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RESEARCH ARTICLE

COMPARATIVE STUDY ON PLASMA NITRIDING IN CATHODIC CAGE WITH CONVENTIONAL NITRIDING OF THE AUSTENITIC STAINLESS STEEL 316

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ABSTRACT

The present work is based on a comparison between nitriding plasma technique described as CCPN (Cathodic Cage Plasma Nitriding) and the conventional DCPN (DirectCurrent Plasma Nitriding). Here the nitriding process applied on the AISI 316 stainless steel was investigated under the following conditions:constant pressure of 5mbar at temperatures of 400, 450 and 500°C. The cathodic cage used allowed the deposition and thermal treatment in three-dimensional way on samples and guaranteed excellent deposition rate and the growth of the layersonactivated thermal surfaces. The nitriding process appliedwith the cathodic cage produced the same properties related to the conventional one (DCPN) by eliminating common problems associates with this procedure, especially, the edge effects. The thickness of the nitrided layer obtained by the usage of the cathodic cage was closer to the one obtained by DCPN process, however with lower adhesive wear when is compared with ionic nitriding. The ideal temperature in nit riding mixture of 80% N_2 - 20% H_2 for the procedure with the cathodic cage was 450°C. These also contributed to thickening the layers and improve themicro hardness as well as the wear resistance of the material.

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INTRODUCTION

Austenitic stainless steels are widely used in the industry field because these materials present high performance when they are submitted to harsh environment due to their excellent general corrosion resistance (Novak, 1977; Lo *et al*., 2009; Antunes *et al*., 2010; Karimi *et al*., 2012). However, one drawback of these steels is that they still present some limitation regarding to their insufficient corrosion resistance and poor conductivity due to the formation of oxide layers (Feng *et al*., 2011; Yang *et al*., 2014) which can lead to undesirable degradation under specific applications. It has been reported that the application of plasma nitriding technique son the austenitic stainless steel 316 have been improved in a considerable way its surface properties such as hardness, wear and corrosion resistances (Li *et al*., 2012; Kaijie *et al*., 2015).

So far, it is evident that the application of this procedure has the aim of obtaining and promotes suitable properties on the material for desirable applications and extends its lifetime (Zhao *et al*., 2005). Additionally, this is a clean process which allows an optimal control of the phases formed in the nitrided layers as well as its uniformity (Sousa *et al*., 2014). Furthermore, plasma nitriding on austenitic stainless steels at low temperatures represents a good mechanism in order to avoid the formation of chromium nitride due to its lower diffusivity leading to better surface properties (Menthe *et al*., 2000). As mentioned above, it is well known that stainless steels have poor abrasion resistance and attempts have been made in order to promote their hardness, wear and corrosion resistance. These contributed to the development of number of techniques associated with the surfaces modification. Since the 80's, surface modification techniques such as the ones modified by reactive gas and ion bombardment, ion implantation, as well as the deposition of surface films have gone through significant advances (Somers, 1995; Riofano, 2002; Pranevicius *et al*., 2001).

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These advances now use techniques by application of plasma, electron beam, laser chemical and physical vapor deposition. They contributed to gradually replace conventional techniques such as electroplating, galvanizing, liquid nitriding, carburizing and other that generate harmful substances to the environment and have low effectiveness compared with the modern techniques. Direct current plasma nitriding (DCPN) is one of the most conventional surface engineering treatment process used in industry over the past years (Zhao *et al*., 2006). However, this process has shown some shortcoming related to technological development which limits its further application. Among these limitations it is worth to mention the lack of complete understanding of the process and difficulties in maintaining a uniform temperature within the plasma chamber as well as its equipment high cost (Ahangarani *et al*., 2006). Moreover, when the components are treated inside the chamber, they are subjected to arching (Zhao *et al*., 2006), edge effect, hollow cathode effect, and holes (Alves *et al*., 2006; Ribeiro *et al*., 2008; Sousa *et al*., 2007).Despite of those drawbacks, this heat treatment has been receiving great acceptance in industry, i.e. automotive companies (Alves *et al*., 2006).

