Nano-Fabrication by Cathodic Plasma Electrolysis

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Cathodic plasma electrolytic (CPE) techniques are new groups of coating processes, which can be used for fabrication of nanostructured layers on surface of a wide range of metallic substrates. The most exciting visible feature of these atmospheric-based plasma techniques is continuous sparking on processed surface inside an electrolyte. Unlike the anodic part of plasma electrolysis (usually known as plasma electrolytic oxidation (PEO) or micro arc oxidation (MAO)), which is commonly used for oxidation of light metals/alloys such as aluminum, titanium and magnesium, CPE techniques can clean and coat different metals and alloys such as steel, copper, and light metals/alloys with formation of wide range of nanostructures including complex carbides, carbonitrides, intermetallics, and even oxides. It has been observed that the properties of obtained layers depend on the characteristics of achieved nanostructures such as average size, distribution and average coordination number of nanocrystallites. Furthermore, the properties of the processed surface can be tailored by tailoring the nanostructure characteristics. There is limited literature available on the mechanism of CPE and its connection to the morphology of nanostructured layers. This article addresses the two important aspects of CPE, namely characterization of nanostructured layers and mechanism of cathodic plasma electrolysis, which are reviewed in accordance to the morphology of fabricated nanostructures.

Keywords average coordination number, cathodic plasma electrolysis, coating, complex compounds, nanostructure, morphology

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1. INTRODUCTION

Different plasma treatments\textsuperscript{1-8} are increasingly used for surface modification\textsuperscript{9,11} of metallic components, as most of the methods are environmentally friendly.\textsuperscript{12, 13} One that has recently attracted the attention of researchers is plasma electrolysis,\textsuperscript{14,15} which can be classified under atmospheric pressure plasma treatments.\textsuperscript{16-21} Like most of the electrochemical treatment methods,\textsuperscript{22-24} this process consists of immersion of substrate in an electrolyte with a relatively high applied potential (from 200 to 2000 volts).\textsuperscript{25-36} During this process surface of the processed substrate is subjected to continuous sparking\textsuperscript{37, 38} and based on chemistry of the electrolyte and applied mode of voltage, different coatings such as oxides,\textsuperscript{39-41} carbon-based materials, e.g., carbides and carbonitrides,\textsuperscript{42-46} etc.\textsuperscript{47} can be produced. Typical applications of this method are summarized in Table 1.

The processed substrate can behave as the anodic\textsuperscript{48} or cathodic\textsuperscript{49} electrode based on the polarity of applied voltage and hence this method is usually divided into anodic or cathodic electrolytic plasma. Figure 1 shows a schematic division for the process. Pulsed current with bipolar mode\textsuperscript{50, 51} has been used for electrolytic plasma treatment, in which the polarity of electrodes continuously changes. Thus, the type of method (anodic or cathodic) is usually determined by the polarity in which the intensity of applied bipolar current is greater. For example, if the pulsed current with 40\% of duty cycle (\(t_{on}/t_{off} = 40/60 = 0.66\)) and applied cathodic voltage of 600 volts and applied anodic voltage of 300 volts, has been used, the cathodic plasma electrolysis is being used, as the intensity of cathodic side (600 \times 0.4) is higher than anodic one (300 \times 0.6).

The anodic part of plasma electrolysis (frequently recognized as plasma electrolytic oxidation (PEO)\textsuperscript{52-54} or micro arc oxidation (MAO)\textsuperscript{55-58}) is generally used for deposition of an oxide coating on surface of light metals/alloys such as aluminum, titanium and magnesium. The oxide coatings are generally used for enhancing properties of light metals/alloys such as wear,\textsuperscript{59, 60} corrosion,\textsuperscript{61-63} thermal barrier,\textsuperscript{64} etc. Based on the parameters for coating process, the size of formed coating structure vary in the range of few nanometers\textsuperscript{20,65} to several micrometers.\textsuperscript{33} The researchers are interested in the structure of coatings formed by electrolytic plasma process and are actively working towards increasing their understanding of the mechanism for observed structure. Furthermore, formation of nanostructure has opened avenues to produce and study nanocomposite layers by this method.

