

# Mechanical and chemical results in plasma-surface contact a study of sheath parameters

## Abstract

Many works have been carried out on the plasma behavior in touch with a solid surface; when the surface material consists of chemical compounds (e.g. oxides of metals), then the plasma chemistry takes place. The present paper contains the final work of Plasma Laboratory at "Demokritos", which consists of an elaboration of plasma sheath parameters adapted to experimental conditions, a suitable choice of plasma gases (either  $H_2$  or  $N_2$ ), and an electric potential current enforcement on objects. Additionally, a brief theory is given to explain the results, with a short reference to both boundary phenomena in thermonuclear reactors and low pressure plasma of glow discharges, so that to reveal the similarities and differences of those two cases. An extensive examination of the treated objects by XRD method gives results, in agreement with theoretical predictions. Using this improvement on plasma restoration system, (a combination of electric current on metallic object into suitable plasma), it is shown that we have better results on the cleaning and conservation of archaeological objects.

**Keywords:** impurities, plasma sheath parameters, reduction of surfaces, external potential, influence on treatment rate

Volume 2 Issue 1 - 2018

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**Received:** November 22, 2017 | **Published:** January 12, 2018

## Introduction

Plasma always comes in touch with solid surfaces, whatever the way it might be restrained. These surfaces could be:

- The vessel that contains plasma
- The device that produces it
- The devices of measurement that is located into plasma.

As plasma is always in an unstable state, many interactions between plasma and surfaces are created. If the material of the surfaces is simple (made of pure metal), then the interactions are caused by mechanical procedures, whereas if it is covered with chemical compounds (oxides of metals), then the interactions are caused by chemical reactions. These interactions often corrode the surfaces, and sometimes they embody material to them. These procedures sometimes are harmful and consequently avoided, and sometimes are beneficial and consequently wanted. So, to the first category belongs the case when impurities are created into plasma<sup>1</sup> by the corrosion of the surface material, which cause energy radiation and, as a result, the plasma is sometimes interrupted. The application of plasma in cleaning (corrosion) and conservation (embodiment) of archaeological objects belongs to the second category.<sup>2</sup> Since the 1980s many extensive studies, about the interaction of plasma with a surface with which it is in touch, have been carried out,<sup>1-7</sup> even though the negative role of impurities into plasma has been known much sooner. A very large literature is concerned with the plasma sheath.<sup>2,4,8</sup> A lot of information on basic processes of recycling is given in the references.<sup>6,7,9</sup> The subject of sputtering has a large literature too; a series of volumes (Behrisch R, Sputtering by particle bombardment, Springer-Verlag, Berlin, Vol I, 1981, Vol II, 1983, Vol III, 1991) covers the issue in a satisfactory way. Furthermore, an extensive study has been carried out about the arcing, evaporation and atomic and molecular processes,<sup>2,3,10,11</sup> as these consist the plasma-surface interaction basic procedures.

The above physical and chemical mechanisms, with which the plasma acts upon a tangent surface, have the beneficial side, the cleaning and conservation of ancient artifacts. For the first time Daniels and co-workers<sup>12,13</sup> used plasma for the reduction of silver tarnish on daguerreotypes. A further development and improvement was expected during the following years; Veprek and co-workers<sup>14-17</sup> have used an rf produced plasma on cleaning metallic objects; the gases  $H_2$ ,  $N_2$ ,  $CH_4$ , Ar are used for plasma production. The cleaning elaboration with low-pressure plasma is based on intense chemical action of plasma, which reduces the oxidized metals at low temperature beyond the destruction risk. The plasma activity is obviously caused by the plasma ions, which are formed by the ionization of neutral atoms or molecules; the free reduction energy diagrams of ion oxides show that the atomic H is more drastic than the molecular  $H_2$ .

