Chaotic behavior of plasma surface interaction. A table of plasma treatment parameters useful to the restoration of metallic archaeological objects.

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Abstract: In Plasma Physics laboratory of NCSR "Demokritos" the plasma chemistry method has been used for the restoration and conservation of metallic archaeological objects during the last decades. The obtained experience had led us to conclude that plasma parameters and different status of treated objects are so specific, so as to become unique. In the present paper the theoretical and experimental results of our laboratory are summarized. A treatment table of plasma parameters is given, which claims to be useful for the conservators. It is obvious that this treatment table needs to be completed and extended, so that it meets the uniqueness of each artifact. A theoretical study and the treatment of a variety of iron objects are presented.

Keywords: plasma sheath potential, plasma restoration, corrosion, external potential, plasma parameters

1. Introduction

Three decades have passed since Daniels and coworkers used for first time the mechanical and chemical action of the plasma [1] to reduce the tarnish of silver on daguerreotypes. During the 80's, Veprek and coworkers systematized the plasma cleaning and restoring method [2-4], by creating the homonymous plasma reactor, where a low-pressure hydrogen plasma acts upon the artifacts. These procedures were very soon adopted by the Plasma Laboratory of NCSR "Demokritos" due to the many archaeological artifacts, which are found at the Hellenic area. The plasma treatment processes are usually preferred, for the following reasons: the plasma temperature is low and consequently, the destruction risk of artifacts is avoided; the chemical reactions produce steady compounds on the objects (e.g. magnetite for iron objects), which consist the restorating behavior of plasma; finally, the plasma reactor volume allows the simultaneously treatment of many objects.

Many experiments and studies have been carried out [5, 6], at the two plasma reactors of "Demokritos" since the early 90's. Recently, the utilization of an external d.c. electric current on the treated objects have showed very good results [7, 8].

The whole previous meditation leads to the conclusion that plasma cleaning proceedings are chaotic due to multi-parametric behavior of plasma and the complicated corrosion of metallic objects. Thus, the factors which affect the cleaning and restoring can be listed as below.

- The plasma production way, the nature of plasma gas, accompanied with its parameters (plasma density, temperature, pressure ect).
- The kind of metal, and its metallurgy.
- The type of corossion and the corossion rate which are depended on the burial environment of the objects an on the time of their burial.

Consequently, the treatment of every object becomes unique, as the whole method is multiparametric- chaotic.

The purpose of the present paper is to classify the previous results, to add new ones from Plasma Laboratory of "Demokritos" and to draw up a table of treatment methods useful to the restorators.

The paper is organized as following: the new experimental studies are presented in Sec.2; the precedent results, many of which were studied in our laboratory [5-8], are briefly described in Sec. 3 and in Sec.4 treatment tables are given. Finally, in Sec.5 the main results are summarised and concluded.

2. New experimental results

Beyond the previous work, which has been done in the Plasma Laboratory of "Demokritos" during the last five years, the plasma treatment was extended by the enforcement of the d.c potential on restorated objects. In this way, a d.c current passes both through objects and plasma, and proves that the Langmuir probe theory which basically is valid**,** must be modificated.

It is known that the rf plasma production method gives to the electrons much more acceleration than the ions because of the very small electron mass. Furthermore, the electron energy loss by the collisions with ions or neutrals, is negligible due to the small value of the ratio m_e/m_i . In this way, the electron temperature increases considerably (10.000-100.000 K°), while the ion and neutral temperature remains at low levels (about 500 K° for ions and 300 K° for neutrals). Consequently, plasma is not in thermodynamic equilibrium, while the high electron temperature makes plasma more effective for the oxide reduction.

When none external potential is imposed on the treated objects, the plasma sheath theory is valid as it was proved in an extented previous work which was carried out at "Demokritos" Laboratory [7,8]. However, if an external d.c. potential is enforced on the objects, as in our experiment, the Langmuir probe theory is valid with the presupposition that the following thoughts are taken into consideration.