The cathodic part of plasma electrolysis can be used to process different types of metals/alloys and can be applied to fabricate complex coatings such as graphite\textsuperscript{69} and oxides.\textsuperscript{70} Figure 2 illustrates schematic diffusion of small elements from the electrolyte into metallic lattice through nanostructured compound layer and stressed under layer formed by cathodic plasma electrolysis (CPE). It has been observed that the sizes of structures produced by this method are, mostly, in the range of 1 to 100 nm, which is in domain of nanostructures.\textsuperscript{14,71-73} The key aspect of the nanostructures obtained by CPE is that the properties of the processed surface can be tailored by changing characteristics of
TABLE 1

<table>
<thead>
<tr>
<th>Target industry</th>
<th>Industrial component</th>
<th>Plasma Electrolysis</th>
<th>Improvement</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oil industry</td>
<td>Valves, casings, pumps</td>
<td>Surface hardening,</td>
<td>Hardness improvement,</td>
</tr>
<tr>
<td></td>
<td></td>
<td>nanocomposite coatings</td>
<td>distribution control for</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>nanocomposite coatings</td>
</tr>
<tr>
<td>Aerospace industry</td>
<td>Light alloys, turbines</td>
<td>Nanocomposite coatings</td>
<td>Thermal barrier applications,</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>lifetime increasing</td>
</tr>
<tr>
<td>Electrical industry</td>
<td>Wires</td>
<td>Cleaning</td>
<td>Surface characteristics for</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>post coatings</td>
</tr>
<tr>
<td>Tool industry</td>
<td>Industrial components under</td>
<td>Nanocrystalline plasma</td>
<td>Hardness, wear resistance,</td>
</tr>
<tr>
<td></td>
<td>high wear conditions</td>
<td>electrolytic saturation and</td>
<td>life time and in some cases</td>
</tr>
<tr>
<td></td>
<td></td>
<td>nanocomposite coatings</td>
<td>corrosion resistance</td>
</tr>
</tbody>
</table>

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These nanostructures (such as shape of nanocrystallites),71, 72 It has been observed that by reducing average size of the nanostructures, properties of the surface (such as corrosion and wear resistances) will improve significantly.74, 75 This method can also be used for surface cleaning of different metallic substrates.73,76–79 Table 2 compares routine carburizing processes and plasma electrolysis.

CPE has shown promise to produce nanostructured surfaces with desired properties, the mechanism and its relation to effective factors of process80 and morphology of nanostructured layers is an important aspect. This article reviews the nanostructures formed by CPE and current understanding of the involved mechanism studied by the authors and others researchers. This review comprises four sections (except this section), which focus on the cathodic part of plasma electrolysis for formation of nanostructured layers (primarily coating aspect and not for cleaning). Cleaning procedure by this method has been well studied previously.14,76–79 The authors intend to review open literature in nano-coatings deposited by cathodic plasma process and the findings from their own research.

It is notable here that the term “applied potential” or “applied voltage” which has been used through this paper means the highest applied potential during CPE. In the case of pulsed voltage, it means the peak of applied voltage on the cathodic direction. Exceptions have been determined in the case of used anodic potentials.

2. PERFORMANCE OF CATHODIC PLASMA ELECTROLYSIS

2.1. Electrolyte

There are two effective factors on the process: (a) composition of electrolyte (b) mode of applied current.15,81,82 Aqueous based electrolytes can be used for deposition of coatings by this process,83 but most of the used electrolytes have been with organic based electrolytes for fabrication of nanostructured carbide-based layers. CPE is characterized by diffusion of high-energy atoms from electrolyte (such as carbon, nitrogen, etc.) under a relatively strong electrical field toward the surface of the sample. During processing, the atoms continuously diffuse into the lattice of metallic substrate, thereby creating intrinsic stresses in the affected lattice. This results in increase in hardness of the processed surface and simultaneously (in combination with localized elevated temperature of surface) in formation of a compound layer consisting of nanocrystalline carbides, carbonitrides, etc.84,85 The primary constituent of an organic based electrolyte is carbon, so the formed layer will consist of carbide-based compounds. Carbamide (Urea), Glycerol, Triethanolamine, Formamide, etc.82 are examples of organic electrolytes that can be used for fabrication of nanostructured layers.