In Plasma Laboratory of "Demokritos" a program similar to the programs above runs with great success during the last two decades.<sup>7,18</sup> Two plasma reactors with different dimensions operate,<sup>19</sup> on which we have applied our conceptions, which are basically the enforcement of a d.c potential on the metallic object itself, or on a suitable metallic basis for non conductive artifacts; sometimes the external potential is placed so that it floats (floating), and other times it gives electric current with a circuit. A detailed elaboration of potential sheath parameters, after having adapted it to our conditions, and a proper choice of plasma production gases, is the main purpose of the present work; furthermore, by using the XRD diagnostic method on a large number of excavated and artificially pre-corroded metallic objects, we attempt to understand and interpret the experimental data in agreement with theory, by providing the appropriate chemical reactions.

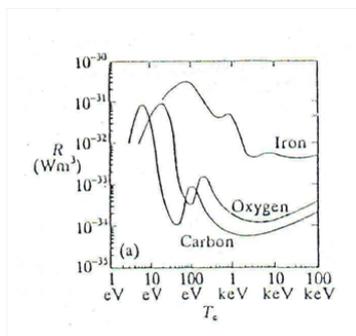
A brief outline of the paper is the following: the mechanisms of plasma impurities are analyzed in Section 2. The sheath potential parameters are briefly elaborated and presented in Section 3. The treatment (cleaning-restoration) device is described in Section 4. Consequently, the preparation of the samples and the experimental results are given in Section 5. Finally, the findings are discussed and conclusions are carried out in Section 6.

## Plasma impurities

Impurities arise from the tangent solid surfaces and, through transport processes, can get into the interior of the plasma. The presence of impurities there can enhance radiation losses and disperse the ions in the reacting plasma, which both result in making difficult the thermonuclear fusion process.<sup>3</sup> Two causes are involved in radiation losses; the first is the enhancement of bremsstrahlung due to the higher value of the ionic charge for impurities. The second is the radiation, which occurs through the atomic processes of line radiation and recombination. If the transport effects are negligible, then in the steady state, a given impurity species radiates power, which is proportional to the electron density  $n_e$  and to the impurity density  $P_R$ ; if  $P_R$  is the radiated power density we have,

$$P_R = n_e \cdot n_i \cdot R$$

$R$ , the radiation parameter, is affected from the temperature of electrons. In Figure 1 the change of  $R$  versus the electron temperature  $T_e$ , for three elements appears.<sup>3</sup>



**Figure 1** Radiation parameter  $T_e$  vs the temperature of electrons  $T_e$ .

The bigger maximum appears at low temperatures, which is something that explains the big energy radiation of impurities when the plasma starts-up. Another smaller maximum appears at higher temperatures. Generally but more evidently for light impurities the principal maximum appears at a low temperature, whereas for higher temperatures the radiation is greatly reduced. This occurs because at high temperature, electrons are successfully released from the impurity ions and, when the ions are completely stripped, only bremsstrahlung radiation operates. Consequently, a brief description of mechanisms, which produce impurities from surfaces' material, is given. In fact, it is possible for the surface material to be introduced into plasma with processes such as sputtering, arcing and evaporation.

## Sputtering

Sputtering is the transfer of momentum from the rapidly moving ions, either hydrogen or impurities, which strike on a solid surface, resulting to the release of atoms. It is possible that sputtering occurs from neutral atoms, due to resonant charge exchange between an energetic ion and a cold neutral. This impact by ions or atoms leads to erosion of surfaces, which creates problems in the Tokamak reactor. On the contrary, it is very beneficial in the process of cleaning archaeological artifacts. If a rapidly moving ion or neutral atom strikes on a solid surface, successful collisions among lattice atoms take place. Sputtering occurs when these successful collisions provide one atom of the surface with enough energy to exceed the surface binding energy. Thus, sputtering decreases with increasing sublimation energy of the solid and increases with increasing energy that is transferred from the incident ion to the lattice atom. For light ions, such as hydrogen and helium, the yielded sputter is small due to

low energy transfer, and the energy is dissipated mainly in inelastic processes.

