COMPARISON OF DIRECT CURRENT AND CATHODIC CAGE PLASMA NITRIDING TECHNIQUES[1]

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Abstract

Over the last decade, various plasma nitriding techniques exploring shielding of parts were used in order to eliminate problems in the conventional nitriding technique as edge effects and non-uniformity heating. The cathodic cage plasma nitriding (CCPN) is a technique that uses a same shielding as active screen but with better efficiency and control of process because multi hollow cathodes formation. In this work, the CCPN technique was compared with conventional technique called direct current plasma nitriding (DCPN) during nitriding of both AISI 316 and AISI 1020 steels. Rods with 8.0 mm in diameter were cut to various heights: 1, 3, 5, 8 and 10 mm and nitrided at temperature of 773K, 723K and 673 K using both (DCPN) and (CCPN). Influence of parameters as pressure, position and time of treatment were also evaluated. Unlike of the DCPN, the samples nitrided by CCPN did not have restriction rings in the layer and the hardness on surface is independent of the height of the samples. Further it was observed that the CCPN has a nitriding rate higher than the DCPN when the pressure for the occurrence of the effect of hollow cathode is properly used. These results shows a better efficiency of the CCPN when compared with the conventional technique, evidencing also that the application of such a new technique eliminates problem as thermal gradient and edge effect.

Keywords: Plasma nitriding; Hollow cathode; Stainless steels; Hardening.

COMPARAÇÃO ENTRE AS TÉCNICAS DE NITRETAÇÃO POR PLASMA DE CORRENTE CONTÍNUA E DE GAIOLA CATÓDICA

Resumo

Nas últimas décadas, varias técnicas de nitretação por plasma explorando blindagem das peças foram utilizadas com o intuito de eliminar problemas existente na nitretação iônica convencional como efeito de bordas e aquecimento heterogêneo. A nitretação por gaiola catódica (CCPN) é uma técnica que utiliza uma mesma blindagem que na técnica de nitretação por tela ativa mas com melhor eficiência e controle do processo devido à existência de multi cátodos ocos. Neste trabalho, a técnica de CCPN foi comparada com a nitretação iônica convencional (DCPN) durante a nitretação dos aços AISI 316 e AISI 1020. Cilindros com 8,0 mm de diâmetro foram cortados em alturas de 1, 3, 5, 8 and 10 mm e nitretados em temperaturas de 773K, 723K and 673 K usando as duas técnicas. Influência de parâmetros como pressão, posição e tempo de tratamento foram também avaliados. Ao contrário da DCPN, as amostras nitretadas por CCPN não apresentaram anéis de restrição na camada e a dureza da superfície é independente da altura da amostra. Também foi observado que a CCPN possui uma taxa de nitretação maior que a DCPN quando a pressão do efeito de cátodo oco é propriamente utilizada. Esses resultados mostram uma melhor eficiência da CCPN quando comparada com a técnica convencional, evidenciando ainda que a aplicação dessa nova técnica elimina problemas como gradiente térmicos e efeito de bordas.

Keywords: Nitretação iônica; Cátodo oco; Aço inoxidáveis; Endurecimento de aços.

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INTRODUCTION

When ionized nitrogen species are used for metallurgical surface modification to improve wear, hardness and fatigue resistance of ferrous and non-ferrous materials, they can be used in two different ways: (i) ion implantation, which consists of a small ion flux with a high average energy per ion, (ii) plasma-assisted nitriding (PAN), which consists of a large ion flux with average energy per ion sufficient to cause sputtering (sputtering), defects in the crystal lattice of the material and other important events to accelerate and/or improve the process. These processes offer the possibility to vary widely the properties of surfaces through the control of plasma parameters (electron density, energy and distribution function). The combinations of these parameters give rise to different PAN techniques.[1-4]

The precursor technique, called Direct Current Plasma Nitriding (DCPN) or ion nitriding, as patented in 1931 by J.J. Egan in the U.S. and by Berghaus in 1932 in Switzerland. Its commercial use began in the 60’s, making good progress in the 70's.[5] But limitations related with edge effect by electric field on workpiece surface and hollow cathode effect has motivated the introduction of new techniques for plasma-assisted nitriding.[4] It was found that due changes of the electric field on edges of the piece resulting in non-uniformity of layer. Also parts with different area/volume ratio have different heat transfer behavior.[6-8] To solve or reduce these problems, adjustments in the conventional technique were developed in the present work by the Cathodic Cage Plasma Nitriding (CCPN). It is a technique that uses a same shielding as active screen plasma nitriding (ASPN)[9-12] but with better efficiency and control of process because multi hollow cathodes formation. The difference between DCPN, ASPN and CCPN techniques are illustred in the Figure 1.