Some additives are usually added to these electrolytes for enhancement of electrical conductivity of the electrolyte. As seen in Figure 3, electrical conductivity of electrolyte has an important role in energy consumption of CPE process. These additives can be sodium carbonate, sodium nitrate, sodium chloride,
<table>
<thead>
<tr>
<th>Type of Current</th>
<th>Surface pressure (Pa)</th>
<th>Substrate bias (V)</th>
<th>Type of applied current</th>
<th>Current density (mA.cm⁻²)</th>
<th>Surface temperature controllability</th>
<th>Maximum hardness improvement</th>
<th>Load bearing ability</th>
<th>Other</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plasma implantation</td>
<td>0.01-1</td>
<td>10-50 kV</td>
<td>Pulsed (0-400 Hz)</td>
<td>1-4</td>
<td>Fair</td>
<td>~ 400%</td>
<td>Fair</td>
<td>Also usable for nonmetallic substrates</td>
</tr>
<tr>
<td>Arc discharge</td>
<td>0.4-4</td>
<td>80</td>
<td>D.C.</td>
<td>Good</td>
<td>~ 400%</td>
<td>Fair</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Plasma Electrolysis</td>
<td>Atmospheric pressure treatment</td>
<td>200-700</td>
<td>D.C. and Pulsed</td>
<td>200-800</td>
<td>Fair</td>
<td>~ 1000%</td>
<td>Excellent</td>
<td>Ability to fabricate nanocomposite layers</td>
</tr>
</tbody>
</table>
etc. It is important to select an appropriate additive in order to achieve a uniform layer with desired chemistry. For pure carburizing, the additives containing nitrogen (such as sodium nitrate) should not be used as it can form nitrides or carbonitrides. Additives that are more efficient in increasing of electrical conductivity of the electrolyte are preferable due to lower water content in an organic electrolyte.

Water content plays an important role while using organic electrolyte with CPE. Water dissolves the additives in the electrolyte and helps chemical reactions that occur at the processed surface. CPE process results in evaporation of water from the electrolyte, so it is necessary to add water at regular interval to maintain chemistry of the electrolytic bath. But it is critical that the water content does not exceed a certain amount in the organic electrolytic bath, generally not more than 5%. Higher amounts of water content in electrolyte can limit capability of coating process to form nanostructured carbide based layers, due to oxidation of the surface. The oxide layer also has a nanometric structure and may be useful for some other purposes rather than increasing the hardness for surface of different metals/alloys.

Usage of aqueous based electrolytes for cathodic plasma processes with different applied potentials has been reported in literature. These electrolytes can be used to fabricate nanostructured layers as well as nanoparticles by use of CPE. Aqueous electrolytes consist of appropriate dissolved mineral components (e.g., aluminum chloride) for fabrication of desired nanostructured coating (e.g., intermetallic compounds of aluminum containing layer).

The authors have used statistical methods for optimization of electrolyte composition with desired target of uniform coating and smaller nanocrystal size. It was seen that the coating with lower average size of nanocrystallites, exhibits better electrochemical and mechanical properties. This is consistent with nano-structured coatings that have been reported in literature deposited by using various technologies. The distribution and its deviation from normal status is also an important issue for this kind of nanostructured coatings. It was revealed that the best properties achieved by the normal distribution of nanocrystallites and this kind of distribution is fully accessible by precise controlling of CPE effective factors.

A study was conducted by use of DC current to optimize process parameters for plasma electrolytic nitrocarburising (the content of nitrogen is higher than the content of carbon in compound layer) with the goal of improving corrosion resistance of 316L austenitic stainless steel. Applied voltage was the primary factor to achieve higher corrosion resistance of the 316L substrate, due to formation of thicker modified layer. Treatment time was the second effective factor in ranking, while electrical conductivity of the electrolyte and carbamide concentration had similar effects. The study showed that optimal processing parameters for the CPE system were 1050 g/L for carbamide concentration, 360 mS/cm for electrical conductivity of electrolyte, 260 volts for applied direct voltage and 6 minutes of treatment time. The corrosion resistance increased by \( \sim 50\% \) as compared with the unprocessed substrate.

Plasma electrolytic carburizing process (the content of nitrogen is lower than the content of carbon in compound layer) was studied by using pulsed current, with a target of achieving small size of nanocrystalline carbonitrides on the surface of commercially pure titanium (CP-Ti). The process parameters in the order of their significance can be ranked in following order; (1) applied pulsed voltage (2) frequency (3) treatment time and (4) temperature of electrolyte. The estimated optimized conditions are 15 KHz for applied frequency, 50 °C for temperature of electrolyte, 500 volts for applied voltage and 30 minutes for treatment time. The average size of nanocrystalline carbonitrides was \( \sim 67 \) nm, which resulted in improvement of corrosion and wear resistance as compared to the unprocessed substrate.

Temperature of electrolyte must be controlled by a cooling circuit. It has been observed that it is important to control the temperature of the electrolyte. First, higher electrolyte temperature can lead to decomposition of organic constituents such as carbamide. Second, electrolyte temperature also affects micro quenching of nanocrystallites on the processed substrate, thereby affecting its size and properties. Micro-quenching aspect is discussed in more detail in later section.