## Arcing

Basically arcing is caused from the sheath potential and can occur between plasma and surfaces. The proper feature of the arc is the material evaporation from the cathode and the following ionization that gives the passing of current. Always an arc starts at a sharp point of surface, where the electric field is intense although the applied potential has the same value everywhere. The initial voltage for arc initiation is enhanced and is very depended on the state of the surface; after the arc has started, the required voltage decreases in the range of 5-10Volts and depends on the electrode material exclusively. As the current flows to the surface, one localized point is heated due to Joule phenomenon, and electrons are produced at the surface due to thermionic emission and field emission. The arc, which is caused from an external potential, is called power arc. If the plasma touches a surface, the plasma sheath potential is created, which can produce a unipolar arc. The sheath potential is in the range of 3 to 5Volts, and the local electron temperature must be only 3-5eV to sustain the arc.

As the arc operates, the sheath potential accelerates the electrons away from the solid surface. Then, the sheath potential is reduced due to current flow, and the electrons move across the sheath with big flow (in the tail of the maxwellian distribution). If we add the electron flow, which approaches, and the other, which is removed to the surface, we have the total electron current,

$$= s \cdot n_e \cdot e \sqrt{\frac{T_e}{2m_e}} \left( e \frac{eV_c}{T_e} - e \frac{eV_s}{T_e} \right)$$

$n_e$  The surface area,  $n_e$  the number electron density,  $V_s$  is the critical potential for the arc to operate, and  $V_c$  is the potential of sheath. If we consider the energy balance between arc energy, and Joule heating and thermal conduction, we are able to determine the current, which is capable of sustaining the arc with value of few Amperes.

The appearance of arcs causes erosion on the surface material. Thus, material pieces leave the surface in the form of neutral atoms, ions, solid and molten drops.

Within a vacuum tube (e.g. diode) the erosion rate of surface by arcing has been measured, for a variety of metals. The conclusion is that the erosion is proportional to the passing charge. Thus, the mass alleviation due to erosion is

$$m_{er} = \lambda \cdot Q$$

Where the erosion rate factor  $\lambda$ , depends only on solid material and is measured in  $Kgr/Cb$ . In Table 1 the erosion rate values for few metals are given.<sup>3</sup> In our experimental device the arcing is considered as the basic mechanism, which affects the treatment rate of archaeological objects. This can be easily understood, as it is briefly stated above, that the enforcement of an external current increases the arcing and consequently, the surfaces erosion-cleaning.

**Table 1** Erosion rate of metals

Metal	Symbol	Erosion rate $x10^{-7} Kgr/Cb$
Carbon	C	0.17
Molybdenum	Mo	0.47

Table continued

Chromium	Cr	0.4
Titanium	Ti	0.52
Tungsten	Tu	0.62
Iron	Fe	0.73
Nickel	Ni	1
Copper	Cu	1.15
Silver	Ag	1.5

### Atomic and molecular processes

Many atomic and molecular reactions occur as the incoming gas touches the plasma. For simplicity, we consider hydrogen as the discharge cleaning gas. In this case the main atomic reactions are the excitation, ionization and charge-exchange (Table 2). It is evident that the main molecular reactions have been previously done, and are tabulated in Table 3. Plasma temperature and density affect very strongly the reaction rate of the processes above. Atomic and molecular processes are indispensable to understand the plasma chemical cleaning, and, although they are not an easy subject, they have been extensively studied today.

**Table 2** Atomic reactions

Reaction	Name
$H+e \Rightarrow H^*+e$	Excitation
$H+e \Rightarrow H^++2e$	Ionization
$H^++H \Rightarrow H+H^+$	Charge Exchange

**Table 3** Main molecular reactions

Reaction	Name
$H_2+e \Rightarrow H+H+e$	Dissociation
$H_2+e \Rightarrow H+H^++2e$	Dissociative Ionization
$H_2+e \Rightarrow H_2^++2e$	Molecular Ionization
$H_2^++e \Rightarrow H+H$	Dissociative Recombination
$H_2^++e \Rightarrow H^++H^++2e$	Dissociative Ionization