To overcome these undesirable limitations and effects on ion nitriding process, new improvements on DCPN techniques were developed such as radio frequency (RF) plasma nitriding, pulsed dc plasma nitriding and plasma immersion ion implantation which have been successfully scaled up at industrial applications (Gredelj *et al*., 2002; Baldwin *et al*., 1998; Mahboubi *et al*., 1996). ASPN (Active Screen Plasma Nitriding) shows more advantages over the DCPN in laboratory scale. The nitriding in active screen developed a new device called cathodic cage or ionizing cage that obtain uniform treated surfaces (Sousa *et al*., 2014; Ribeiro *et al*., 2006; Sousa *et al*., 2007). The ions formed in the vicinity of the cage are strongly accelerated towards the walls of the cage leading to atoms spraying. This favors the combination of the energized particles from the plasma to forming the compounds that will be deposited or diffused on the sample surface (Sousa *et al*., 2014).

In this study, the same principle of ASPN was used but with a modified experimental arrangement. It was based on the appearance of the hallow cathode effect produced in each cage bore to enhance the sputtering and deposition of compounds formed in the plasma over the surface of the samples (Li *et al*., 2002). The aim of the present study is comparing the effect of plasma nitriding process variables with the use of cathodic cage and without the use of the cathodic cage by making correlations between them from the different characteristics of the formed layers.

MATERIALS AND METHODS

The material used in this study was the austenitic stainless steel AISI 316 produced by Arcelor Mittal (São Paulo / SP) in the form of cylindrical bar with 12.7 mm in diameter and 3 m in length. Table 1 shows the nominal chemical composition of this alloy. The bars were cut into cylinder specimens with diameter of 12 mm, height of 3mm with upper and lower surfaces rectified to ensure parallelism between them. For the methodology of this work, two systematic studies of nitriding in Cathodic Cage (NCG) were developed. The first aimed on the intension of understanding the nitriding mechanism for this new technique while the second raised the intention to make the comparative analysis between them through temperature variations at constant pressure and nitriding mixture. The stainless steel AISI 316 samples were nitrided during 5 hours at temperatures of 400, 450 and 500 °C in nitriding mixture of 80% N_2 - 20% H_2 and constant pressure of 5mbar. The nitriding process with active screen was performed using the same configuration of the conventional nitriding chamber, but with the addition of an austenitic stainless steel AISI 316 cage. This apparatus presents thickness of 0.8 mm mounted on the sample holder, as shown in Fig. 1. The cage dimensions are 112 mm in diameter and 25 mm height. The diameter of the holes is 8 mm and the distance between centers of adjacent holes is 9.2 mm. The samples were placed on a 57 mm in diameter and 3 mm thick alumina disc to ensure electrical insulation and radial arrangement.

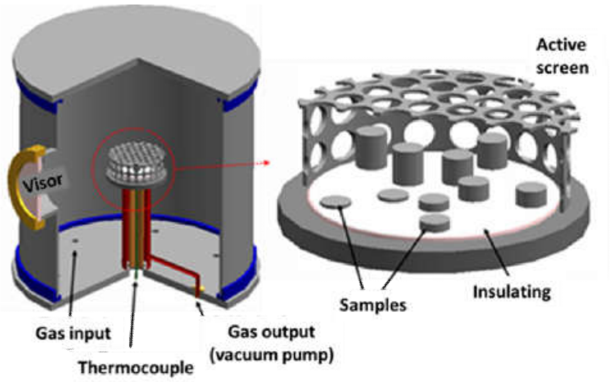

Fig. 1. Sectional view of the treatment reactor and detail of the cathode cage showing the spatial arrangement of the samples (Sousa *et al*., 2007)

