

Cast iron plasma nitriding in $N_2/H_2/Ar$ working gas: the role of auxiliary gases (H_2/Ar) in the growing kinetics of compound layers

Luis César Fontana ^{1*} 

David Pascoal Sudaia ¹

Abel André Cândido Recco ¹

André Olah Neto ¹

Paulo César Borges ²

Wilson Luiz Guesser [†]

Abstract

Present paper sets out to investigate the role of $N_2/H_2/Ar$ working gas in plasma nitriding of nodular cast iron. The proportion of $N_2/H_2/Ar$ proved to be a relevant parameter in the growing kinetics control of the $\gamma'-Fe_4N$ e $\epsilon-Fe_3N$ compound layers. X-ray diffraction and optical microscopy were used in order to characterize the compound layers. Results indicate that there are no generation of compound layers if the treatment is performed through plasma of pure N_2 . However, even small percentages (~10%) of auxiliary gases (H_2/Ar), added to the working gas, are enough to generate compound layers as thick as $10\mu m$ (at $500^\circ C$, and 3,0 h). In addition, it is possible to obtain $\gamma'-Fe_4N$ monophasic compound layer when the nitriding process is carried out in low proportion of nitrogen in the $N_2/H_2/Ar$ working gas mixture.

Keywords: Plasma nitriding; Nodular cast iron; Working gas.

1 Introduction

Plasma nitriding is a well-known surface treatment process which aims to generate nitride layers in order to increase the surface hardness of metals. In general, the nitrided layers are constituted by a compound layer (white layer) and a diffusion zone [1,2]. Only a few papers on nitriding of nodular cast iron are found in the literature, although this material has been widely used in the automobile industry and other applications for structural parts. Nodular cast iron is a low-cost manufacturing material and show technical features such as good machinability and hardenability. In general, products built with nodular cast iron show good mechanical resistance associated to good toughness and shock resistance, even in their raw state. Despite the properties that make the cast iron a very useful material, it would be possible to expand its applications through increasing the wear resistance, in order to promote a longer useful life of parts subjected to relative motion and friction. This increase in wear resistance can be obtained through surface treatments, such as plasma nitriding [3-5]. Cast iron plasma nitriding may improve several surface properties as wear resistance, corrosion resistance, fatigue, among others. Dong et al. [6] shown a two steps process: first, the process is carried out in a poor N_2 plasma atmosphere ($5\% N_2 + 95\% H_2$) which produce a thick hardened case (up to $300\mu m$)

through the sharp edges of spheroidal graphite cast iron; the second step of the treatment consist in plasma nitriding in a rich N_2 atmosphere ($25\%N_2+75\%H_2$) just for growth a compound layer as Fe_4N . The authors conclude that the two-stage nitriding process can form a dual layer with a large thickness of the diffusion layer on cast iron substrate, which is critical to the retention of the sharp edges of cast iron component. Writzl et al. [7] investigated a duplex surface treatment on compacted graphite iron (CGI), which consist in plasma nitriding followed by laser hardening. They concluded that the duplex treatment greatly increases the layer scratch resistance. Santos et al. [8] studied plasma nitriding of pre-textured surfaces of components made in pearlitic gray cast iron. They show that plasma nitriding carried out at low temperatures and short times, can increase the surface hardness without change roughness pattern of the previously textured surface. Another interesting research was carried out by Wollmann et al. [9], which investigated the rolling contact fatigue (RCF) of plasma nitride ductile cast iron. They have concluded that brittle thin layer formed after plasma nitriding may reduce the RCF life, so that, it is necessary prevent the growing compound layer, during the plasma nitriding, when the treatment aims to rolling contact fatigue application. Regarding to the plasma parameters

¹ Laboratório de Plasmas, Filmes e Superfícies, Centro de Ciências Tecnológicas, Universidade do Estado de Santa Catarina, UDESC, Joinville, SC, Brasil.

