

# A Phenomenological Model of Nanocrystalline Coating Production Using the Plasma Electrolytic Saturation (PES) Technique

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**Abstract.** *The Plasma Electrolytic Saturation (PES) technique is a relatively new process, which uses a high DC voltage power supply with a related organic electrolyte. Within the phenomenological model, the mechanism of the nanocrystalline coating formation processes has been developed to clarify the controlling variations of the procedure. Within the informative model, a feedback parameter for the formed surface state estimation was established. This parameter is the power spectral density of the current. The voltage versus current characteristics of the treatment within the plasma region depend on the main electrolysis conditions, such as current density, electrolyte concentration and agitation rate. Application of the control algorithm of the parameters could increase the efficiency of the plasma electrolytic saturation and nanocrystalline coating formation. In this process, the electric field strength, “E”, within the surface region reached a value of between 106 and 108 V/m, which was sufficient for initiation of ionization processes in the vapor envelope. The ionization phenomena initially appeared as a quick sparking in scattered gaseous bubbles and then transformed into a uniform glow distributed throughout the vapor plasma envelope. Because of the hydrodynamic stabilization of the vapor envelope in the region of 180–210 V, the current dropped and the glow discharge transformed into intensive arcing, accompanied by a characteristic low-frequency acoustic emission.*

**Keywords:** *Plasma treatment; Glow discharges; Nanostructure; Dielectrics; Diffusion.*

## INTRODUCTION

The Plasma Electrolytic Saturation (PES) technique is a new method in surface treatment. This technique should be considered as a preferred group of surface engineering and nanocrystalline coating formation, due to the presence of the electrolysis of a liquid environment and the production of an electrical discharge on the work piece surface [1].

It is well known that the electrolysis of aqueous solutions is accompanied by a number of electrode reactions. The liberation of hydrogen and cation reduction can also occur on the cathodic surface.

Recently, numerous investigations have taken into account using special correction factors, e.g. ‘current yield’ or ‘electrode shielding’ coefficients, in the case

of a plasma environment and, also, plasma formation. However, such a simplification is not always justifiable, since, under certain conditions, the results obtained from the treatment are influenced considerably by the processes that occur in the plasma environment surrounding the electrode [1].

For PES, the electrolyte composed of treatment related ions (e.g. carbamide for nitrocarburizing and borax for boronizing treatments) and KCl or Na<sub>2</sub>CO<sub>3</sub> or NaOH, which are utilized to obtain appropriate solution conductivity, is solved in distilled water. In the plasma electrolytic treatment, water content influences the experimental parameters. For example, in plasma electrolytic nitrocarburizing (PEN/C), less than 5% H<sub>2</sub>O causes an increase in the critical voltages for plasma envelope stabilization, while more than 10% H<sub>2</sub>O leads to an increase in the slope of the voltage-temperature curve [1]. The final gained properties of the treated samples contribute to the role of applied experimental parameters [2].

By applying voltage in the first step of the treat-

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ment, the potential rise leads to current elevation. The current rise is limited by a gaseous envelope covering the cathode surface. In areas where the electrode remains in contact with the liquid, the current density continues to rise, causing local boiling of the electrolyte adjacent to the electrode.

By forming a continuous vapor plasma envelope of low electrical conductivity, almost all of the voltage across the circuit is now dropped in this near-electrode region. The ionization phenomena appear initially as a quick sparking in separate gaseous bubbles and then continue to form a uniform glow distributed throughout the vapor plasma envelope, due to the high applied voltage in the formed thin film near the electrode. Due to the dielectric properties of the formed envelope, the current drops sharply and the glow discharge transforms into intensive arcing accompanied by acoustic emission [1].

In PES treatment, the high temperature of treatment affects the surface hardening procedure [3,4], thus, this technique was termed "heating in electrolytic plasma". Furthermore, the phenomenon of electrolyte components diffusion into the surface of the electrode was also noticed. During previous studies, these effects were used to develop a set of processes directed to the surface saturation of bulk materials with various alloying elements [5,6], thus new innovations for the industrial application of the technique, termed Plasma Electrolytic Saturation (PES), developed. However, further investigation of the plasma electrolytic processes requires an understanding of the physical and chemical background of the plasma phenomena and nitrocarburized layer formation. In order to find out the principles of the plasma electrolytic processes, reviewing and finding a phenomenological model in the generic term of Plasma Electrolytic Saturation (PES) is required. Therefore, the purpose of this work is to clarify the Plasma Electrolytic Nitrocarburizing (PEN/C) procedures as a kind of PES technique. These procedures chiefly consist of electrolyte decomposition, dielectric discharge phenomenon, heat transfer from the plasma environment to the carbon and nitrogen particles and, finally, diffusion route, respectively. These concepts, as a model of the Plasma Electrolytic Saturation (PES) technique, can provide asset information for the researchers to take control over the treatment.