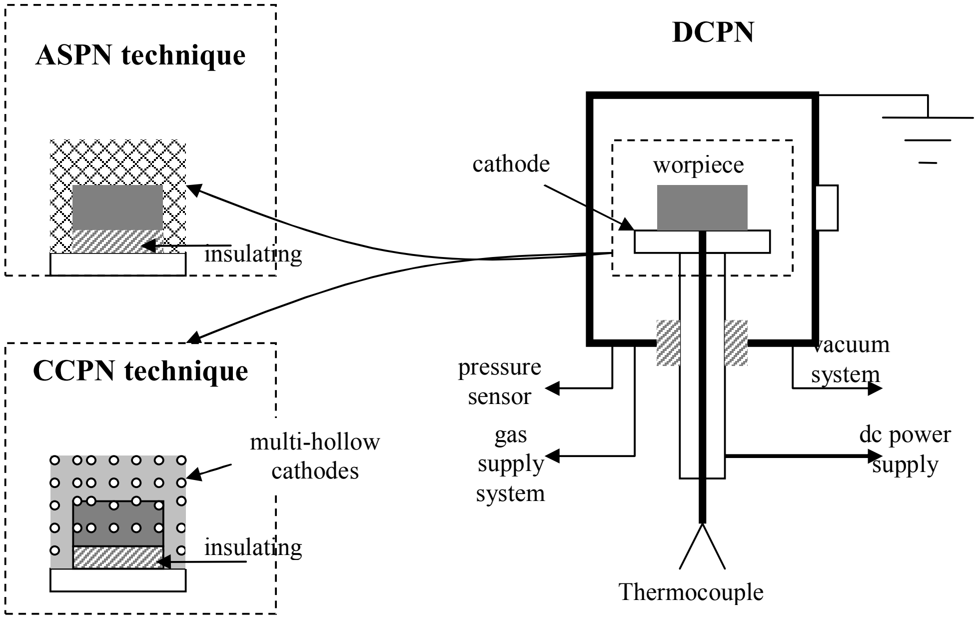


Figure 1. Difference between DCPN, ASPN and CCPN techniques.

In CCPN, the entire workpiece is surrounded by a metal cage with holes at cathodic bias. The workpiece to be treated are insulated from cathodic cage and the anodic chamber walls. Thus, the workpieces are in a floating potential or subjected to a relative lower bias voltage.[13] The holes in the cage plays two roles, i.e. to heat the components to the nitriding temperature by radiation from the hollow cathode discharge and to provide the active nitriding species to the component surface.

Since plasma is not formed on the component surface, many of the practical problems associated with DCPN techniques are overcome. In the CCPN many of the existing models established for DCPN technique may not be the dominant mechanisms for nitrogen mass transfer. Instead, a modified "sputtering, deposition and diffusion" model like in ASPN has been proposed to explain the nitrogen mass transfer.[10-12] During processing have found material transferred from the internal wall of the holes to the surface of glass samples, suggesting that the sputtering and redeposition mechanism was involved in the treatment.[14] Electrons accelerated to some internal wall of the holes will turn repelled by the other wall opposite also polarized and so sucessivelly. This zig-zag motion produce high density of ions within holes if the distance minimum between the wall (distance between cathode-cathode - $d_{c\text{-}c}$) is approximately 2.5 times greater than the thickness of the sheath (d) required by Paschen's law:[15]

$$V_B = \frac{C_1 pd}{C_2 + \ln pd}$$

where, V_B is the breakdown voltage, C1, C2 are constants that depend on the type of gas and p is the pressure value. Thus, between the internal wall of each hole the ion density of plasma is higher than in another parts. It is maximum when the hollow cathode occur, characterized by the high brightness. In this moment the temperature rises abruptly.[7,16] The sputtering on wall holes surface is produced by bombardment of nitrogen ions, aided by local heating effect caused by the hollow cathode, are responsible for the mass transfer of the to the surface of the part. A study of iron deposition on glass surfaces using an atmosphere of N2-75%H2 and temperature of 400° C for 2 hours, showed that the film thickness varied inversely with pressure. For a range from 75 Pa to 250 Pa, the quantity of iron varied from 6.8 to 0.9 at%, respectively.[17] But the decrease in pressure necessarily requires a change in power to maintain the same temperature. In this case, for the power between 268.7 and 117.6 W, the efficiency (power / quantity of iron deposited) was from 3×10^{-4} to 6×10^{-3} (W / atFe%) with higher value at lower pressures.[17] For nitriding of stainless steel surfaces during 10 h, using the same conditions, it was obtained thickness of layer ranging from 6.6 to 5.0 μm.