For microcopy analysis, the samples were polished sequentially with sandpaper grain size of 120, 220, 320, 400, 600, 1000 and 1200 and finalized with diamond paste of 6, 3 and 1μm. Microhardness tests were applied on the samples in order to measure the variation of the resistance from the surface to the center of the specimens. Additionally, x-ray diffraction was performed for identification and characterization of the compounds presented on the nitrided sample surfaces treated with the cathodic cage. The adhesive wear tests by rotating sphere were performed on a wear machine "Callus Test" by applying a load of (13N ~ 1.325, 15gf). The wear tests were conducted in non-lubricated condition (adhesive wear) at room temperature. Each sample was tested in a total time of 50 minutes, and every 5, 10, 15, 20 and 25 minutes, the tests were suspended for diameters measurements of the spherical groove appeared to determine the wear volume. The analysis was performed by plotting the mass loss (volume) versus the traveled distance in meters.

RESULTS AND DISCUSSION

Microstructures features and micro hardness measures of layers formed

As a comparison parameter for this study, previous researches already done by Oliveira *et al*.(2003)by using conventional nitriding chamber process without cathodic cage, was taken into account here.

Table 1. Nominal chemical composition of material

Steel	Composition (%)						
	Cr	Ni	Mo	C	Mn	Si	Fe
AISI 316	17.10	10.80	2.37	0.05	1.77	0.47	Balanced

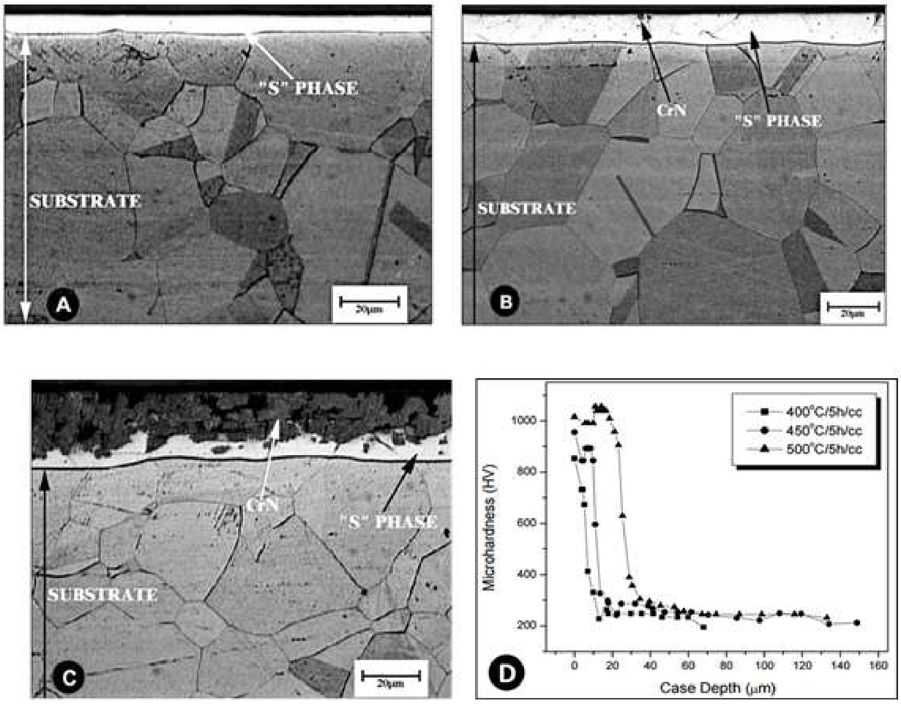

Fig. 2.Optical microscopy analysis of the cross section of the steel AISI 316 samples nitrided without the usage of the cathodic cage at (a) 400, (b) 450, (c) 500 °C and (d) the microhardness profile as function of the depth (24)