² Universidade Tecnológica Federal do Paraná, UTFPR, Curitiba, PR, Brasil.

[†] W. L. Guesser, In memoriam, UDESC, Joinville, SC, Brasil

*Corresponding author: luis.fontana@udesc.br



influences, other papers have been demonstrated that the voltage waveform (e. g. pulsed plasma, DC plasma, and bipolar plasma) has a great influence on the growing kinetics of the nitride layers and diffusion zone [10,11].

Compound layers growing kinetic, during plasma nitriding of metals parts, can be controlled through several parameters, such as: voltage intensity, temperature, work pressure and composition of the working gas. Present paper sets out to investigate the kinetics of formation of nitride layers in an N_2 plasma with different proportions of auxiliary gases Ar/H_2 . Changing the composition of the working gas would allow us to modify the plasma reactivity and the energy provided to the cathode surface (parts to be treated). For example, the cathode heating depends on the energy provided by ions from the plasma. In addition, the ion bombardment can activate the atomic diffusion on the surface of cathode. On the other hand, this bombardment can cause re-sputtering of adsorbed nitrogen atoms, which may reduce the concentration of these atoms on the surface to be treated. Therefore, the bombardment intensity is a very important parameter to improve the treatment efficiency, since it can activate the diffusion of reactive atoms adsorbed on the surface. However, excessive bombardment may produce excessive spraying of nitrogen adatoms. Therefore, the physicochemical characteristics of the working gas atoms can work as a control parameter in plasma nitriding processes.

Hydrogen has been frequently used as a component in the working gas because it can perform different roles in the plasma nitriding process. Among the beneficial effects of hydrogen in the working gas, it can be highlighting the reduction of oxides and organic compounds pre-existing on the metal surface and the increasing in the plasma ionization rate. In the specific case of cast iron plasma nitriding, active hydrogen generated in $N_2/H_2/Ar$ plasmas can promote a “cleaning” on the surface of the parts. Diverse species produced into the plasma, as atomic hydrogen and excited H_2 , can react with carbon on surface, resulting in volatile hydrocarbons, which may be eliminated through the vacuum pumping. The removing of carbon atoms from the surface allows increase the nitrogen adsorption on surface. This nitrogen adatoms can, subsequently, diffuse toward the parts core, which contribute to the growing of nitride layers. Another benefit of eliminating carbon atoms from the surface, through its reaction with hydrogen from plasma, is the improvement the nitrogen interstitial diffusion, once the carbon and nitrogen act as competitive elements at interstices of the iron crystal lattice [12,13]. Additionally, an increase in the plasma ionization rate is observed when the proportion of hydrogen in the $H_2/(H_2+N_2)$ mixture is around 25% [14]. Therefore, the use of hydrogen in the working gas atmosphere can improve the plasma properties and can improve the absorption of nitrogen on the surface of parts. Thus, it is possible to control the formation of different nitride phases (ϵ - $Fe_{2,3}N$, γ - Fe_4N , besides the diffusion layer) through the change in the concentration of H_2 in the N_2/H_2 gas mixture in the plasma atmosphere [15,16].