In general we can say that combining voltage and pressure it's possible the occurrence of hollow cathode effect for all the holes.[18-20] When this effect occurs, all the holes shine with greater intensity. There is a compromise between the pressure, voltage and diameter of the hole. The pressure may not be so large that does not allow the transfer of material to workpiece. The hole must have diameter sufficient to occurrence of the hollow cathode effect (typically between 6 – 10 mm). This can be obtained experimentally by varying the voltage until a high brightness appears in the holes. In the internal walls of the hole occur the same events of the DCPN but intensified by the hollow cathode effect. The multiple hollow cathode effect increases the sputtering and deposition rate. The material removed by sputtering is transferred to the surface of the workpiece. These atoms can also react with nitrogen atoms to form stable and metastable compounds before being deposited. The next step is the diffusion of species on the surface to reach the thermodynamic equilibrium. The excess nitrogen from these interactions diffuses into the piece.

EXPERIMENTAL

The samples (diameter: 8 mm and height: 10 mm) were machined and then annealed. The metallographic analysis was accomplished, where the top surfaces of the samples were ground, using sandpapers from 220 to 1200 mesh, and polished with alumina (0.3 µm). They were further cleaned ultrasonically in acetone bath and dried before placement into to vacuum chamber.

The system used for plasma nitriding consists of a high voltage DC source (maximum output 1500 V, 2 A), a vertically mounted cylindrical vacuum chamber (40 cm in diameter and 40 cm in height, made of stainless steel), gas input and evacuation components and process parameter sensors and controllers, as shown in Figure 2a. Samples were positioned onto worktable (CCPN) as indicated in Figure 2b and onto isolating substrate as indicated in Figure 2c. The cage was made of austenitic 316 stainless steel (diameter: 76 mm and height: 25 mm), containing a removable cover.

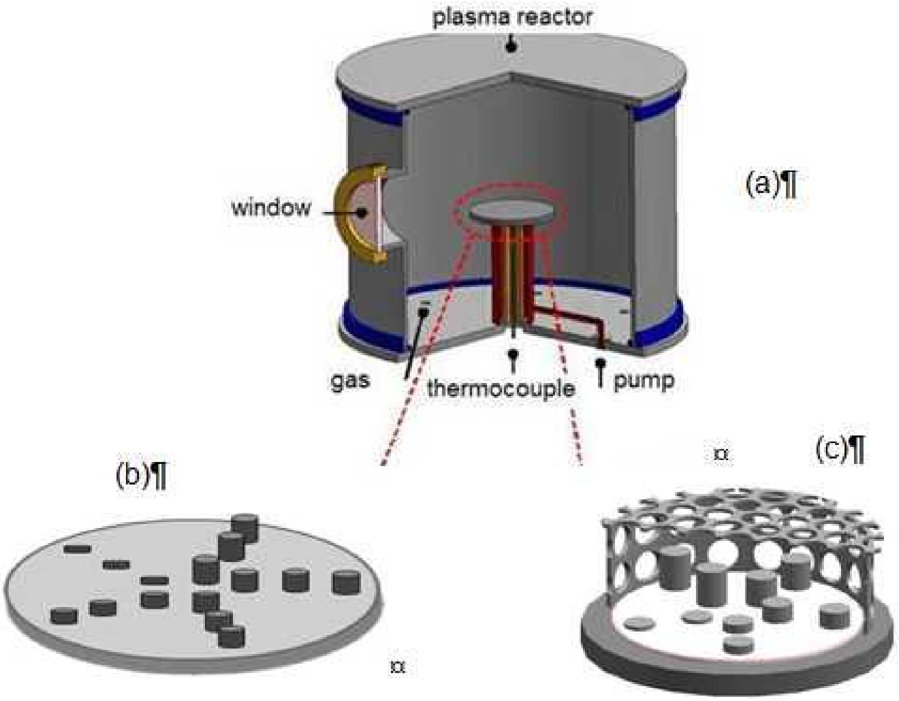


Figure 2. System used for plasma nitriding (a) showing detail of positioning of sample on worktable for (b) DCPN and (c) CCPN.