## EXPERIMENTAL PROCEDURE

Disc substrates made of AISI 316L steel with a diameter of 25 mm and thickness of 3 mm were ground and polished with SiC abrasive paper to obtain a mirror finish. Table 1 shows the analysis of the substrates.

In this study, the Plasma Electrolytic Nitrocar-

burising (PEN/C) treatment was carried out in a 2 liter capacity pyrex bath. The substrates were biased with negative voltages of 200 volts. An AISI 316 stainless steel coupon of dimensions 15 mm×30 mm forms the anode of the system and test pieces were cathodically biased, using a 20 kW DC power supply with high (500 V) potential and (40 A) current capability.

The treatment electrolyte was an aqueous solution of 65% wt. carbamide [ $\text{CO}(\text{NH}_2)_2$ ], 27% wt. water ( $\text{H}_2\text{O}$ ) and 8% wt. chemically pure sodium carbonate ( $\text{NaCO}_3$ ). Sodium carbonate was added to provide the desirable conductivity. PEN/C treatment was performed at a temperature of around 700°C. The surface temperatures of the samples were measured using a thermocouple inserted into the sample, approximately 500 mm below the surface, by drilling a hole.

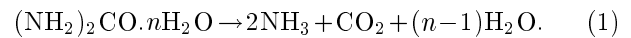
After the PEN/C treatment, the obtained samples were washed with distilled water and dried. The produced nanocrystalline coatings were examined by means of an X-ray diffractometer and a Scanning Electron Microscope (SEM), to observe the produced nanocrystalline grains.

The cross sectional image was taken by means of SEM. In order to protect the formed layers during the polishing processes, the treated sample was electroplated in Watt's nickel bath.

## RESULTS AND DISCUSSION

### Plasma Constitution

The source of diffusional carbon and nitrogen particles is the electrolyte which surrounded the work piece. The plasma environment is also initially obtained from a gaseous sheath around the cathode. Above 180 V, a significant amount of gas was generated, due to the ohmic heating of the solution vaporized near the sample's surface, according to the following equation:



Therefore, the gaseous products form a vapor envelope over the cathode's surface. After the electrolyte has been vaporized, the gaseous atmosphere will transform to a plasma environment. Therefore, after a while, due to the formation of a dielectric barrier, it becomes a stable saturated environment, called "plasma" [1]. The plasma environment generated in the gaseous envelope produces a number of active species, carbon and nitrogen radicals. They bombard the sample surface and provide an inward aggressive diffusional flow.

In the plasma formation procedure, the dielectric barrier discharge is an atmospheric pressure environment which yields a uniform discharge within the plasma envelope, as mentioned above [7]. In this circumstance, the carbon and nitrogen ionized particles

**Table 1.** Analysis of substrates.

Substrate	C	Si	Mn	P	S	Cr	Mo	Ni
<b>AISI 316L</b>	0.030	0.750	1.860	0.450	0.030	18.0	2.530	14.0

provide a saturated sheath on the cathode surface, alike to that of a low pressure glow discharge [8]. It is worth noting that such a powerful discharge is fairly uniform in the radial direction, which is suitable for surface engineering applications. The maximum magnetic field strength bringing about the dielectric discharge was found in front of the work piece, at about 1.8 cm from the cylinder axis [9].

The mentioned procedure for practical systems can be analyzed via current-voltage region monitoring. As mentioned above, the plasma environment initiation can be identified by the critical voltage [10]. Thus, it can be calculated against the critical field strength,  $E_{c1}$ , for breakdown across the gaseous envelope, as shown in the following equation from the impact ionization theory:

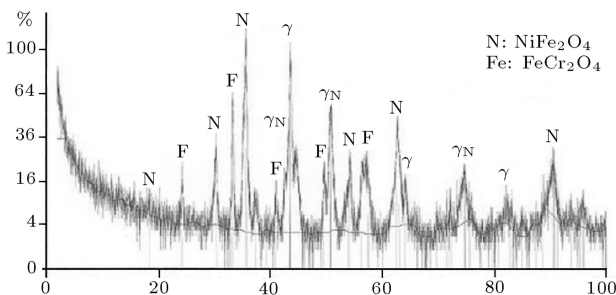
$$E_{c1} = bp \ln \frac{\alpha}{ap}. \quad (2)$$

Here,  $a$  and  $b$  are constants,  $p$  (Pa) is the vapor pressure and  $\alpha$  is the impact ionization coefficient of the vapor species [1]. Therefore, the voltage breakdown can be considered as the point at which the plasma discharge has been commenced.

