemical technology providing local treatment with radio plasma jet (RPJ)^{1, 2}. The radio plasma jet operates with a nozzle connected to the rf power that is flowed through by gas. The rf discharge is ignited inside the nozzle electrode. The excited and ionized gas flows through the nozzle and creates a plasma channel. A supersonic plasma jet is achieved by a suitable pressure

difference. The interaction between the active plasma channel and the object surface is used for film deposition or surface etching. The working conditions of the supersonic RPJ were as follows:

reactor pressure:	1–300 Torr (mmHg)
flow rate of the gases:	10–103 sccm (standard cubic centimeter per minute) in respect to the nozzle diameter (0.2–5 mm)
rf frequency:	13.56 MHz (Megahertz)
rf power:	25–500 W (Watt)

RPJ could be ignited in the air atmosphere with some special types of nozzles, e.g. with a hollow hypodermic needle or with a rf gliding arc².

The advantage of RPJ, compared to other methods, consists in an accelerate modification of small surfaces or localised cavities. The minimum surface areas for a treatment is about 1 mm² without the necessity to use a second electrode (single pole discharge). Choosing the area and the intensity of the treatment, RPJ allows plasmachemical conservation of historical composites (artefact made of different materials, e.g. metals, glasses, ceramics). Using the RPJ discharge we considered also:

- 1 the combination of different plasma jets and the combination of RPJ with other discharge types³,
- 2 the development of suitable jets working at atmospheric pressure (plasma pencil)^{2, 3},
- 3 the study of the system plasma in solution^{2, 3}.

The corona discharge, the barrier discharge and the gliding glow discharge can be used for local surface treatment. These kind of discharges provide non-destructive low temperature applications at atmospheric or lower pressure. Our investigation on these types of discharge focused toward the treatments of textiles, glass corrosion films and paintings on this material.

The low pressure rf discharge being successfully applied to the reduction of metal can be used for the low temperature plasma chemical vapour deposition of the protective conservation films of SiO_x (Silicium-Oxides), Si_xN_y, (Silicium-Nitride), PTFE (polytetrafluorethylene) etc., as well as for plasma etching. This technology is useful for a variety of materials and can be carried out on the whole object surface. The application of the reduction of corrosion com-

pounds on historical metal artefacts is sufficiently known and discussed in detail in many publications⁴⁻⁶. With direct monitoring of the undergoing processes and the help of various diagnostic methods we expect further development of the low pressure discharge method.

order to remove corrosion compounds from former plasmachemical reactions⁷. We study also phenomena arising from interaction between RPJ, supersonic RPJ and solution for the application on archaeological and historical glass, metals, and tissues^{2,3} (Fig. 1a, 1b).

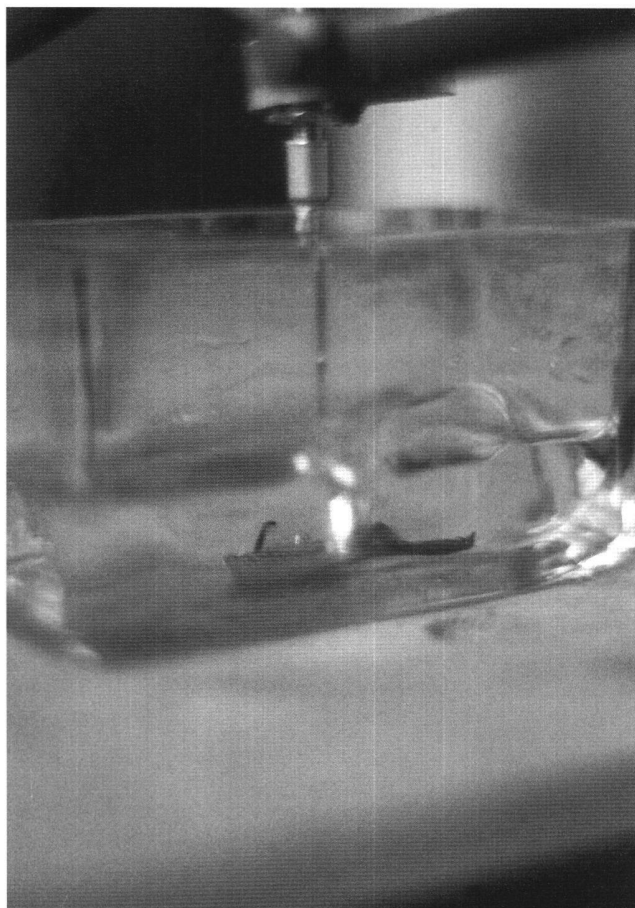


Fig. 1 Plasma pencil – RPJ in combination with 1% solution of Complexon III for applications on

a) historical glass (used gasses were argon, nitrogen, C_5F_8 , mixture of argon and SF_6)

b) bronze object (used gasses were argon, mixture of argon and hydrogen).

Parts of the objects, such as degraded textile, paper, glasses etc., which are sensitive to the plasma exposure (heating, ion bombardment, ultra-violet radiation) can be treated in an afterglow plasma being less aggressive due to active reactants situated between the electrode and the object, reducing the bombardment of the surface.