The cage walls thickness is 0.8 mm, with holes diameter of 7.6 mm and distance between the centers of adjacent holes of 9.2 mm. The working temperature was 773 K, for both steels.

The nitriding time was 3 h to 1020 steel and 5 h to 316 stainless steel. Before nitriding, the system was pumped down by a two-stage rotary pump until a residual pressure of about 1 Pa was reached. To determine the optimal condition of pressure and gas composition, a systematic variation it was performed. Thus, gas mixture with the composition of 20% N_2–H_2 for DCPN process and 80% N_2–H_2 for CCPN was introduced and its flow adjusted to 10 sccm using a mass flow controller. Also the treatment pressures of 360 Pa and 250 Pa for carbon and stainless steel, respectively, measured by a barocel capacitance manometer, was adjusted manually.

The phase composition and texture was analyzed using X-ray diffraction (XRD). The analyses described here were performed using Cu Kα lines (wavelength: 0.154 nm), operated at 40 kV in a XRD instrument (Shimadzu, XRD-6000). Optical microscope was used to observe morphology and thickness of nitrided layer. Finally, microhardness profile was carried through to evaluate uniformity and the appearance of edge effect.

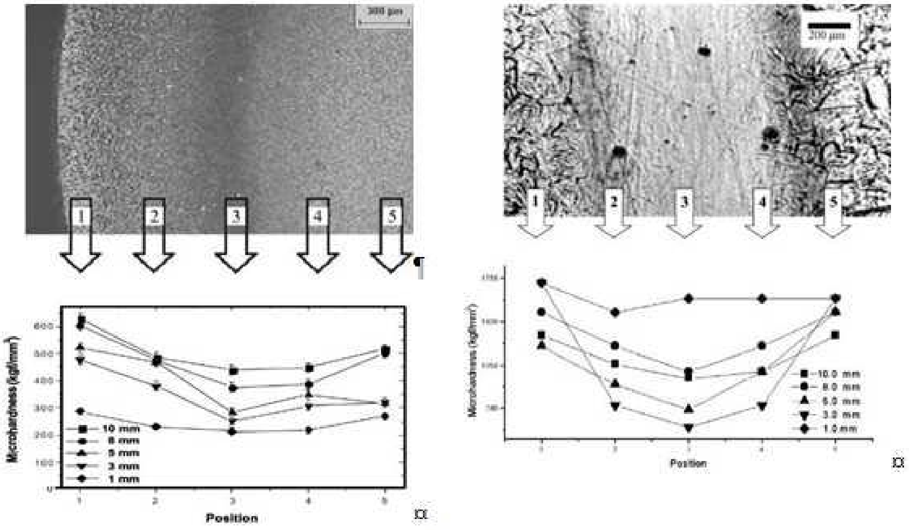
RESULTS AND DISCUSSION

Both steels presents ring on surface after nitriding by DCPN. This effect is not observed for steel nitride by CCPN. The Figure 3 shows a typical characteristic surface for DCPN and CCPN.

(a) (b) (c) (d)

Figure 3. Typical characteristic after nitriding by DCPN for (a) AISI 1020 steel, (b) AISI 316 steel and by CCPN for AISI 1020 and AISI 316, (c) and (d).

It is observed a more defined ring at stainless steel than carbon steel. We observed in previous studies that this phenomenon is associated with the concentration of nitrides former elements steel. This region is characterized by the decline or extinction of the nitrided layer and thus we call of restriction ring. It is also observed a dependence of position, width and hardness profile of the ring with the height of samples. In the Figure 4 is showed this behavior for different height for both steels.



(a) (b)

Figure 4. Behavior of the width and hardness of the ring as function of height of sample for (a) AISI 1020 steel and (b) AISI 316 steel nitrided by DCPN.

Note that the curve of hardness has a different behavior. Except for samples of 1 mm height, the fall of hardness inside the ring is greater for samples with lower height. One explanation for this fact is that the cathode sheath in the edge is the result of two contributions, the sheath of worktable and the sheath of surface sample itself. For sample of 8 mm and 10 mm height, the hardness curve has a similar behavior because the contribution of worktable for both cases is small. For sample of 1 mm height the sheath of worktable covers the sample decreasing the contribution of sheath of the surface sample. In this case the restriction ring is tenuous. In respect to nitriding kinetics, it was observed a higher layer depth in CCPN for same condition of treatment. Also, the dispersion on thickness value (difference between maximum and minimum value) in sample with different height is lower in CCPN than in DCPN. The Table 1 and 2 shows the thickness value for all temperatures used in this experiment of the nitrided layer on sample with different height for AISI 1020 and AISI 316 steels, respectively.