### Plasma sheath parameters

The atoms of a neutral gas, which contact an absorbing surface, flow towards the surface with the thermal velocity. Only a numerical factor makes the difference between the thermal velocity and acoustic velocity. When the plasma is in touch with the surface, the flow velocity towards the surface is likely close to the acoustic one, but the understanding of this behavior is more complicated. The electron

thermal velocity is bigger than the ion one, by the square root of the mass ratio.

$$u_{th,e} = \sqrt{\frac{m_i}{m_e}} \cdot u_{th,i} \tag{1}$$

However, due to an electrical field, which is developed into plasma, the electron and ion flux becomes equal by decreasing the electron flux and increasing the ion one. The final flux is defined from electron and ion pressure combination, and is restrained by ion inertia. The initial electric field is located at a narrow sheath in touch with the surface, whose thickness is some Debye lengths. One small electric field, called pre-sheath, extends more deeply into the plasma.

The Poisson equation gives the electrical potential,<sup>2,3,8</sup>

$$\nabla^2 \cdot \varphi = \frac{e}{\epsilon_0} (n_e - n_i) \Rightarrow \frac{d^2 \varphi}{dx^2} = \frac{e}{\epsilon_0} (n_e - n_i) \tag{2}$$

Where  $n_e$  and  $n_i$  are the electron and ion number density respectively.

Considering that  $\varphi=0$  at sheath edge, the electrons distributed by Boltzmann are:

$$n_e = n_0 \cdot e^{-\frac{e\varphi(x)}{T_e}} \tag{3}$$

If we take into consideration the energy balance for ion out and into sheath,

$$\frac{1}{2} m_i u_i^2 = \frac{1}{2} m_i u_0^2 - e\varphi \tag{4}$$

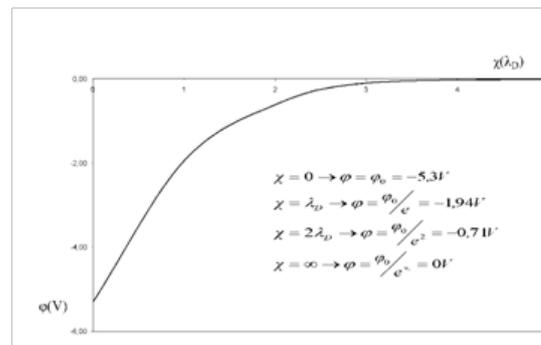
And the ion flux constancy,  $n_i u_i = n_0 u_0$ ,

After suitable elaboration,<sup>6,7</sup> we end with the equation of potential;

$$\varphi = \varphi_0 \cdot e^{-kx} \tag{5}$$

With  $k^2 = \frac{1}{\lambda_D^2} \left( 1 + \frac{T_e/m_i}{u_0^2} \right)$  and  $\varphi_0 = -2.65 \frac{T_e}{e}$

Approximately, it could be taken  $k \cong \frac{1}{\lambda_D}$  and the last is represented graphically by Figure 2.



**Figure 2** Sheath potential dependence from distance x.

From energy balance equation (4), we obtain,

$$u_i = \sqrt{u_0^2 - \frac{2e\varphi}{m_i}}$$

Taking into consideration the equation (5) and the relation  $\varphi_0 = -2.65 \frac{T_e}{e}$ , it results that,

$$u_i = \sqrt{u_0^2 + 5.3 u_0^2 e^{-kx}} \text{ or } \ln n_e = \ln n_0 + \frac{e\varphi(x)}{T_e} \tag{6}$$

Figure 3 shows the dependence of the ion velocity from distance x.

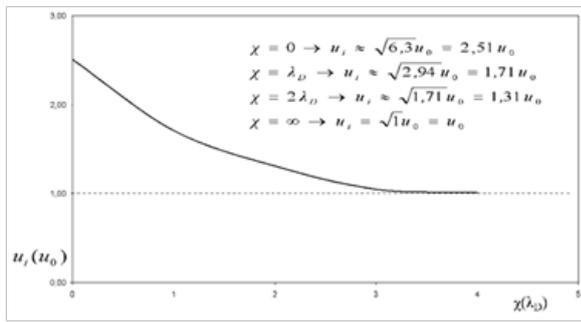


Figure 3 The ion velocity change versus the distance from the surface.