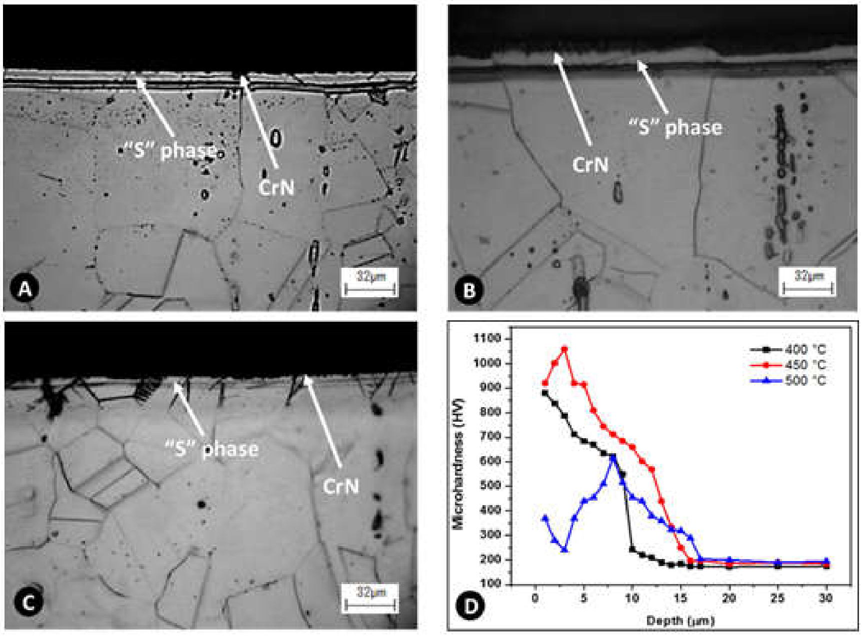

Fig. 3.Optical microscopy analysis of the cross section of the steel AISI 316 samples nitrided with the usage of the cathodic cage at (a) 400, (b) 450, (c) 500 °C and (d) the microhardness profile as function of the depth

They found produced nitrided layers in different configurations on an austenitic matrix by increasing the temperature of the treatments. The samples nitrided at 400 and 450 °C presented a single phase layer known as phase "S" or "expanded austenite", as shown in Fig. 2. (a) and (b). On the other hand, sample nitrided at 500 °C, showed the formation of a dark layer of chromium nitride on the phase "S" layer, see Fig. 2. (c).They confirmed these results by x-ray diffraction technique, not shown here. They also showed that the micro hardness profile on the nitrided layers was affected by the heat treatment attested temperatures. The nitrided layer at 500 °C showed the higher levels of microhardness as well as achieved a greater depth, see Fig. 2. (d). They concluded that this happened due to the presence of chromium nitrides and higher concentration of nitrogen in the clear layer ("S" phase). Mentioning again, all these results can be find in Oliveira et. al. reference 24. Fig. 2.Optical microscopy analysis of the cross section of the steel AISI 316 samples nitrided without the usage of the cathodic cage at (a) 400, (b) 450, (c) 500 °C and (d) the micro hardness profile as function of the depth (Oliveira *et al.*, 2003). For the tests performed with the use of cathodic cage, Fig.3. shows the microstructures of AISI 316 steel nitrided during the time of 5 hours, in a nitriding atmosphere of 80% N_2 + 20% H_2 at temperatures of (a) 400, (b) 450 and (c) 500 °C, keeping the pressure constant at 5mbar.

It is easy to see the presence of nitrided layers produced on an austenitic matrix (substrate). For the samples subjected to nitriding process at 400 °C, it was formed a single phase layer - phase "S" or "expanded austenite", while that in samples at 450 and 500 °C, this occurred early and increased the formation of a dark layer of chromium nitrides on phase "S".

The microhardness profile is shown in Fig.3. (d) as a function of the nitrided layers depth. It is evident that in all cases of heat treatment, there was effectiveness in order to increasing the surface hardness of the steel and that nitriding temperatures affect the micro hardness levels. The nitrided sample at 450 ° C showed the higher level of micro hardness as well as a greater depth of treatment. This was possible due to the presence of chromium nitrides and high concentration of nitrogen in the light layer ("S" phase). For the research done without the cathodic cage, the temperature in which was achieved the higher level of resistance, was at 500 and 450 °C.