### 2.2. Applied Current

Mode of applied current is a key factor for CPE process. The applied current or potential is directly related to the localized temperature of surface, which is important to control the properties of phases formed on the substrate. It is necessary to control the applied current to tailor surface elemental composition and to obtain desired nanostructured layer. In general, applying an adjusted pulsed current can lead to more uniform coating with desirable properties. Although there are studies on exotic use of pulsed current for CPE such as pulse on pulsed currents, but the most effective factors of pulsed current mode are frequency, duty cycle \( \left( t_{on}/(t_{on}+t_{off}) \right) \) and polarity of processed substrate (monopolar or bipolar).
Plasma electrolytic saturation process used in bipolar pulsed current mode with glycerol-based electrolyte showed that higher applied cathodic voltages accompanied with lower anodic voltages, and in combination with lower duty cycle ratio (cathodic direction to duty cycle of anodic direction) was more appropriate to achieve nanocrystallites with smaller size.\textsuperscript{81} Distribution of nanocrystallites exhibited a Gaussian-shape (near normal distribution). Samples with high height to width ratio on the distribution curves, exhibited nanocrystallites with lower average size and lower aspect ratio (length-to-diameter ratio).\textsuperscript{96}

The surface composition of substrate was not an important factor for CPE; however, substrates with higher melting points act better in the process.\textsuperscript{102} One of the most interesting facts related to CPE, is that the morphology and distribution of nanocrystallites is not only directly proportional to mechanical properties of deposited nanolayers (also reported for other methods for deposition of nanostructured layers), but also is directly proportional to electrochemical properties of the nanolayers, which is rarely observed in other methods.\textsuperscript{98}

Use of plasma electrolysis on $\gamma$-TiAl alloy substrates for fabrication of nanostructured coating by bipolar pulsed current showed that certain factors have strong effect on the properties of achieved layer.\textsuperscript{90} The factors include applied current (ratio of duty cycle for cathodic direction to anodic direction between 0.2 to 0.4), frequency of pulsed current (range between 5 and 15 kHz), and treatment time (10 to 30 minutes). The study showed that higher frequencies in combination with lower duty cycle ratio (cathodic direction to anodic direction) and treatment time resulted in complex nanocrystallites with smaller size.

A study on skewness and kurtosis of Gussian distribution curves of nanocrystallite size revealed that current density and duty cycle of the pulsed current significantly affect the average size of hard nanocrystallites.\textsuperscript{95} Furthermore, higher current densities and lower duty cycles of the pulsed current are, in general, better for deposition of hard nanocrystallites with smaller sizes. These two factors also affect the surface roughness of coated substrate.

Different pulsed current modes can be used during CPE processing. Figure 4 illustrates the pulsed currents which have been used for CPE; namely triangular,\textsuperscript{103} rectangular\textsuperscript{104} and sinusoidal.\textsuperscript{105} The studies revealed that nanocrystallites had some defects (such as pores and cracks) were deposited by use of triangular and rectangular modes. Triangular mode resulted in diffused layer with higher hardness as compared to rectangular and sinusoidal modes, which was related to higher electrical field around the substrate in triangular mode. Sinusoidal mode resulted in better mechanical and electrochemical properties than triangular and rectangular modes, which was related to denser and more uniform compound layer formed on the processed surface. Also, sinusoidal mode resulted in smallest average size of nanocrystalline carbides and minimum percentage of average cracks density than the other modes of applied pulsed current.

![FIG. 4. Schematic diagram of different (a) triangular (b) rectangular (c) sinusoidal pulsed currents. (Reprinted with permission from Aliofkhazraei and Sabour Rouhaghdam,\textsuperscript{143} Copyright 2010: Wiley-VCH Verlag GmbH & Co. KGaA.)](image-url)
3. MECHANISM OF CATHODIC PLASMA ELECTROLYSIS

The break down voltage of gaseous envelope around the substrate is directly related to the applied voltage.\(^{73}\) Hence, CPE behaves similar to conventional electrolytic process up to a certain voltage, which obeys ohmic law by linear resistance electrical circuits. Gupta et al.\(^{14}\) have shown theoretical and experimental behavior of cathodic electrolytic process in aqueous electrolyte by use of DC current. Deviation from Faraday’s law is observed after a certain critical voltage and at a breakdown voltage spark is seen on the surface of the substrate. In fact critical voltage is a critical point that the current-voltage diagram shows deviation form a linear trend of increasing. In case of pulsed current the critical voltage for a given system may increase as compared to the DC current (but the necessary power for reaching sparks on the surface of cathode remains approximately constant). For example, by applying pulsed voltage with 50% of duty cycle, the critical applied voltage for sparking can be two times higher with respect to similar conditions without pulsed current. It is worth while mentioning that the anodic part of plasma electrolysis (e.g., PEO treatment) does not show this behavior, and sparking begins at a constant value of applied voltage and is not dependent on DC or AC source for a given electrolytic system.\(^{106-109}\)