Now, the Boltzmann distribution (3) gives,

$$\ln n_e = \ln n_0 + \frac{e\phi(x)}{T_e} \text{ or}$$

$$\ln \frac{n_e}{n_0} = -2.65 \cdot e^{-kx} \tag{7}$$

Figure 4 represents the dependence of the electron number density from distance x.

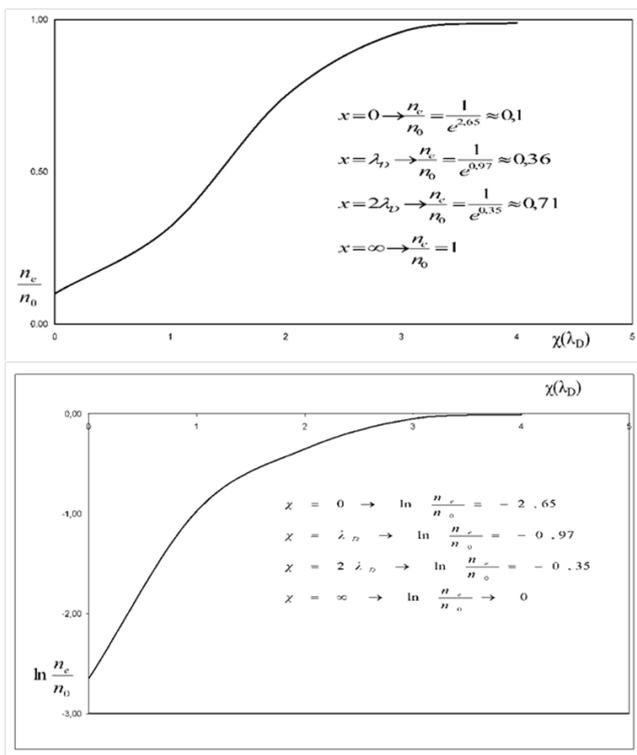


Figure 4 The electron number density versus the distance x.

Finally, the ion flux constancy for into and out of the sheath, by combination with equation (6), gives,

$$n_i = n_0 \cdot \frac{1}{\sqrt{1+5.3e^{-kx}}} \tag{8}$$

Figure 5 shows the ion density charge, as the distance x from the surface increases.

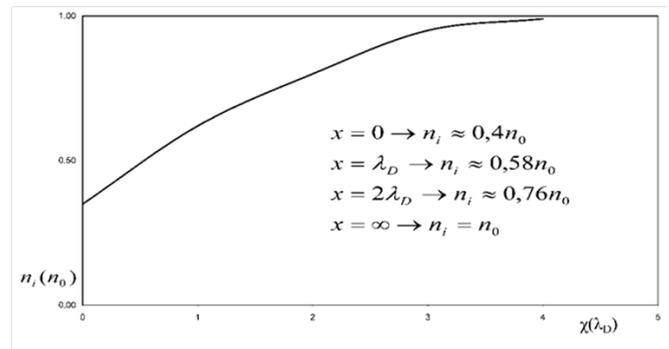


Figure 5 The ion density versus distance x.

Figures 4 & 5 show that on the surface (x=0), as well as at the whole sheath thickness, ion concentration is bigger that the electron one.

### Description of the treatment device

Objects are cleaned by particle bombardment into the plasma discharge. There are various types of cleaning discharge, as glow discharge, pulsed discharge and discharge excited by radiation at the electron cyclotron frequency. The most widely used technique is the glow discharge, due to its effectiveness and simplicity. The dc glow discharge is commonly combined with rf radiation at 10–30MHz. The rf radiation gives sufficient ionization, allowing the glow discharge to be operated at lower pressure (typical value 10Pa), when collisions into the sheath become fewer and ions strike with bigger energy.

At plasma laboratory in the Research Center “Demokritos”, two equivalent systems are installed to the above treatment device (Figure 6).