Furthermore, the use of argon (inert gas) in the plasma atmosphere, in addition to nitrogen, gives rise to Ar^+ ions, which can bombard the surface during plasma nitriding. Even low Ar percentage, as 10%, is sufficient to promote some sputtering from cathode and surface heating [17]. According to Fancey et al. [18], in an N_2/Ar plasma, Ar^+ ions are responsible for more than 90% of the bombardment on cathode surface. The atomic mass of Ar (39.9 g/mol) has a value of almost 70% of Fe mass (55.8 g/mol), so that the Ar^+ bombardment on ferritic surface can effectively transfer moment to the Fe atoms [19]. Thus, argon bombardment increases the vibrational energy in the metal’s crystal lattice at region close to the surface. Furthermore, Ar also can contribute to increase the dissociation of molecular nitrogen (in plasma) and the maximum dissociation may occurs when the $Ar/(Ar+N_2)$ ratio is around 0.5 [20]. This mechanism contributes to supply atomic nitrogen to the cathode surface and contribute to the formation of thicker nitride layers and diffusion zone. The main variable for increasing diffusivity in solids is the temperature, as shown in Equation 1 [21] (where D is the diffusivity, D_0 the diffusion coefficient, Q_d is the activation energy, R is the molar gas constant and T is the absolute temperature). The surface bombardment through Ar^+ ions contribute to increase the localized temperature at surface of the cathode, consequently it can increase the diffusivity of the nitrogen atoms adsorbed there, as predict Equation 1. On the other hand, the Ar^+ bombardment can provoke pulverization of adsorbed nitrogen atoms, so that Ar^+ hitting on surface can produces a competitive process between the adsorption and desorption of nitrogen atoms. It is difficult to find an optimized condition for nitriding due to many concurrent effects, as there are many interdependent variables in the plasma nitriding process, such as: voltage, applied voltage waveform, plasma and surface temperature, gas mixture, working gas pressure, surface chemical composition, among others shape conditions.

$$D = D_0 e^{-\frac{Q_d}{RT}} \quad (1)$$

Considering the attributes of argon and hydrogen as additional gas in the atmosphere of plasma, as discussed above, present paper set out to investigate the use of auxiliary gases H_2/Ar for surface treatment of nodular cast iron. The use of both gases H_2/Ar , besides N_2 , may produce synergistic effects on the growing kinetics of compounds layers and on the guidance of crystalline phases of nitrides.

2 Materials and methods

Nodular cast iron samples were treated in plasma with different proportions of $N_2/H_2/Ar$ working gas. The plasma was generated inside a vacuum chamber, built in stainless steel, with dimensions of 300 mm in diameter and 300 mm in height, containing three glass windows that allows the plasma visualization. The samples temperature measurement

was carried out through a thermocouple k-type housed into a standard sample. The N₂/H₂/Ar proportion was driven by Mass Flow Controllers, which allow the flow control of each gas through the chamber. The total gas flow was kept constant at 50 sccm. The working gas pressure into the chamber was adjusted through a butterfly valve placed between the chamber and the vacuum pump. The plasma was generated using a power supply which could provide adjustable voltage between 0 and 1000V. The treatment time was 3.0 hours, and the working gas pressure was adjusted between 1.5Torr and 2.5Torr in order to keep the temperature of the samples at 500 °C (Table 1 show the treatment parameters). The discharge current intensity depends on the voltage, the working gas composition and pressure, among other variables (e. g. cathode area/geometry, anode-cathode distance, etc.). In this work the discharge current range was between the values of 70 mA and 155 mA.

The chemical composition (%weight) of the nodular cast iron samples, used in this work, is the following: 3.86%C; 2.49%Si; 0.40%Mn; 0.025%W; 0.008%S; 0.023%Cr; 0.004%Sn; 0.5% Cu; 0.041%Mg. This material contains a large amount of carbon, most of which is in the form of graphite, which is the stable form of carbon in iron. Carbon atoms can also occupy interstitial sites in the crystalline iron lattice and so, it can make difficult the nitrogen diffusion during the plasma nitriding, as discussed above, in the introduction. The samples were hand-sanded (up to 1200-grain sandpaper) and polished with 0.3 μm alumina. After the nitriding treatments, the specimens were sectioned perpendicularly to the nitrated surface. The samples were then embedded in Bakelite and again sanded and polished. Subsequently, the samples were etched with 2% nital, during 20s, in order to reveal the nitride layers and other phases in the bulk, which could be visualized through a conventional optical microscope. The final layer thickness values were obtained after 20 measurements on each specimen, from which the means and standard deviations of each series of measurements were calculated. The crystalline phases were determined by x-ray diffraction measurements (λ=1.54 Å; V=40.0 kV).