The mechanism of CPE can be described by linear increase of current due to an increase in applied voltage. After reaching specific value of applied potential (break down potential), random sparks will form on the surface of substrate. Increasing applied potential after this level (approximately 10 to 30 volts) will lead to continuous sparking on the substrate. In this region, current will drop linearly with applied potential as the impedance of nonlinear system of sparking is lower than total resistivity of used electrolyte. In other words, the slope of current-voltage diagram in this region is lower than the linear ohmic region (first step of CPE). Similar behavior has been reported in literature for electrolytic plasma processes.\(^{14,15,43,100}\) The breakdown current density and treatment time are also dependent on the composition of the used electrolyte, but its effects are negligible as compared with the applied potential.

Composition of the gaseous envelope is dependent on the chemistry of the electrolytic bath. In aqueous solutions, water vapor is major component, where as in organic electrolyte, such as for nitro-carburizing chemical reactions affect the composition of gaseous vapor. Some of the possible reactions in organic electrolyte include:\(^{15,43}\)

\[
\begin{align*}
2H^+ + 2e^- & \rightarrow H_2 \quad [1] \\
HCONH_2 & \rightarrow NH_3 + CO \quad [2] \\
HCONH_2 & \rightarrow HCN + H_2O \quad [3] \\
(C_2H_4OH)_3N & \rightarrow 2CH_4 + 3CO + HCN + 3H_2 \quad [4]
\end{align*}
\]

Increasing the applied potential will not only affect chemical reactions on the surface of the cathode, but will also affect local evaporation rate of the used electrolyte due to localized heating of electrolyte in vicinity of the cathode.

The regime of potentials which forms stable gas envelope and spark around the substrate has been exploited by CPE for numerous surface treatments by use of organic and inorganic electrolytes. Formation of sparks on the surface will lead to synthesis of nanocrystallites, which will remain in the nanometric
range due to rapid quenching in electrolyte at near room temperature. Higher applied potentials or higher electrical fields around the substrate provide higher powers for ion bombardment on the processed surface and can lead to deeper diffusion zone into the depth of the substrate. In lower applied potentials, only small diffusive atoms can become accelerated in plasma envelope and diffuse into the surface of cathode. Higher applied potentials can provide sufficient energy to bigger diffusive atoms, such as Aluminum and Silicon for bombardment onto the substrate. It is proposed that these atoms become ionized in a very short time of sparking and accelerate toward the cathodic surface under strong electrical field. Similar mechanism has been reported by other researchers.\textsuperscript{14,15,43}

4. AVERAGE COORDINATION NUMBER

4.1. Simulation of ACN for Nanostructured Layer

The average coordination number (ACN) of atoms depends on the size and shape of fabricated nanoclusters. Large amount of surface atoms will decrease the ACN of nanostructured layer with simultaneous increase of dangling bonds. Hence, the ACN can be estimated from the amount and size of the surface atoms. Direct relation of the ACN to physical and chemical properties of materials, such as catalytic properties of nanostructures,\textsuperscript{110} metallic manners of materials,\textsuperscript{111} photoemission properties,\textsuperscript{112} ionization potentials,\textsuperscript{113} electronic states concentration,\textsuperscript{114} atomic packing factor and crystalline structure\textsuperscript{115} have been extensively studied. Evaluation of distribution, average size and geometrical shape of nanostructures from their ACN can help in estimation of catalytic activity of nanostructures.\textsuperscript{116}

As we have discussed in the previous sections, CPE nanostructured layer consist of different nanocrystallites and nanoclusters.\textsuperscript{81,83} Their atoms could either be at the surface or in internal layers. The coordination number of different atoms can be assigned as $Z_S$ and $Z_I$ for surface and internal atoms, respectively. $Z_S$ describes only surface bonds and is not related to the internal bonds of surface atoms. $n_S$, $n_I$ and $n_T$ denote the number of surface, internal and total atoms, respectively ($n_T = n_S + n_I$). Surface, internal and total ACN of nanostructured layer can be described as:

$$
\bar{Z}_S = \frac{\sum_{i=1}^{n_S} Z_S}{n_S} \quad [5]
$$

$$
\bar{Z}_I = \frac{\sum_{i=1}^{n_I} Z_I}{n_I} \quad [6]
$$

$$
\bar{Z}_T = \frac{\sum_{i=1}^{n_S} Z_S + \sum_{i=1}^{n_I} Z_I}{n_T} \quad [7]
$$