The presence of phase "S" or "expanded austenite" with high nitrogen content in solid solution or chromium nitrides formation are responsible for the increase in the wear resistance of the layer. By doing a comparison on the magnitude of orders on y-axis scales in both graphs of the Figure 4, it is well remarkable that there was a considerable increasing on the wear resistance of the AISI 316 austenitic stainless steel under plasma nitriding treatment with the usage of the cathodic cage.

The difference on this axis is close to 100 times less of mass loss for the treatments performed with the cathodic cage. Furthermore, it clear that the conditions with the cathodic cage at 450 °C gained more resistance giving supports to the microhardness results. Fig. 5. shows the spherical groove obtained during the wear test after 20 minutes at (a) 400 and (b) 450 °C. It is verified for these cases that the wear mechanism was purely of the adhesive type, characterized by plowing the presented surfaces.

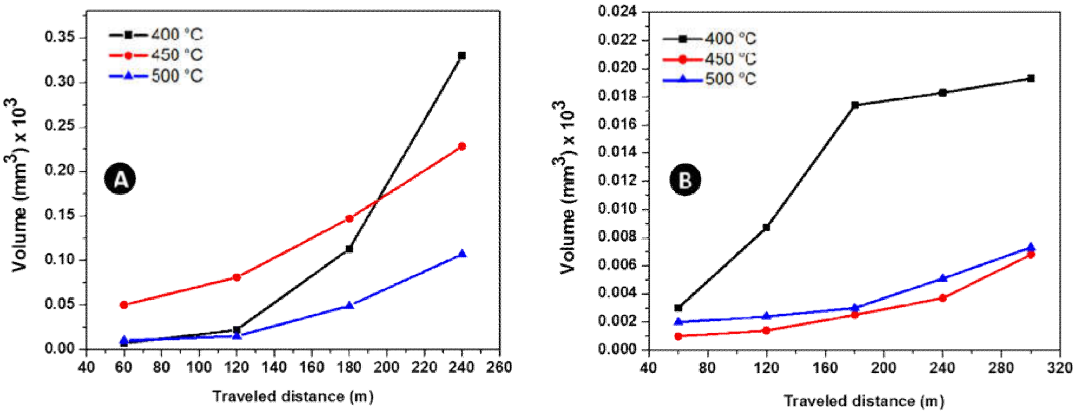

Fig. 4.Mass loss in relation with the traveled distance for (a) nitrided steel AISI 316L samples without the cathodic cage and (b) with application of the cathodic cage

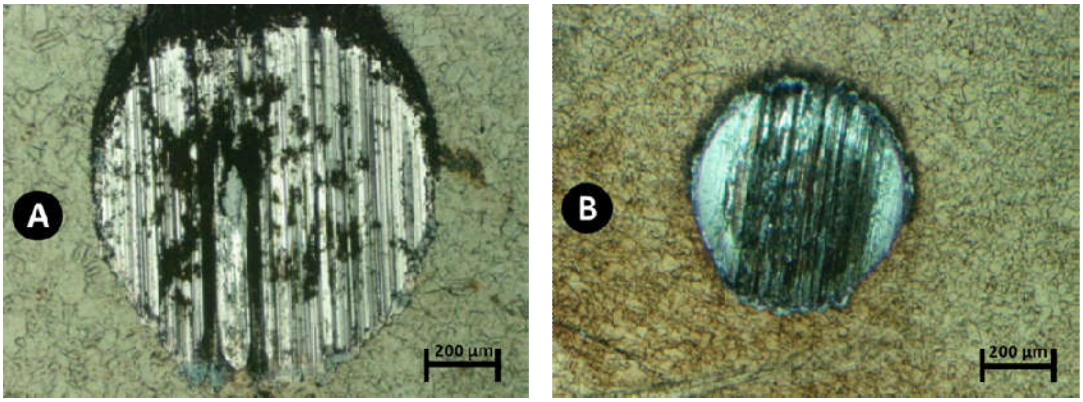

Fig. 5. Spherical groove obtained during the wear test at (a) 400 and (b) 450 °C.