3 Results and discussion

Results analysis and discussion are made by correlating the thickness of nitride layers and the respective crystalline

phases formed, γ'(Fe₄N) and/or ε(Fe₂₋₃N) accordingly to the plasma parameters used for the treatments of cast iron samples.

Figure 1 shows XRD and layers thickness results for samples treated in four working gas composition: 1- pure nitrogen; 2, 3- containing just one auxiliary gas in the N₂ plasma (N₂/H₂ or N₂/Ar); 4- containing both auxiliary gases (N₂/[H₂+Ar]). Results shown that there is no compound nitride layer formation if the treatment is carried out with pure nitrogen plasma. As the nodular cast iron may contain high concentration of carbon atoms at interstitial sites, the interstitial diffusion of nitrogen atoms may be low. However, when 20% of hydrogen is added to the plasma atmosphere (0.8N₂/0.2H₂), it is observed the generation of nitride compound layers with approximately 8μm thickness, composed by ε-(Fe₃N) and γ'-(Fe₂N) phases. It is important to point out here that hydrogen in the working atmosphere, in the range of 10%-20%, increases the plasma current. Higher plasma current implies in greater ionic bombardment on the cathode surface and greater plasma reactivity. The increasing in the plasma reactivity can be correlated to greater dissociation of molecular nitrogen and generation of excited atoms and molecules. In addition, hydrogen can contribute to eliminate carbon atoms from the cathode surface, by forming C_xH_y hydrocarbons. In short, the hydrogen as an auxiliary gas in the plasma atmosphere may contribute to generation of nitride layers on cast iron through indirect mechanisms, such as: 1- surface decarburization of parts, during the plasma nitriding, through formation of volatile hydrocarbons; 2- there is an increase in plasma current, which may intensify the generation of active species in the plasma, such as atomic nitrogen and excited molecular nitrogen. High reactive nitrogenous species may increase the concentration of nitrogen on surface, which may activate the atomic diffusion toward the core (as provided by Fick's laws).

In turn, the use of argon as an auxiliary gas can generate more dense plasma. The argon contributes to increase the plasma electron density, that is, it increases the ionization rate. The gas mixture of 40%N₂/60%Ar can generate plasma with high density and high electronic temperature [22]. Figure 1b shows that the plasma nitriding carried out with working gas proportion of 40%N₂/60%Ar can generate nitride layers with 6,2 μm thickness, composed by phases ε-Fe₃N and γ'-Fe₄N. As already has been discussed in the introduction, the Ar atoms have atomic mass close to Fe atomic

Table 1. Plasma parameters used for surface treatment of nodular cast iron

| Working gas composition | %N ₂ | %H ₂ | %Ar | V _{plasma} ±10 (V) | Time (h) | Temp. ±5(°C) | Pressure ±0,2(Torr) | I _{plasma} ±10 (mA) |
|------------------------------------|-----------------|-----------------|-----|--------------------------------|----------|-----------------|------------------------|---------------------------------|
| N ₂ | 100 | - | - | 440 | 3.0 | 500 | 2.2 | 70 |
| N ₂ /H ₂ | 80 | 20 | - | 440 | 3.0 | 500 | 2.5 | 95 |
| N ₂ /Ar | 40 | - | 60 | 440 | 3.0 | 500 | 1.5 | 80 |
| N ₂ /H ₂ /Ar | 80 | 10 | 10 | 440 | 3.0 | 500 | 2.1 | 105 |
| | 70 | 20 | 10 | 440 | 3.0 | 500 | 2.0 | 120 |
| | 60 | 20 | 20 | 440 | 3.0 | 500 | 1.9 | 125 |
| | 20 | 20 | 60 | 440 | 3.0 | 500 | 1.6 | 155 |