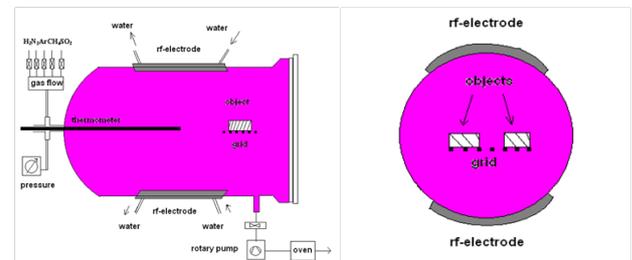


Figure 6 The treatment arrangement.

The bigger one consists of a closed cylindrical tube made of glass (pyrex), in which plasma is produced. The tube has the following geometrical dimensions and characteristics: 100cm length, 50cm diameter, a metallic door which closes air-tightly the tube, through which the objects that are to be cleaned are entered, and the other cylinder end has a suitable sheath for the thermometer to be placed. Another port allows the manometer’s adjustment, while the gases are introduced through a series of flow meters. The pyrex tube is evacuated through a rotary pump.

Three windows (ports) are opened on the cylindrical-curved surface, which allow us to enforce the external potential and enter suitable Langmuir probes for plasma parameters’ measuring.. Two big copper sheets placed opposite to one another on the cylindrical-curved surface, enter the rf power into the cavity; the RF generator operates at 27,12MHz. Due to RF power heating, the electrode system is cooled with a closed water system.

The whole device, which is described above, is isolated into a rectangular aluminum netting (Faraday cage) for the surrounding to be protected from RF radiation. Typical values for plasma parameters are tabulated on Table 4.

**Table 4** Typical plasma parameters

Plasma parameter	Symbol	Typical value
Pressure	p	1 Torr
rf frequency (standard)	f	27,12MHz
rf power	w	1kW
Plasma temperature	T	300°C
Treatment gas		H <sub>2</sub> , N <sub>2</sub>
Plasma density	n <sub>e</sub>	10 <sup>15</sup> m <sup>-3</sup>
Enforced potential	φ	20V

## Experimental results

### Measuring of the bunk plasma parameters ( $T_e, n_e, I-V$ )

A thin Langmuir probe is used for the measuring of plasma parameters; from the probe characteristic ( $I-V$ ) it was calculated that;  $T_e=1,8eV$ ,  $n_e=10^{10}m^{-3}$  and plasma potential  $I-V$ . It is remarkable to comment that we used the object itself for these measuring, taking its characteristic  $I-V$ ; for  $T_e$  the same value (close by  $1,8eV$ ) was found, whereas for  $T_e$  big inclination has appeared. The first result (for  $T_e$ ) indicates that the enforced object may obey to electrical probe theory (big surface probe). It is in agreement with the Langmuir probe relations,  $I_e=I_{eo} \cdot \exp\left(\frac{eV_p}{K_B T_e}\right)$  and  $\ln\left(\frac{I_e}{I_{eo}}\right)=\frac{e}{K_B T_e} V_p$ , where the current ratio is independent from probe surface  $T_e$  (and consequently the  $T_e$  value), whereas the current itself is proportional to  $A$ .

The same must be expected for the plasma density, as the relation  $\frac{n_e=A I_e}{A \cdot \exp\left(\frac{eV_p}{K_B T_e}\right) / z_{m_i} N_i}$  shows independence from surface A. But here we have measured the  $n_o$  value with enough difference at the two cases; explanation may be given if the electron saturation current  $I_{eo}$  is taken into consideration; it is truth that the  $u_i$  experimental measuring is very inaccurate, and in the present study the value from the object characteristic was taken more credible for the following reasons; the object characteristic reaches the saturation more rigorously, and the measuring represents the average density value.

The ion velocity  $u_i$  and the superiority of the ion number density  $n_i$  of plasma, comparing to the electron one  $u_e$ , are among the factors that affect the plasma chemical and mechanical actions on oxidized surfaces. This is obvious from the equations (6), (7) and (8) which are presented graphically by the figures 3, 4, 5. The above occur when the surface is in contact with plasma, without external electric potential enforced on it.