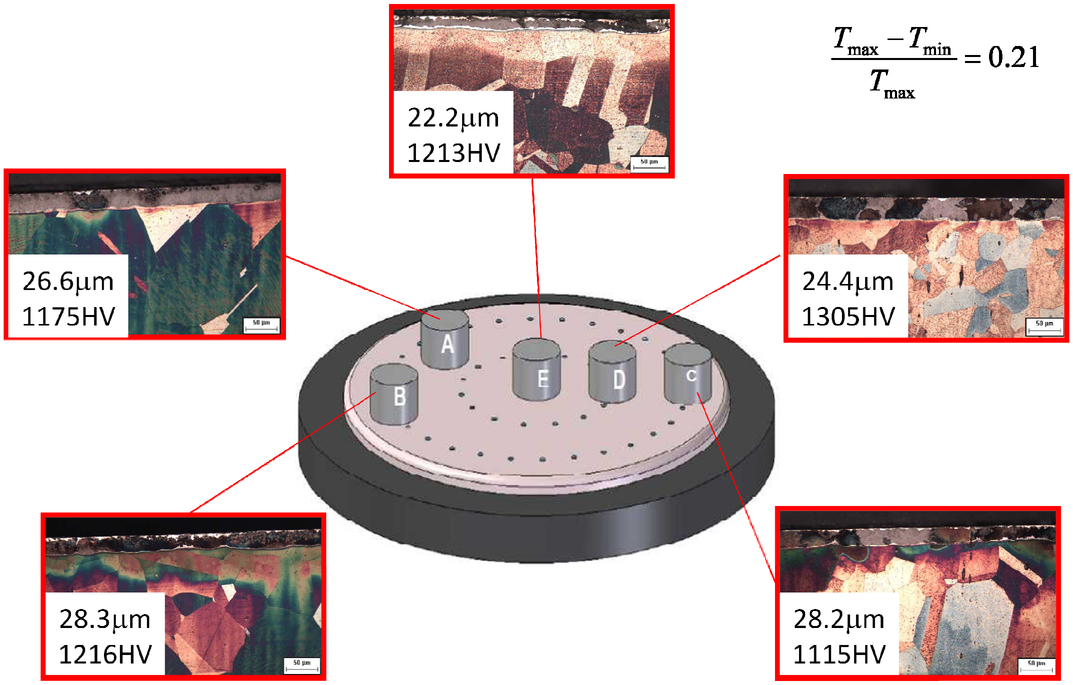
Table 1. Thickness of the nitride layer for AISI 1020 steel nitrided at pressure of 360 Pa, during 3h

Height samples (mm)		Temperature (K)					
		673	773	843	673	773	843
		CCPN			DCPN		
1	Thickness (µm)	136,6	90,3	141,2	38,9	48,4	68,8
3		105,7	93,7	206,7	34,5	42,0	75,3
5		138,5	109,5	186,1	35,7	55,9	92,9
10		138,2	171,9	212,8	61,2	61,3	98,2

Table 2. Thickness of the nitride layer for AISI 316 steel nitrided at pressure of 250 Pa, during 5h

Height samples (mm)		Temperature (K)					
		673	723	773	673	723	773
		CCPN			DCPN		
1	Thickness (µm)	7,8	22	49,1	1,3	16	24,5
3		8,5	23	50,9	2,1	17,4	28
5		10	28	52,2	3,5	23,5	36,4
10		12	32	53,4	4,4	29,5	45,8

However when it is compared samples of the same height nitrided at different positions of the worktable there is greater dispersion in the value of thickness for the treatment of CCPN. For sample nitrided by DCPN the dispersion was lower than 5% maximum value. For sample treated by CCPN this value was 21% maximum value. The Figure 5 show the dispersion for AISI 316 steel nitrided by CCPN. This result indicates a strong dependence of the uniformity of the process with the size and distribution of holes in the cage in the CCPN. Samples placed near the walls of the cage are favored with higher deposition rate than those near the center of the cage. Care it should therefore necessary to ensure symmetry of the holes in relation to parts.



$$\frac{T_{\max} - T_{\min}}{T_{\max}} = 0.21$$

Figure 5. Dispersion of thickness value for AISI 316 steel of same height sample nitrided by CCPN at different position on worktable.

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