mass and, therefore, the Ar⁺ bombardment can efficiently transfer energy to the iron surface. The Ar⁺ bombardment may also produce sputtering of atoms from the surface of the cathode. The sputtering of Fe atoms may activate another nitriding mechanism which consist in formation of the metastable FeN phase in the atmosphere near to the surface. The FeN can condensate on surface of the cathode, and it could be decomposed in ϵ -Fe₃N and γ' -Fe₄N, known as K lbe model [23]. However, results shown that it is generated thicker compound layer (approximately 11 μ m, Figure 1B) if the plasma nitriding is carried out with both auxiliary gases (Ar, H₂), at proportion about 80%N₂/10%H₂/10%Ar. In this case, Figure 1A show that the nitrided layer contain both ϵ (Fe₃N) and γ' (Fe₄N) phases. The greater thickness of the layer can be attributed to the effects produced by both auxiliary gases (Ar, H₂), in association to the main working gas N₂, which favor the formation of the nitride layers as discussed above. Table 2 presents numerical values of layers thickness and the respective crystalline phases generated.

Figure 2 shows results of samples treated in N₂/H₂/Ar plasma, where the concentration of H₂ was kept constant at 20%. The Ar percentage was between 0 and 60%, with N₂ balance. Figure 2b show that the maximum compound layer thickness occurs for argon percentages of 10% and

20%. The layer thickness decreases for nitriding carried out in plasma with high Ar content (60%) associated to low N₂ content (20%); furthermore, this working gas composition favor the growing of Fe₄N single phase as shown in the X-ray diffractogram (Figure 2a). This result is particularly interesting because the ϵ (Fe₃N) phase is brittle and can compromise the performance of nitrided parts [24]. Table 3 show numerical values for the layer thickness, with the respective standard deviation values, and the corresponding crystalline phases.

Figure 3 show a comparison between samples treated in plasma containing high proportion of nitrogen (60% to 80% of N₂, with balance of auxiliary gases H₂-Ar). It is observed the formation of both ϵ (Fe₃N) and γ' (Fe₄N) crystalline phases (Figure 3a) and the generation of compound layers with thickness above 10 μ m (Figure 3b). However, no significant changes have been observed on layers thickness and in the XRD peaks intensity, corresponding to the ϵ and γ' crystalline phases. So that, it can be stated that the kinetics of compound layer formation is not affected by small changes in the proportion of H₂-Ar mixture, during plasma nitriding of nodular cast iron, if the plasma atmosphere contains high N₂ percentage (between 60% and 80% of N₂).

Figure 4 shows optical micrographs of the cross section of nodular cast iron samples, after plasma nitriding