In the present experiment, an additional external D.C. electrical potential is imposed on the treated objects, and a current goes through them. As a result, the above theory must be modified. However, beyond each modification of theory, it is obvious that on the treated object with negative potential, the ion velocity  $u_i$  and the ion number density  $n_i$  are increased. On the contrary, on the objects with positive potential, the same physical quantities are decreased. A direct measurement of these quantities in the narrow limits (boundaries) of the sheath potential is impossible. For this reason, the conclusions will

be studied indirectly, using the effects that took place on the plasma treated objects.

More experimental measurements were also carried out by a variation of the treatment time. The aim is the time influence on the treatment to be studied, because the saturation of phenomena hides the rate of change.

### Preparation of samples

The samples used in this work were selected to be corroded iron objects which had been exposed to the environment for a period of 10 years.

Four types of plasma treatment were applied:

- A reducing plasma treatment of 100% H<sub>2</sub> at a pressure of 1 to 1.2Torr, and at a temperature range of 240°C to 280°C. The purpose of the experiment is to confirm the agreement between results and the theoretical foresights from Section 3.
- A plasma treatment of 100% H<sub>2</sub> at a pressure of 1 to 1.2Torr, and at a temperature range of 240°C to 280°C, while an external D.C. potential was applied to the treated coupons, so that each coupon behaves as the negative and the positive electric pole of a closed d.c. electrical circuit. By this intervention the difference of the results from the theory has been searched.
- A plasma treatment of 100% N<sub>2</sub> at a pressure of 0.50Torr and at a temperature range of 260°C to 300°C. The purpose is now to check the effect of nitrogen plasma on the samples; the purpose is also to show the difference from the hydrogen action, as well as to study the nitriding of objects.
- A plasma treatment of 100% N<sub>2</sub> at a pressure of 0.50Torr and at a temperature range of 260°C to 300°C, while an external D.C. potential was applied to the treated coupons, so that each coupon behaves as the negative and the positive electric pole of a closed D.C. electrical circuit. The aim of this experiment is also the research of the effectiveness of the external potential on cleaning and restoration when the plasma gas is nitrogen.

During each of the above treatment process, the outer oxide layer became more porous and therefore less hard by transformations or transformations and reduction in the case of H<sub>2</sub>. The layer was removed mechanically (by means of a scalpel) until the original surface of the samples was revealed. The identification of crystalline phases within the oxide layer, before and after each stage of treatment of the samples, was followed by means of X-ray diffraction method (XRD). A Siemens model D500 (CuK<sub>α</sub> radiation, 40kV, 35mA) automatic diffractometer was used for this work. 50-200mg of powder from the external oxide layer was removed mechanically. Samples of the objects before treatment were also analyzed as reference samples for the plasma treatment effect.

## Results

Results from XRD spectra from each category of samples are shown in Table 5. It must be noted that the results are not only qualitative, but there is the ability to obtain semi-quantitative measurings; taking the asterisk as an arbitrary unit and considering a linear numbering-system. It was obvious that the presence of soil minerals from the environment, such as calcite, quartz, feldspars, was dominant in all spectra before and after plasma treatment. In addition, the main iron corrosion identified, before any treatment, was goethite FeO(OH) and hematite  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>.

Table 5 XRD results

Gas Treatment	Treatment	Sample	Goethite FeO(OH)	Hematite $\alpha$ -Fe <sub>2</sub> O <sub>3</sub>	Maghemite $\gamma$ -Fe <sub>2</sub> O <sub>3</sub>	Magnetite Fe <sub>3</sub> O <sub>4</sub>	Soil minerals (CaCO <sub>3</sub> , SiO <sub>2</sub> , feldspars etc)
H <sub>2</sub>	no treatment		*	*			**
	reference sample	C1		*		*	**
H <sub>2</sub>	sample as the positive	C2 (+dc)		*		*	**
	pole of the electric circuit						
H <sub>2</sub>	sample as the negative	C3 (-dc)		*		**	**
	pole of the electric circuit						
N <sub>2</sub>	reference sample	S1	*				**
	sample as the positive	S2 (+dc)		*	*		**
	pole of the electric circuit						
N <sub>2</sub>	sample as the negative	S3 (-dc)			*		**
	pole of the electric circuit						