Firstly, when a voltage is applied on the treated object with reference to the earth, the simple probe with very large surface is formed. From plasma sheath theory [7, 8] is known that the ion current density to the object surface, is

$$j_i = n_0 . e . c_s \qquad (1)$$

with n_0 the plasma number density and c_s is the ion sound speed.
It is possible to approach,

$$c_s^2 \cong \frac{T_e + T_i}{m_i} \cong \frac{T_e}{m_i} \cong \upsilon_0^2$$

where υ_0 is the ion velocity at the sheath edge.
Similarly, the electron current density to the object surface, is $j_e = -\frac{1}{4} \cdot n_e \cdot e \cdot \bar{c}_e$. Taking into consideration that $n_e = n_0 \cdot e^{\frac{e\phi(x)}{T_e}}$ and $\bar{c}_e{}^2 = \frac{8T_e}{\pi m_e}$, the electron current density is

$$j_e = -\frac{1}{4} \cdot n_0 \cdot e \cdot \left(\frac{8T_e}{\pi m_e}\right)^{1/2} \cdot e^{\frac{e\phi(x)}{T_e}} \qquad (2)$$

The current I to the object (probe) is $I = (j_i + j_e) \cdot S$ where S is the projected surface area into the plasma.
By substitution of ion and electron current density from (1) and (2), the current I which is biased to voltage V is

$$I = j_i \left(1 - e^{\frac{e(V - V_f)}{T_e}}\right) \cdot S \qquad (3)$$

V_f is the floating potential, which is equal to the external enforcemed potential, so that the current I vanishes. Since the object (probe) dimensions are large compared to the ion and electron gyro-radii and the Debye length, the area S is determined as following: $S = \frac{1}{B} \cdot \int \vec{B} \cdot d\vec{S}$.

When the probe is biased negatively enough, all ellectrons are repulsed while what remains is the ion current. This current is not affected by the voltage and is known as ion saturation current. The ion current is saturated because the bias potential gathers all ions across the surface sheath and the ion flux is determined by the flux of ions which enter into the sheath at the ion sound velocity. When the probe potential becomes larger than the plasma potential, there is no sheath and the electrons strike on the object surface with the thermal distribution of velocities. In this case the electron current is saturated by value $I_{es} = \frac{1}{4} n_0 e \bar{c}_e \cdot S$, with $\bar{c}_e$ the electron thermal velocity.

Figure 1 shows the typical probe characteristic (I versus V), which presents three regions: the ion current saturation, the exponential electron distribution and the electron current saturation.

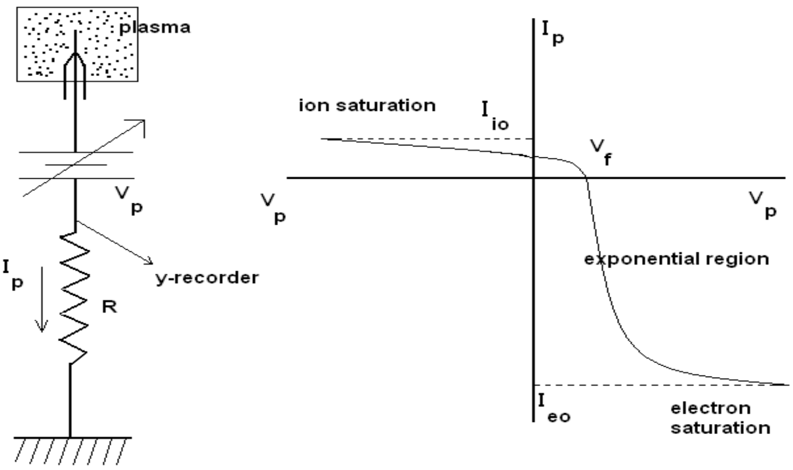

Figure 1. The Langmuir probe and its characteristic.

If plasma is non-magnetized (as the plasma we use to treat corroded objects), it follows the above simple theory; the characteristic $I-V$ draws the two saturation regions with the ratio of electron to ion saturation current is equal to ratio of electron thermal velocity to ion sound speed.

However, in our experiment the probe's metallic surface into the plasma has been replaced with the treated objects , which have much more area than the probe's one. In spite of this big difference the Langmuir probe theory is valid in a very satisfactory way, and the measurements give currents proportional to the object area. Figure 2 whows the d.c. current, which passes through the objects and the plasma.

As Figure 2 shows, a big ohmic resistance R is necessarely lined at the circuit to reduce the current I , which is measured on the value of some Amperes. The negatively charged object (cathode) attracts plasma ions, which strike on the surface with increased velocity; then, while the ions take free electrons from the cathode, reductive reactions take place as following:

$$3Fe_2O_3 + 2H^+ \Rightarrow 2Fe_3O_4 + H_2O$$

or $$Fe_2O_3 + 2H^+ \Rightarrow 2FeO + H_2O$$

On the contrary, the positively charged object (anode) attracts the plasma electrons, which strike on the surface and reduce the oxides as the reactions show:

$$6Fe_2O_3 + 4e- \Rightarrow 4Fe_3O_4 + O_2$$

or $Fe_2O_3 + 2e- \Rightarrow 2FeO + \frac{1}{2}O_2$

From the above chemical reactions it is obvious that the external d.c. potential makes the plasma much more active and reduce the object oxides to more stable compounds (magnetite) as the XRD examination can confirm.