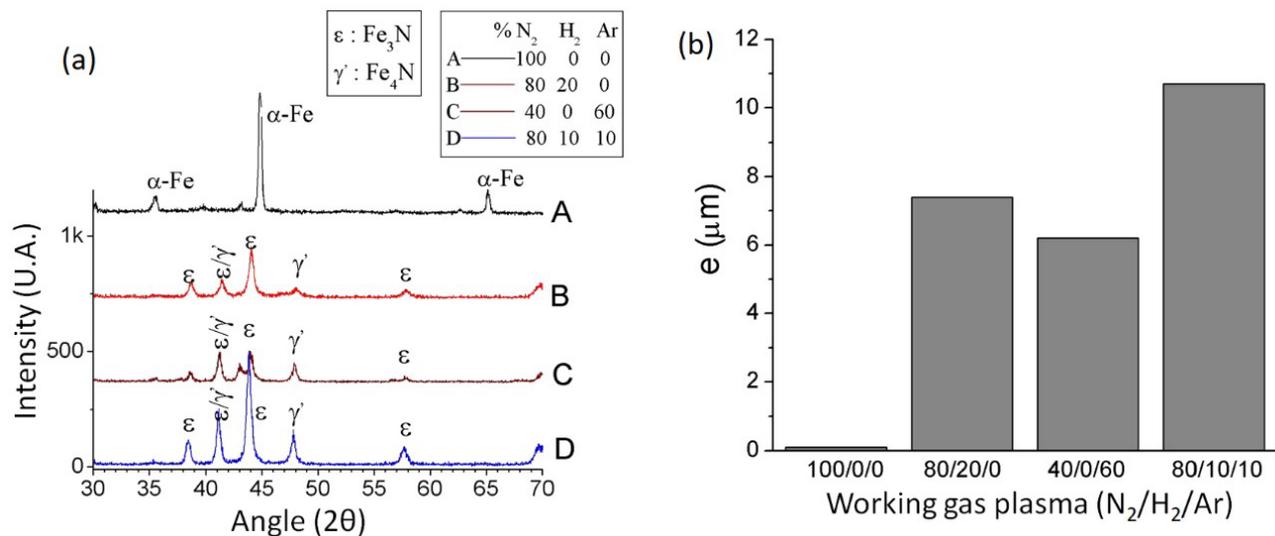


Figure 1. (a) XRD results for cast iron samples treated through plasma generated in different working gas composition N₂/H₂/Ar (t=3,0h, T=500°C); (b) Compound layers thickness.

Table 2. Thickness and crystalline phases of Nodular Cast Iron samples treated by plasma nitriding, carried out in different compositions of the working gas (N₂/H₂/Ar)

| | Working gas composition (%) | | | Layer thickness (μm) | Standard deviation (μm) | Phases |
|---|-----------------------------|----------------|----|----------------------|-------------------------|--------|
| | N ₂ | H ₂ | Ar | | | |
| 1 | 100 | – | – | – | – | α-Fe |
| 2 | 80 | 20 | – | 7.4 | 1.6 | ε+γ' |
| 3 | 40 | – | 60 | 6.2 | 1.1 | ε+γ' |
| 4 | 80 | 10 | 10 | 10.7 | 1.4 | ε+γ' |

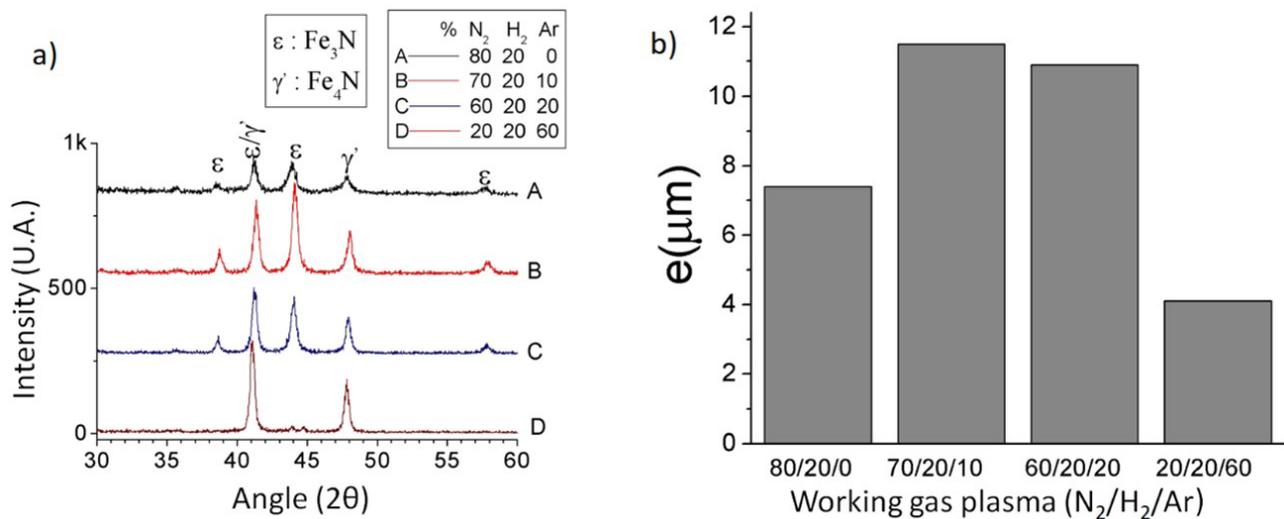


Figure 2. (a) XRD results for samples treated in plasma with different proportions of working gas N₂/H₂/Ar, keeping the H₂ percentage constant at 20%; (b) the compound layers thickness.