Wear testing

Fig. 4. (a) and (b) shown the results of wear tests done on the nitrided steel AISI 316L samples without the cathodic cage and with the cathodic cage respectively. The tribological properties of the layers formed were evaluated under conditions of simple metal-metal sliding. The wear rates of the layers varied with the final thicknesses and microhardness of the nitrided layers. From this plot it is visible that the plasma nitriding treatment with the presence of the cathodic cage was well effectiveness in increasing the wear resistance when compared with the nitrided samples without the cathodic cage.

X-Ray diffraction analysis

In Fig. 6. (a), (b) and (c) are shown the XRD patterns related to the nitrided layers formed on the AISI 316 stainless steel with the cathodic cage at 400, 450 and 500 °C respectively. At temperatures of 400 to 450 ° C is noticeable the presence of Fe_4N phase (') peaks - with N content of 19.3 atomic% (white layer in Fig. 3. (a)). When this nitrogen content reaches 19.5 atomic%, nitrides of the type Fe_2-3N ( ) are formed, seeFig.6. (b) (450 ° C). When chromium nitrides are present in large quantities, as case of the studied AISI 316 steel, other nitrides are formed, such as Cr N and Cr_2N.

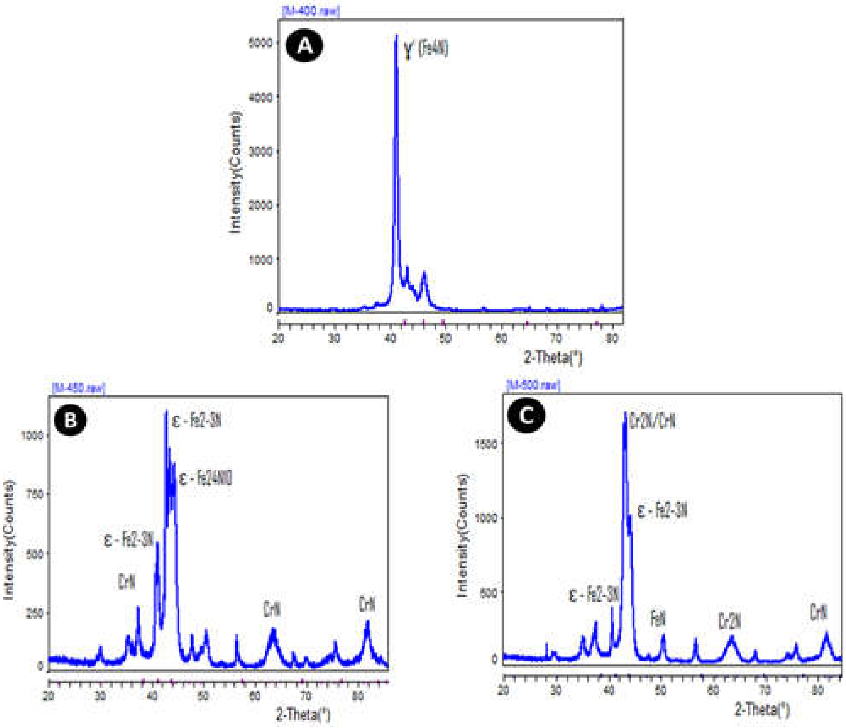

Fig. 6. XRD of the AISI 316 stainless steel after nitriding process at (a) 400 ° C, (b) 450 ° C and (d) at 500 ° C during 5 hours