In a CPE system, there are three primary sources for atoms to form a nanostructured layer, namely substrate, electrolyte and chemical reactions in sparking region. The proportional changes in coating thickness with bombarded atoms from electrolyte\textsuperscript{83} in CPE will lead $(n_T/n_I)$ to be constant. Further more, $n_T$ and $n_I$ will change unidirectional, i.e., $n_T$ will increase with increase in $n_I$ (in the case of changing one effective factor of coating process). For example, if all of the processing parameters assumed to be constant and just duty cycle of pulsed current is changed, by increasing the duty cycle, the total $(n_T)$ and hence internal $(n_I)$ atoms of the layer will increase simultaneously, but the surface atoms $(n_S)$ of the layer will also depend on the distribution of porosities and their size over the nanostructured layer.

4.2. ACN Changing Trend

The strong relation among different properties of CPE nanostructured layers with their characteristics of nanocrystallites\textsuperscript{98} can be studied by studying distribution of ACN. A correlation between processing parameters with properties of nanostructure can be made by estimating the changing trend for different expressions of Equ. 7 with change in processing parameters. The changing trend of total and internal atoms due to change in processing parameters has been extensively studied and reported by the authors.\textsuperscript{75,81,83,87,117} In accordance with Equ. 5 to 7, as $n_T$ and $n_I$ are proportional, changing trend of ACN can be determined by $n_SZ_S/n_T$. Distribution of surface atoms can be determined by analyzing the surface porosities. Authors have done investigations on distribution and size of porosities by SEM analysis of micro/nanostructures on the surfaces and the cross sections (with enough measurements for minimizing statistical errors).\textsuperscript{65,82,83} Image analysis measurements were used to determine relationship of size and distribution of porosities with processing parameters and results are summarized in Table 3. It is necessary to emphasize that change in porosity with processing parameter are in agreement with experimental observations on properties of the deposited nanostructures. For example, frequency and duty cycle of pulsed current are inversely proportional to the properties of nanolayers, especially corrosion resistance.\textsuperscript{72,117} It is well known that corrosion resistance is affected by the surface activity of porosities or the amounts of dangling bonds which is related to the average coordination number of the nanostructured layer. Table 3 shows that $n_I$ decreases with increase in duty cycle, i.e., increase in surface porosity and hence leads to decreased corrosion resistance.

| Table 3 |
|---|---|---|
| Increasing (▲) of processing parameter | $n_T$ | $n_S$ | $\bar{Z}_T$ |
| Frequency | ▲ | ▲ | ▲ |
| Duty cycle | ▲ | ▼ | ▼ |
| Treatment time | ▲ | ▼ | ▼ |
| Current density | ▲ | ▼ | ▼ |
| Applied potential | ▲ | ▲ | probably |

*) ▲ = increase, ▼ = decrease, ▼ = approximately constant
5. MORPHOLOGICAL ASPECTS OF ACHIEVED NANOSTRUCTURES

5.1. Growth Kinetics and Size Effect

Phase analysis, X-ray diffraction patterns and growth kinetics for nanocrystalline coatings have been reported in some researches.\textsuperscript{75,87,118} Based on the composition of electrolyte, different hard layers can be deposited. Usage of nitrogen containing organic electrolyte causes the formation of complex carbonitride with the general formula of $MC_xN_{1-x}$ ($M$ = substrate metal). Based on the experiments, the amount of $x$ in this general formula is mainly related to the factors affecting the coating process such as the peak of applied voltage and the frequency of pulsed current rather than the ratio of carbon to nitrogen (C/N) in electrolyte. These factors affect the plasma medium and its containing species differently and thus cause different amounts of carbon and nitrogen atoms to accelerate toward the sample. It was revealed that average $MC_xN_{1-x}$ nanocrystallites sizes start from near 4 nm to higher values. Presence of dense nanocrystalline coatings has been confirmed by field emission scanning electron microscope (FESEM) and transmission electron microscope (TEM) images in Figure 6.\textsuperscript{43} Direct current has high growth rate while its average size of nanocrystallites (ASN) is relatively bigger and its layer has more porosities. Applying pulsed current will cause the growth rate to decrease and denser layers can be achieved. Bipolar pulsed currents will decrease the growth rate more than monopolar pulsed currents do. As the vector shown in Figure 7 illustrates, increasing the frequency of applied pulsed current is similar to decreasing its duty cycle for lowering the growth rate and hence, decreasing the ASN and the amount of porosities. Unlike the direct current, monopolar pulsed current (generally pulsed current) will affect more on the growth rate rather than bipolar pulsed current.