The results obtained after each plasma procedure differ as follows: as far as the hydrogen plasma treatment is concerned, the sample (C1), which was treated without any additional d.c. potential, shows the expected results (absence of goethite and appearance of magnetite) that we have already established in our previous work.<sup>18</sup> Since an additional d.c. enforcement is applied on the samples treated in hydrogen plasma, the sample with the positive potential (C2) shows the same results as the reference sample. At the same time, on sample (C3), on which the negative potential is applied, the presence of magnetite is elevated, which shows that plasma action is increased.

On the other hand, the samples treated in nitrogen plasma differ from each other. S1, which is the reference sample, shows no plasma effect even after 3 hours of treatment. The results from S2, which is the sample with the positive additional potential, shows the presence of hematite and maghemite, while S3, with the negative potential, shows the presence of magnetite only. The presence of hematite or maghemite is accomplished because of dehydration of iron hydroxides to the trivalent iron oxide Fe<sub>2</sub>O<sub>3</sub> (hematite or maghemite) which took place according to the reaction  $2\text{FeOOH} \rightarrow \text{Fe}_2\text{O}_3 + \text{H}_2\text{O}$ . Even though, the nitrogen plasma treatment shows less action than

the hydrogen one, in the case of the additional negative potential, the presence of maghemite only leads us to conclude that the negative enforcement amplifies the action of nitrogen ions due to the elevated ion concentration and velocity.

In the case of hydrogen plasma treatment, the final products were hematite and magnetite. Magnetite is the most stable (thermodynamically) oxide of iron, which is a product of the reduction of hematite according to the reaction  $3\text{Fe}_2\text{O}_3 + 2\text{H} \rightarrow 2\text{Fe}_3\text{O}_4 + \text{H}_2\text{O}$ . This leads us to the conclusion that, in addition to the dehydration of oxyhydroxides, a reduction due to hydrogen action has taken place. On the contrary, in nitrogen plasma treatment, the final products were hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>) and maghemite ( $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>). By evaluating the above results, it is concluded that only dehydration of oxyhydroxides has taken place,<sup>20</sup> and no reduction reaction has occurred. Generally, the nitrogen plasma is much less reductive than the hydrogen one due to released electron from the nitrogen atom, as it becomes ion. However, the nitrogen plasma had significant effects on the pure metal, by giving a visible epidermis (layer) of nitrogen on coupon's surface (nitriding) (Figure 7).



**Figure 7** Coupons after plasma treatment. The nitrogen one seems to have a metallic azure colour in its cross section (nitriding).

## Conclusion

The plasma parameters' elaboration (Section 3) came out with pre-conditions, suitable for surfaces without external dc potential. Equations 6, 7 & 8, show that the ion velocity  $u_i$  on the surface is increased and that ion number density  $n_i$  is bigger than the electron one  $n_e$ . Taking into consideration that the two factors ( $u_i$  and superiority of ion concentration) affect positively the chemical reactions, the plasma restoration ability can be easily understood.

According to predictions that originated from the above theory, when we apply negative potential on a corroded sample, faster and more evident results are expected. On the contrary, if the applied potential is positive, results are expected to be weaker.

Another significant result is the difference of plasma action according to the nature of plasma gas. When plasma gas is hydrogen, an intense chemical action is noticed. On the contrary, when plasma gas is nitrogen the phenomena are feeble (no reduction is noticed); the above outcome is caused because hydrogen atoms offer electron for reduction, while nitrogen atoms do not.

Although nitrogen does not reduce iron oxides, a significant action on the pure metal was noticed, by changing its colour. This plasma action is useful to metallurgy.

## Acknowledgements

The authors would like to thank the technical personnel of the Laboratory for their assistance during the experiment.

## Conflicts of interest

Authors declare there is no conflict of interest.

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