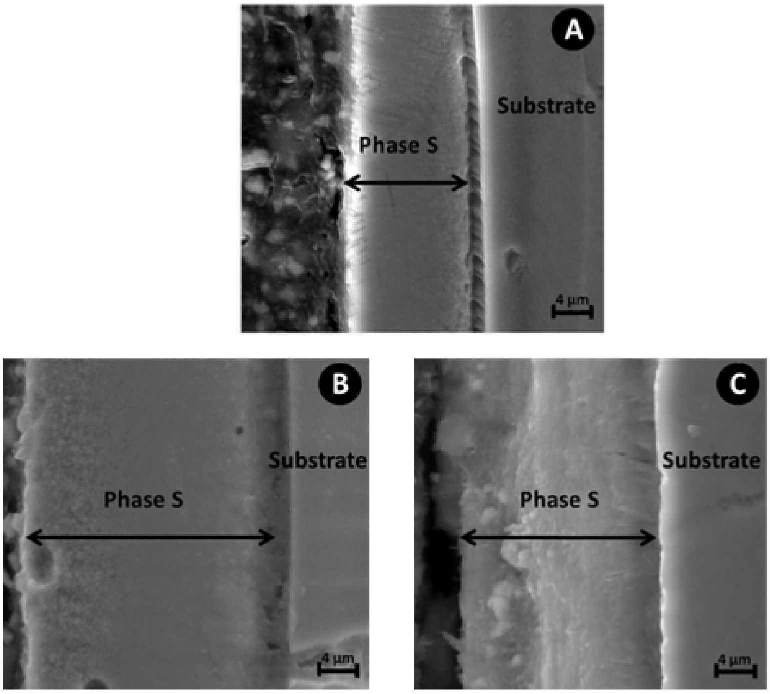

Fig. 7. SEM images of the samples subjected to plasma nitriding at (a) 400, 450 and 500 °C

The peaks shown in Fig.6. (c) (500 °C) are due to the oversaturation of nitrogen in the austenite matrix driven from the chromium nitride closer to the grain boundaries. Some researchers also suggest that the nitride layer obtained at a low temperature corresponds to a body-centered tetragonal structure. Also it is observed that when the nitriding temperature is increased to 500 °C, chromium nitrides (CrN and Cr_2N) were detected, Fig. 5.Spherical groove obtained during the wear test at (a) 400 and (b) 450 °C. corresponding to the formation of the dark phases in the nitrided layer (See Fig. 2. and Fig. 3).

SEM analysis of the samples after nitriding process

Fig. 7. shows the results of SEM analysis of the AISI 316 stainless steel after plasma nitriding with the usage of the cathodic cage at temperatures of (a) 400, (b) 450 and (c) 500 °C during 5 hours at a constant of 5 mbar. It is noted that the samples treated at 400 °C, Fig. 7. (a) presents the formation of a uniform layer. This is characteristic of interstitial diffusion related to nitrogen which formed the phase "S". However, the thickness of this layer is approximately 9 µm suggesting that this temperature was not enough to guarantee suitable

mechanical resistance under this condition when compared with the other temperature treatments. This can be confirmed by Fig. 4. (b). For the temperature of 450 °C, Fig. 7. (b), the layer is also uniform created from the same mechanism mentioned before. The treatment at this temperature promoted the formation of the thicker layer, approximately 19 µm, compared to the other two conditions. This support the results of mechanical properties of the process applied at this temperature which presented higher resistance, elevated values of microhardness and lower mass loss, see Fig. 3. (d) and Fig. 4. (b).The morphology of the layer formed at 500 °C, Fig. 7. (c), explain the unusual behavior of the measured microhardness shown in Fig. 3. (d). It can be observed that there was deterioration of the layer due to the formation of chromium nitride (Cr_2N/CrN) and iron nitrides of the type $Fe_{2-3}N$ ( ).

Conclusion

The cathodic cage acts as multi-cathode device, allowing the deposition and/or the treatment of the bulk material associated with an excellent deposition rate and contribute to increasing the layers growth in thermally activated surfaces, as the ion nitriding. The cathodic cage produces the same properties relative to the conventional plasma nitriding (DCPN). However, the former process helps to eliminate common problems associated with the procedure, like edge effect, providing the formation of uniform three-dimensional layers. The thickness of nitriding layer obtained in cathodic cage was close to that obtained with ion nitriding, however there was a lower adhesive wear when compared to ion nitriding. The optimum temperature for the nitrating mixture of 80% N_2 - 20% H_2 with cathodic cage nitriding was 450 ° C (possible to obtain thicker layers, higher microhardness and lower wear). In cathodic cage nitriding there was a further increase in wear resistance in relation to conventional procedure.

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