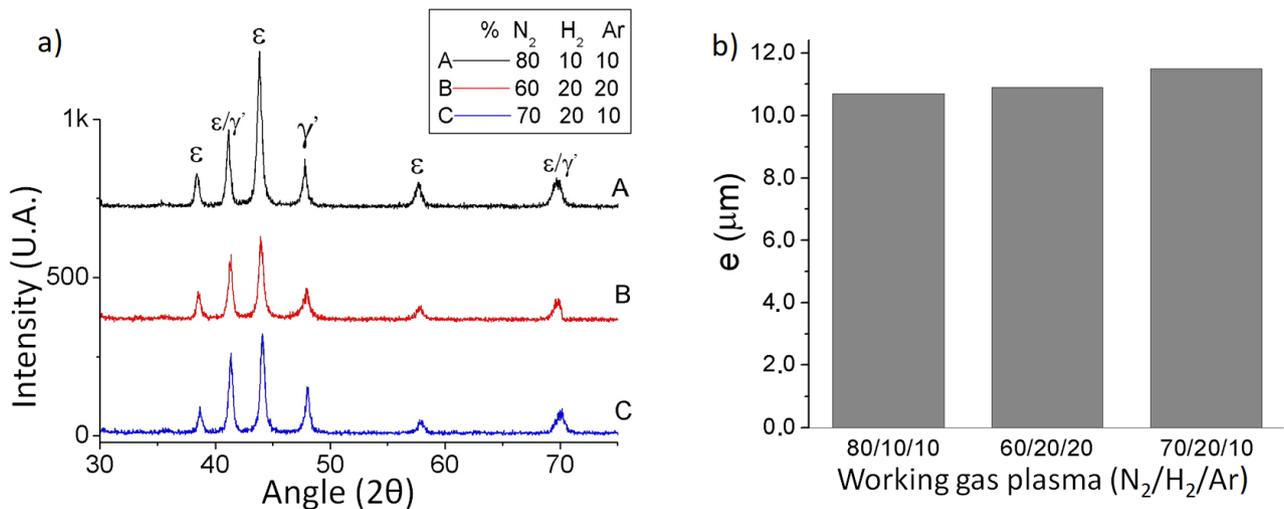


Figure 3. Results of compound layers obtained through plasma nitriding carried out in N₂/[H₂+Ar] working gas. The percentage of each auxiliary gas, H₂ and Ar, was 10% or 20% and N₂ balance. (a) XRD results; (b) compound layers thickness.

Table 3. Nitride layers thickness as a function of the composition of the working gas plasma; the H₂ percentage was kept at 20% (500 °C / 3h)

| Working gas (%) N ₂ H ₂ Ar | | | Compound Layer (μm) | Standard deviation (μm) | Crystalline Phases |
|--|----|----|---------------------|-------------------------|--------------------|
| 80 | 20 | 0 | 7.4 | 1.6 | γ'+ε |
| 70 | 20 | 10 | 11.5 | 1.7 | γ'+ε |
| 60 | 20 | 20 | 11.0 | 1.7 | γ'+ε |
| 20 | 20 | 60 | 4.1 | 0.5 | γ' |

carried out at 500°C, for 3.0h, in two different atmospheres: (a) with low percentage of auxiliary gas (80%N₂ / [10%H₂ + 10%Ar]) and (b) with high proportion of the auxiliary gas Ar (20%N₂/20%H₂/60%Ar). The nitriding carried out in nitrogen-rich plasma favors the generation of thicker layers (Figure 4a), which are composed by two phases, γ' e ε.