### Nanocrystalline Formation

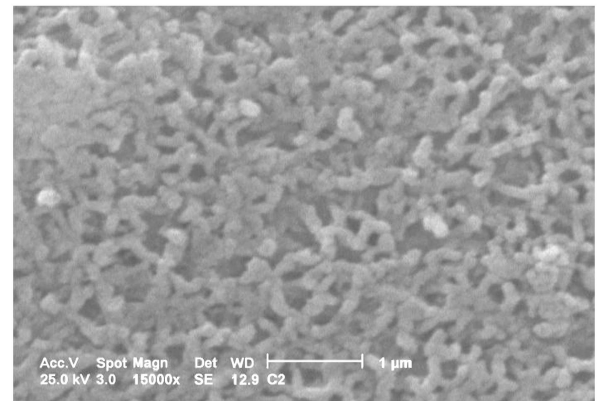
The analytical and morphological aspects of the produced coating are firmly correlated to the plasma characteristics [11,12]. It has become clear that formation of nanocrystals on the surface provides a range of interesting properties caused by compact and dens nanostructures.

Figure 1 illustrates the XRD pattern of the treated sample, showing the main peak intensities of  $\gamma$  (austenite),  $\gamma_N$  (expanded austenite) and spinel oxides. The sample microstructure consists of a magnetite/chromite layer and an expanded austenite

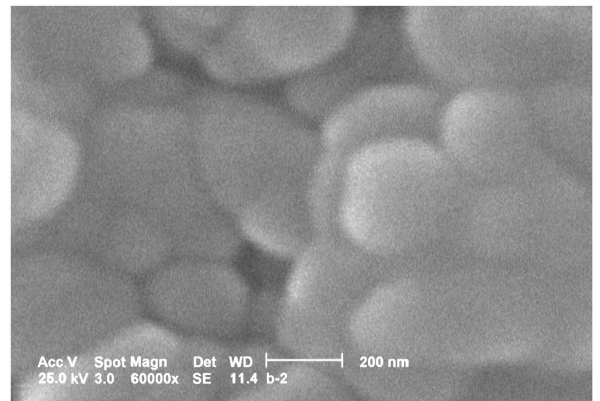
**Figure 1.** XRD pattern of the PEN/C treated sample.

diffusion layer, which possesses porous nanocrystalline grains (Figure 2).

Investigations illustrate that the microstructural, nanocrystalline and, consequently, final corrosion and mechanical properties of the nitrocarburized coatings depend strongly on applied experimental parameters [13]. Inasmuch as the experimental parameters, such as applied voltage, surface temperature and treatment duration play a considerable role in plasma environment characteristics, a profound precept of how plasma characteristics are affected by experimental parameters can provide beneficial information. It is, therefore, necessary to have a simulation that is fast enough to be able to run many times, in order to obtain the statistical averages of the properties for a given set of process conditions.



(a)



(b)

**Figure 2.** SEM photographs of the surface nanocrystals formed by PEN/C treatment at (a) 15000 X and (b) 60000 X.

Since the carbon and nitrogen particles obtain their activation energy from the density of thermal power transferred to them and their activeness determined the surface temperature and, consequently, the final nanocrystalline morphologies, heating plays the most important role in the final surface characteristics of the plasma electrolytic nitrocarburizing procedure [14]. Notification should be given to the fact that only convective heat transfer from the plasma to the carbon and nitrogen particle was considered in the model. The density of the thermal power transferred to the particle by convection can be expressed as:

$$O_c = N_u \cdot \lambda_g \cdot \frac{T_g - T_{ps}}{\pi d_p}, \quad (3)$$

where  $N_u$  is the Nusselt number,  $\lambda_g$  is the thermal conductivity of the plasma gas,  $T_{ps}$  is the particle surface temperature, and  $T_g(X, Y)$  is the plasma gas temperature. The Nusselt number depends on the Reynolds number in the following way:

$$N_u = 2 + 0.6\text{Re}^{0.5} \text{Pr}^{0.33}, \quad \text{Re} \leq 2, \quad (4)$$

$$N_u = 0.5\text{Re}^{0.5} \text{Pr}^{0.3}, \quad 2 < \text{Re} < 500, \quad (5)$$

where  $\text{Pr}$  is the Prandtl number. Equation 4 is the well-known Ranz-Marshall expression and Equation 5 is an experimental approximation for turbulent flow conditions [15,16].