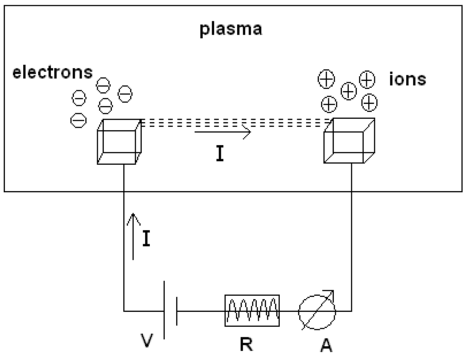

Figure 2. The external dc potential circuit during plasma treatment.

3. Previous results

Many inferences have been taked out from the early experimental work in our laboratory, as the plasma cleaning method is in operation during the last two decades. An excavated nail fron the Holy Monastery of Simonopetra of Mount Athos before and after plasma treatment is shown in Photo 1.

Photo 1. An excavated nail before and after plasma treatment.

The factors and parameters, which affect the plasma cleaning, are too many and as a redult, it is impossible to mention them without the risk of forgetting one. The present work has the ambition to start the drawing of some treatment tables in order to achieve the classification of the chaotic state. Firstly, the kind of the material used e.g. iron, copper, silver e.t.c are presented; secondly, the corrosion depth, which is separated in three sizes for practical reason: lightly corroded, moderately corroded and heavy corroded; the corrosion depth depends on the time and the environment where the object is being corroded. Another parameter, which strongly affects the cleaning, is the plasma gas; gases such as H_2, N_2, CH_4 as combinations of various gases were used, except for N_2 and CH_4 due to identification of CN^- on the pyrex surface. Along with the plasma gas, the other plasma parameters, as plasma pressure, the plasma density, the rf absorbed power and the ion temperature, are listed. Consequently, the treatment time is a remarkable factor; practically, three period of treatment times were used, periods of 10hours, 10-20hours and a period that exceed 20 hours of treatment.

4. Summation-Elaboration Tables

The factors and parameters, which were mentioned in Sec.3 have been tabulated on cleaning Tables I, II and III.

Table I. Plasma treatment table for iron objects

	Iron objects		
	Light corroded	Medium corroded	Heavy corroded
Gas	H_2	H_2	H_2
Pressure (Torr)	0.8	0.9	0.7
Power (kW)	0.7	1 to 1.2	0.7
Time	8h-10h	10h-20h	more than 20h
Temperature	200˚C to 300˚C	250˚C to 350˚C	200˚C
Gas	H_2, N_2	H_2, N_2	H_2, N_2
Pressure (Torr)	0.4, 0.2	0.8, 0.4	0.4, 0.2
Power (kW)	0.8	1.1 to 1.2	0.7
Time	8h-10h	10h-20h	more than 20h
Temperature	200˚C to 300˚C	250˚C to 350˚C	200˚C
Gas	N_2	N_2	N_2
Pressure (Torr)	0.7	0.9	0.5
Power (kW)	0.8	1.0	0.5
Time	more than 20h	10h-20h	more than 20h

Temperature	200˚C to 300˚C	250˚C to 350˚C	200˚C

Table II. Plasma treatment table for bronze objects

	Bronze objects		
	Light corroded	Medium corroded	Heavy corroded
Gas	H_2	H_2	H_2
Pressure (Torr)	0.8	1.2	
Power (kW)	0.65	1.0	
Time	4h-6h	2h-4h	
Temperature	170˚C-190˚C	230˚C-240˚C	

Table III. Plasma treatment table for silver objects

	Silver objects		
	Light corroded	Medium corroded	Heavy corroded
Gas	H_2	H_2	H_2
Pressure (Torr)	0.8	0.8	0.8
Power (kW)	0.7	0.7	0.7
Time	2h-4h	6h-8h	10h-12h
Temperature	210˚C	210˚C	210˚C

It is obvious, that the above tables need to be expanded not only for other kinds of materials but also by taking into account other parameters which were mentioned in section 1, so that a useful plasma treatment manual for restorators will be completed.

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