Higher frequencies will lead to higher densities of sparks on the surface, which cause lower dimensions of volcano-like structures and thus decrease the roughness of the coating. One of the important applications of these coatings is in anti-abrasive industrial parts and hence, lower roughness values are among their advantages. As indicated in other research, achieved nanocrystallites with lower length-to-diameter (L/D) ratio also showed lower ASN and narrower distribution of nanocrystallites. It was revealed that lower ASN of nanocrystallites can lead to higher band gap energy of the fabricated layer (Figure 8). This kind of size dependency has been observed also for some other kinds of nanocrystallites.\textsuperscript{119-121}

In comparison with used direct current (DC), the pulsed CPE method effectively assists $MC_xN_{1-x}$ nucleation. Nucleation densities of the coatings fabricated by the pulsed CPE were around 100 times higher than those fabricated by direct current. The difference in $MC_xN_{1-x}$ growth characteristics by two kinds of CPE method could outcome from the difference in the distribution of sparks and the amount of diffusive elements. As the power of plasma for bombardment of diffusive elements is directly related to the peak of applied voltage, the pulsed current can improve the concentration of saturated layer on the surface of the sample. The concentration of diffusive elements will be changed along the compound layer gradually while it has been observed that the slope of their change in diffusive layer is higher than...
5.2. Correlation among Nanostructure and Properties of Layers

It has been proved that the properties of obtained nanolayers are in close relation with their morphological characteristics. These morphological characteristics can be characterized by the shape of nanocrystallites and size distribution of nanostructured layers. It has been discussed in previous sections that the morphological characteristics depend on the processing parameters such as applied potential and current density; hence tailoring these factors can lead to nanostructured layers with desired properties. The average sizes of nanocrystallites for CPE treated surfaces can vary from few nanometers to 100 nm; but usually it is less than 70 nm. Distribution of nanocrystallites usually shows a Gaussian shape, and a Gussian distribution with no kurtosis and skewness can enhance electrochemical and mechanical properties of deposited nanocrystallites layers to a high degree. Figures 10 and 11 show different examples of deposited nanostructures by CPE and their relative distributions.

Statistical tools were used to study relation between properties of the nanostructured layers, and length-to-diameter ratio of nanocrystallites (L/D) and height-to-width (H/W) of the Gaussian distribution curve. It was observed that the nanocrystallites with high H/W ratios have lower average nanocrystallite size and lower L/D ratios. Higher H/W ratios indicate tighter distribution of the nanocrystallites around a specific average size, which have exhibited better corrosion and wear resistances.

5.3. Electrochemical Properties of Nanostructured Layers

As per the research done by the authors on CPE, applied voltage and treatment time are the most significant factors that have effect on electrochemical properties of nanostructured layers. The electrochemical properties of the CPE processed substrate have been studied by potentiodynamic polarization (PDS) and electrochemical impedance spectroscopy (EIS). The polarization resistances of carburized 316 stainless steel substrate with CPE at different conditions varied between 153.4 KΩ.cm² and 635 KΩ.cm² as compared to an unprocessed substrate with maximum polarization resistance of around 10 KΩ.cm². Obtained results indicate that the corrosion resistances of obtained layers are in inverse relation of their ASN, e.g., a treated substrate (316 austenitic stainless steel) with ASN ~ 73.5 nm exhibited corrosion resistance ~ 218.6 KΩ.cm² as compared with a treated substrate with ASN ~ 47.7 nm with corrosion resistance ~ 548.4 KΩ.cm². The research revealed
that the CPE conditions for achieving maximum polarization resistance were 700 volts for the peak of applied cathodic voltage, 15 kHz for the frequency of pulsed current, 40°C for the temperature of electrolyte and 10 minutes for the treatment time. The polarization resistance of the 316 SS substrate increased to 930 KΩ·cm² by applying these parameters.

It has been revealed that the nitrogen diffusion by CPE will postpone the pitting phenomenon of stainless steels in corrosive media. On AISI 304, applied DC voltage of 260 volts completely increased the corrosion resistance, although applied voltage of 245 volts is sufficient for protection against pitting. For AISI 430, nitrogen diffusion by applied voltages near 230 volts can completely increase the corrosion potential and corrosion current density. On AISI 316L, nitrogen diffusion produced by applied voltages among 230 to 260 volts decreases the corrosion rate to some extent and does not improve in corrosion resistance. More than likely, higher amounts of alloying elements (mainly Mo), hinder the effect of nitrogen diffusion in 316L stainless steel.