In practical investigations, it was found that the formed layer consists of much fine grain with the nano-sized crystals [17], suggesting that the PEN/C treatment on the AISI 316L substrate provides nanocrystalline structures according to the applied temperatures. It was also revealed that the applied voltage and, consequently, the treatment temperature determine the surface morphologies and most of the final obtained characteristics as well. As illustrated in Figure 2, the PEN/C-formed layer shows a nanocrystalline surface morphology.

In accordance with the model presented in [18,19], the case structure of a carbonitride layer consists of an expanded austenitic phase. The nitrocarburized layer itself may contain one or more sub-layers of a given nitride/carbide phase,  $\gamma - \text{Fe}_4(\text{N}, \text{C})_{1-x}$  and  $\gamma - \text{Fe}_4(\text{N})$ . The formed nano-structure morphologies depend on the type and concentration of alloying elements, temperature, the partial nitrogen and carbon pressure, etc., as mentioned above. Any sub-layer is characterized by boundary positions as functions of time and nitrogen/carbon concentration range, which determine maximum and minimum nitrogen/carbon solubility at the surface layer; and an effective diffusion coefficient,  $D_k$ ,  $k = 1, 2 \dots n, n + 1$ , where  $n$  is the number of sub-layers constituting the nitrocarburized

zone. The diffusion is considered as the  $(n + 1)$ th sub layer [18].

It should be taken into account that, at high carbon and nitrogen concentrations, a chemical composition gradient may appear. Because of this, carbon and nitrogen atoms cannot move independently. Then, the carbon and nitrogen diffusion coefficients in the formed layer have to be considered as a mean chemical diffusion coefficient ( $D$ ). The influence of the chemical composition gradient can be taken into account in an approximate way, by the following equation [19]:

$$D = D^* \left( 1 + \frac{\partial \ln \gamma}{\partial \ln c} \right), \quad (6)$$

where  $D^*$  is the tracer diffusion coefficient corresponding to dilute solutions;  $\gamma$ , the activity coefficient of diffused particle and  $c$ , the particle concentration. The diffusion coefficients considered in the present study have the meaning of the chemical diffusion coefficient average on the concentration:

$$D = \frac{1}{c_2 - c_1} \int_{c_1}^{c_2} D(c) dc. \quad (7)$$

If the concentration range,  $C_2 - C_1$ , is relatively small, then  $D$  can be considered as an effective chemical diffusion coefficient at an average concentration. Usually, this effective coefficient is experimentally measured. Consequently, the temperature dependence of  $D$  can be expressed in an Arrhenius form:

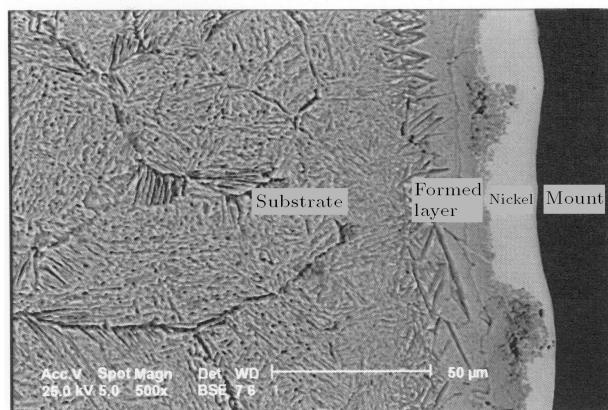
$$D = D^\circ \exp \left( -\frac{Q}{RT} \right), \quad (8)$$

where  $D^\circ$  is called the pre-exponential factor,  $Q$  is the activation energy for diffusion and  $T$  is the absolute temperature [19]. All of the mentioned factors affect the nanocrystalline morphology and sub layer thickness in practice.

An optical image of the cross-sectional view of the coating offers some information about the coating morphology (Figure 3). In this case, it is obvious that the produced coating is characterized by high integrity, because of the appropriate experimental parameters chosen. Therefore, good mechanical and tribological properties are expected.

## CONCLUSION

1. In the PES procedure, due to the formation of a dielectric barrier, the formed envelope becomes a stable environment called "plasma". In the plasma envelope, charged ions are replaced by super radical particles;



**Figure 3.** The cross-section optical micrograph of AISI 316L PEN/C treated sample.

2. The critical voltage for the plasma environment formation can be calculated against the critical field strength,  $E_{c1}$ , for breakdown across the gaseous envelope, as an initiation point for the plasma discharge treatment;
3. The main phases of the PEN/C treatment on AISI 316L are  $\gamma$ ,  $\gamma_N$  and spinel oxides;
4. The microstructure and formation of nanocrystalline grains depend on the applied practical parameters;
5. The carbon/nitrogen concentration range in the produced plasma environment affects the nanocrystalline morphology and sub layer thickness;
6. The appropriate choosing of experimental parameters will provide integrated coatings with high mechanical and tribological performance.

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