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The Perspectives of Plasmachemical Treatment on Ancient Artifacts

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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 *r*adio *p*lasma *j*et (RPJ) or a *supersonic* RPJ. The RPJ reactor operates with a nozzle connected to the *r*adio-*f*requency (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 arc[2].

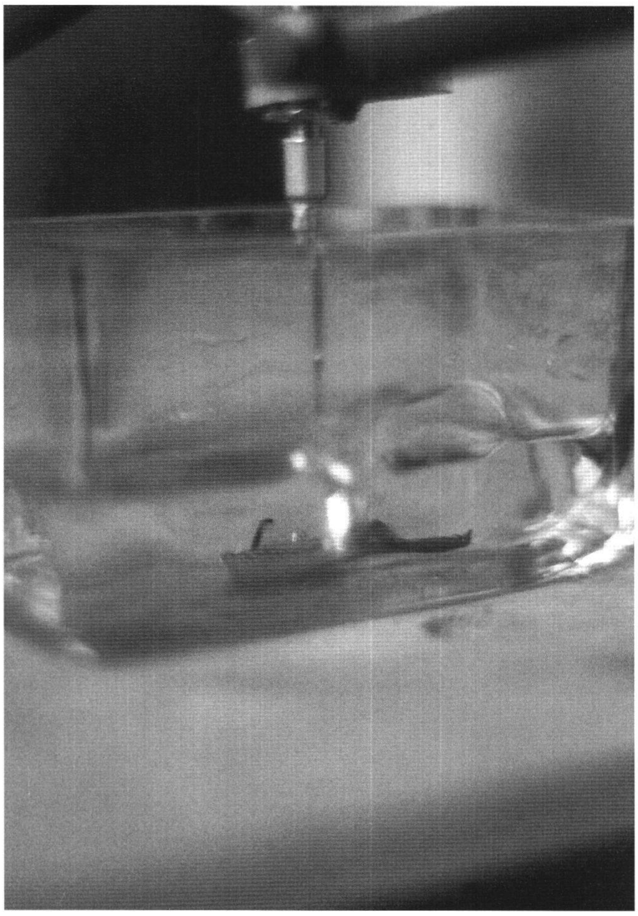
The advantage of RPJ, compared to other methods, consists in an accelerate modification of small surfaces or localised cavities. The minimum surface areas for a treatment is about 1 mm^2 without the necessity to use a second electrode (single pole discharge). Choosing the area and the intensity of the 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 types[3],
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 (polytetrafluoretylene) 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 compounds on historical metal artefacts is sufficiently known and discussed in detail in many publications[4–6]. 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 reactions[7]. 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).



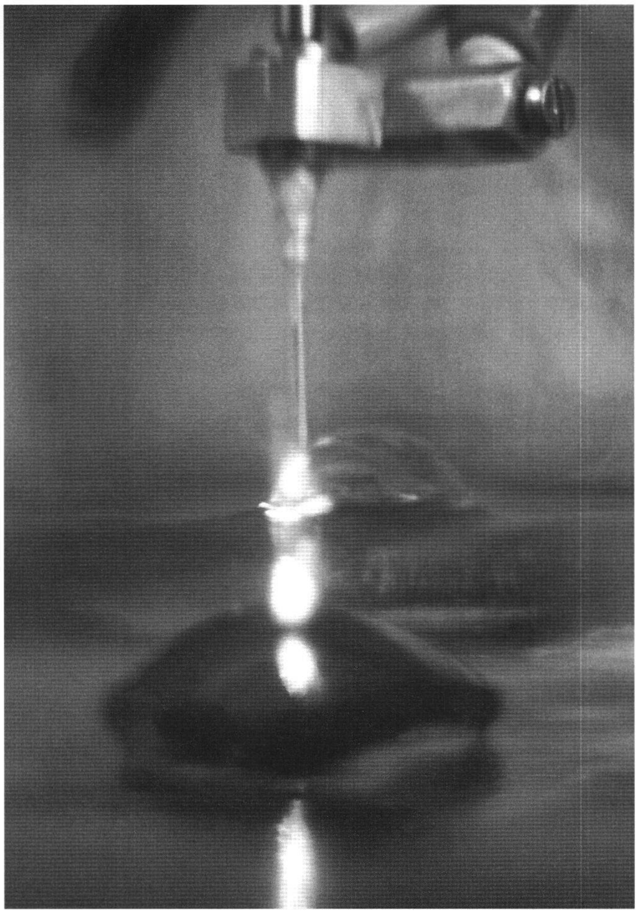


Fig. 1 Plasma pencil – RPJ in combination with 1% solution of Complexon III for applications on

a) historical glass (used gasses were argon, nitrogen, C_3F_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 tissue[6]. 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 silver[5]. 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.

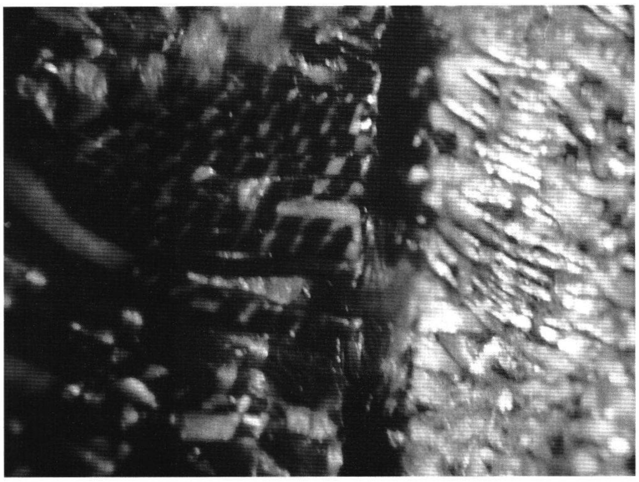


Fig. 2 Brocade plasmachemical regeneration – comparison of metal threads before and after plasmachemical reduction.

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