Carbon diffusion in AISI 304 by CPE increases the localized corrosion resistance. Diffusions produced by applied voltages above 260 volts have shown to enhance the corrosion behavior by fabrication of a surface layer, which could increase protection of passive layer. The authors are investigating the microstructure of the diffused layer to understand the mechanism of observed improvement in corrosion behavior. In contrast, carbon diffusion by CPE can be harmful for AISI 430 and will cause low pitting resistance. Comparing with other methods for fabrication of similar coatings, CPE strongly shows better electrochemical properties.

Corrosion tests also showed that CPE fabricated coatings have enhanced biocompatibility (better than their titanium substrate) and hence CPE can be used to develop coating for biomedical applications. Titanium and its alloys are widely used biomaterials were processed by CPE and corrosion results in simulated body fluids such as Ringer's electrolyte showed enhanced corrosion resistance of the coated substrate than untreated substrates. It has been revealed that CPE processed substrates have more noble corrosion potential ($E_{corr}$), lower corrosion current density ($i_{corr}$) and higher polarization resistance (PR) than untreated samples, which shows that CPE has great potential for biomedical applications.

5.4. Mechanical Properties of Nanostructured Layers

CPE significantly reduced the friction coefficients and wear volume loss of the carbonitrided titanium alloys as compared to the unprocessed substrates. These deposited layers also exhibited high surface hardness, strong adhesion to substrate, and high fracture toughness. Mechanical properties of CPE formed layers are affected by applied voltage, treatment time and current density. The roughness of the nanostructured layers increases by increasing the applied voltage of CPE, but the rate of increase in roughness decreases up to 600V, and increases thereafter. An increase in applied voltage leads to a decrease in ASN and at the same time increases impact of micro and nano sparks on the processed substrate. As per earlier research sparks imploding of the processed surface enhances the surface roughness. But, smaller crystal size will have a tendency to reduce the surface roughness. More than likely, after 600 V both the impact of sparks and crystal size increase due to higher temperature at processed substrate leading to increase in rate of surface roughness. Statistically, the increase in skewness and kurtosis of distribution of nanocrystallites after its normal mode will lead to increase in roughness, which may not be suitable for certain industrial application due higher friction coefficient of rougher surfaces.

It has been observed that thickness of the deposited nanolayer changes linearly with the square root of the treatment time for CPE. It is well known that the thickness of nanolayer
FIG. 11. Distribution curves of nanocrystallites for relative (a) and (b) treated samples which their nanostructures have been shown in figure 10. (Reprinted with permission from Aliofkhazraei et al. Copyright 2009: Elsevier.)

Layer has an affect on mechanical properties of the substrate. Equ. 8 shows the relationship between thickness of deposited layer to the applied voltage for CPE.

$$Th = \alpha V + \beta (V_{\text{Sparking}} < V < V_{\text{Interrupt}})$$  \[8\]

Where $Th$ and $V$ are thickness of influenced layer and applied voltage, respectively. $\alpha$ and $\beta$ are constants. $\alpha$ is related to the treatment time and $\beta$ is related to the modified transmission coefficient of treated media.

The hardness of the nanostructured layer usually decreases gradually with depth of the processed layer into surface of the substrate. The thickness of the obtained layer will not increase after an optimum level of treatment time, which might be related to diffusion limited system after a certain thickness is reached.\(^{43,83}\) Comparing with other methods for applying of similar coating,\(^{140-142}\) CPE can be useful for special industrial parts, which have problems for surface hardening and coating with other methods.

6. CONCLUSION

The setup, performance and properties of CPE have been reviewed with a focus on its use in deposition of nanostructured layers. The importance of design of CPE cell, along with the processing parameters, has been discussed with respect to their influence on properties of nanolayers. The mechanism of CPE has been reviewed; however, authors feel that tremendous opportunity exists in fully understanding the mechanism. Authors have discussed the influence nanostructural characteristics such
as average size, distribution and average coordination number of nanocrystallites on mechanical and electrochemical properties of CPE deposited nanostructures layers. CPE presents a strong potential for various industrial applications, either replacing conventional processes or solving challenging posed by current processes.

ACKNOWLEDGMENTS

The authors would like to acknowledge the financial support for investigations on CPE by Arvandan oil and gas Production Company and Iranian nanotechnology initiative council. The authors would also like to thank Dr. J.A. Curran from Cambridge University for the useful discussions during different aspects of plasma electrolysis.

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