Otherwise, if the plasma nitriding is carried out in nitrogen-poor working gas (low %N₂; high %Ar), it generates smaller thickness layer (Figure 4b). However, this thinner layer is constituted by a single-phase γ', as showed in XRD results (Figure 2a). The Figure 4b, show also that the nitride layer is thicker in the ferrite region (above the graphite) than in the

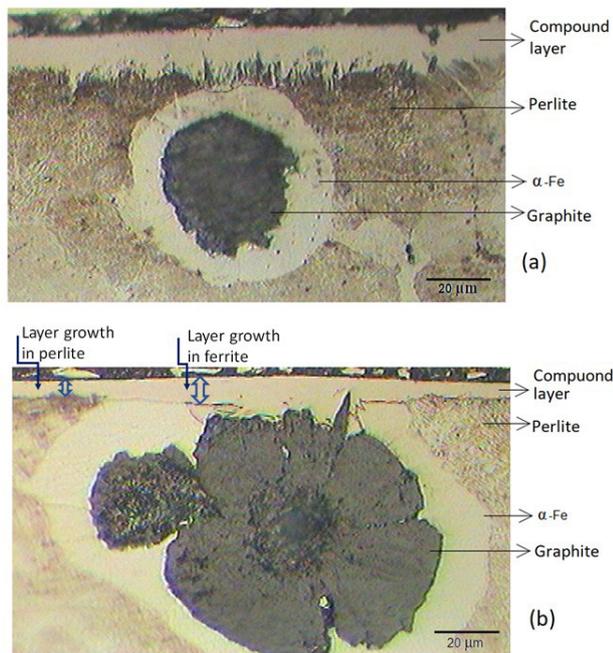


Figure 4. Cross section of nodular cast iron samples, after plasma nitriding carried out at 500°C, for 3.0h, in two different atmospheres: (a) with low percentage of auxiliary gas (80%N₂ / [10%H₂ + 10%Ar]) and (b) with high proportion of the auxiliary gas Ar (20%N₂/20%H₂/60%Ar).

perlite region. This greater thickness of the nitride layer is attributed to the greater nitrogen diffusivity in ferrite structure than in perlite. As the perlite is carbon-rich and the carbon atoms may occupy interstitial sites in the crystal lattice, it can make difficult the interstitial diffusion of nitrogen in the perlite microstructure.

4 Conclusion

Results show that the changing on working gas composition (N₂/H₂/Ar) can induces significantly changes on kinetics of formation of nitride layers during plasma nitriding of nodular cast iron.

Despite the need of a much more detailed model to explain completely the role of H₂ and Ar on plasma

nitriding of nodular cast iron, we would like to highlight the following features:

- Both auxiliary gases, Ar and H₂, produces synergistic effects on plasma nitriding of nodular cast iron and allow the control on case depth. The synergistic effects consist in two hypotheses: 1- better energy transfer from plasma to surface through Ar⁺ bombardment; 2- surface cleaning due to reactions of activated hydrogen (from plasma) with carbon atoms on cast iron surface, so it may create volatiles C-H which may be eliminated through vacuum pump;
- Both, Ar and H₂, induces an increase of discharge current which means an increase in ionization rate in the plasma;
- It is observed an improvement in crystallization and in grow rate of the compound layers (ϵ -Fe₃N and γ' -Fe₄N);
- The use of auxiliary gases, Ar+H₂, in plasma nitriding of nodular cast iron, can generate thick compound layers (ϵ -Fe_{2,3}N and/or γ' -Fe₄N), with thickness in the order of 10 μ m for treatment carried out at 500°C, during 3.0h;
- If there are no auxiliary gases, Ar+H₂, it is observed that there is no formation of compound layer in nodular cast iron nitriding, for parameters used in present work;
- Single-phase layers constituted by γ' -Fe₄N, which are tougher than ϵ -Fe_{2,3}N, can be generated through cast iron nitriding in plasma with low N₂ percentage and high Ar percentage (20%N₂/20%H₂/60%Ar);
- In short, the proportion of the auxiliary gases (H₂, Ar) in the plasma working gas, can be used as a process parameter to control the layer properties, as the thickness and the crystalline phases of nitrides.

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