Taking in account the physical and chemical properties of the plasma in a liquid system a new and successful application was introduced. The selectivity of homogeneous and heterogeneous reactions in solution, activated by low pressure plasma, can be easily regulated. The treatment in solution can be useful for textile regeneration and also for cleaning of surfaces as part of a technological treatment in

Problems of a brocade regeneration and conservation

The plasmachemical treatment of historical composite objects is demonstrated on a piece of cloth consisting of plant material lining and a facial brocade tissue⁶. The treatment by low pressure high frequency discharge in hydrogen or hydrogen-argon mixture was used for the regeneration of the metal threads of silver and various silver-gold alloys. The parameter setting was a power of 100W, a rf frequency of 13.56 MHz and a pressure from 80 to 150 Torr using the same plasma reactor as in the previous examples. The temperature was measured by a mercury thermometer placed on a glass rail. High efficiency of the plasma treatment was

obtained in a temperature range between 95 and 105 °C (Fig. 2). The content of corrosive chlorine and sulphur compounds in the metal threads was reduced to less than 5% and 0.7% respectively. However rests of changed minerals remaining on the metal thread surfaces were identified by electron microscopy. The spots detected, we assume, will be the nuclei of the rapid post-corrosion. Therefore we applied a 2% solution of "Complexon III" to our cloth treatment in agreement with our previous experience from plasmachemical conservation of archaeological silver⁵. In respect to the processes of plasma applied in solution we propose further research on

- 1 adequate steps of plasma-chemical treatments in washing baths,
- 2 further application of the "plasma-liquid" system.

In our recent research on the conservation of a brocade by means of plasmachemical treatment we neglected in a first approach the possible degradation influences on the object. Colour and stability of organic material as well as of the metal threads may change with the duration and intensity of the exposure; high temperature, humidity, ultra-violet radiation, active plasma particles etc. may lead to irreversible changes.

Conclusion

In our paper we have summarized the plasma methods used in our laboratory with respect to the applications on regeneration and conservation of historical and ancient

artifacts. We have introduced new possibilities of plasma applications covering the regeneration of the objects of different materials. Our preliminary results need further investigation.

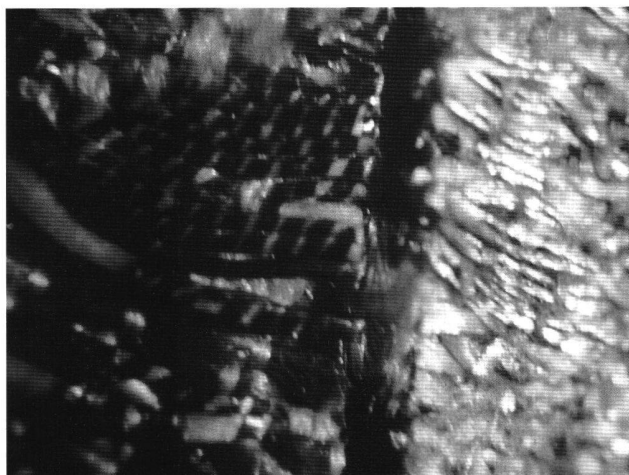


Fig. 2 Brocade plasmachemical regeneration – comparison of metal threads before and after plasmachemical reduction.

Acknowledgement

The present work is supported by the Grant Agency of the Czech Republic, contract 202/94/0490 (PACS 52.80-s).

REFERENCES

- ¹ M. TICHÝ / M. ŠÍCHA / L. BÁRDOŠ / L. SOUKUP / L. JASTRABÍK / K. KAPOUN / J. TOUŠ / Z. MAZANEC / R. J. SOUKUP, *A Study of the Gas Flow in the RF Low-Pressure Supersonic Jet Plasma Chemical System*, in: *Contrib. Plasma Phys.* 34, 1994, p. 765.
- ² MILOŠ KLÍMA / JAN JANČA ET AL., *Perspektivy plazmochemie při aplikaci na historické předměty z různých materiálů*, in: *Proceedings of Seminar in Prag 1996*, Technical Museum Brno, in press.
- ³ MILOŠ KLÍMA / P. SULOVSKÝ, *Corrosion of ancient glasses and their conservation by plasma-treatment*, in: *Proceedings of ENVIWEATH 96*, Brno, Masaryk University Brno, in press.
- ⁴ STANISLAV VEPŘEK / CHRISTIAN ECKMANN / JÖRG TH. ELMER, *Recent Progress in the Restoration of Archaeological Metallic Artifacts by Means of Low-Pressure Plasma Treatment*, in: *Plasma Chem. and Plasma Processing* 8(4), 1988, p. 455.
- ⁵ MILOŠ KLÍMA / M. PTÁČKOVÁ / M. SOUDNÝ / V. RUSNÁK, *Studie stříbrného pražského groše z Královéhradeckého nálezu r.1991 z hlediska konzervačních metod*, in: *Proceedings of Seminar in Luhačovice 1994*, Technical Museum Brno, 1995, p. 81.
- ⁶ MILOŠ KLÍMA / JAN JANČA / ZDENA KUŽELOVÁ / J. MILITKY / V. KOVAČIČ / A. KAŠPAROVÁ / P. SULOVSKÝ, *Nový způsob ošetřování brokátu plazmochemickou metodou*, *Proceedings of Seminar in Olomouc 1995*, Technical Museum Brno, 1996, p. 62.
- ⁷ A. I. MAXIMOV / S. M. KUZMIN, *Some possibilities of the plasma activation of the solution processes*, *Proceedings of International Symposium on High Pressure Low Temperature Plasma Chemistry – HAKONE (Milovy 1996)*, Masaryk University Brno, 1996, p. 282.