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Cathodic Cage Nitriding of AISI 409 Ferritic Stainless Steel with the Addition of CH_4

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AISI 409 ferritic stainless steel samples were nitrided using the cathodic cage plasma nitriding technique (CCPN), with the addition of methane to reduce chromium precipitation, increase hardness and wear resistance and reduce the presence of nitrides when compared to plasma carbonitriding. Microhardness profiles and X-Ray analysis confirm the formation of a very hard layer containing mainly ε-Fe_3N and expanded ferrite phases.

Keywords: *cathodic cage, plasma carburizing, ferritic stainless steel*

1. Introduction

Stainless steel is widely used in engineering due to its high corrosion resistance, despite its low wear resistance and hardness. However, the two latter properties can be improved significantly through ionic nitriding[1,2]. It is well known that nitriding ustenitic stainless steel at temperatures above 723 K produces high hardness and wear resistance, but corrosion resistance decreases substantially due to chromium nitride precipitation, resulting in the reduction of chromium in the matrix. When nitriding is carried out at temperatures below 723 K it produces a supersaturated solid solution of nitrogen called "S phase" or expanded austenite, with high hardness and wear resistance allied to excellent corrosion resistance[3,4]. Nitriding produces a very hard and thin layer, while cementation produces a thick layer that is less hard. The precipitation of chromium nitrite can be inhibited by the addition of small amounts of CH_4. The addition of methane results in a hybrid process which produces a thick double layer, the inner layer being supersaturated by carbon and the outer one by nitrogen, leading to high surface hardness[5-7].

Due to their low hardness, ferritic stainless steels are not normally used in conditions that require wear resistance. However, wear-resistant materials can be obtained either by reinforcing the soft phases with harder phases or by surface-hardening processes. Plasma nitriding stands out among surface-hardening processes because of its effectiveness, relatively low cost and the fact that it is non-polluting. Plasma nitriding can be described as a thermochemical method that introduces atomic nitrogen into the material and allows for the deposition of substrate element nitrides. Nitriding of a material depends on the proper correlation between the dominant mechanisms, the system's treatment parameters and the chemical composition of the substrate[8-10]. The resulting layer can be subdivided into a composite layer – consisting mainly of ε-($Fe_{2-3}N$) and/or γ'-(Fe_4N) phases, which are responsible for the material's good tribological and anticorrosive properties – and a diffusion zone where the nitrogen is dissolved interstitially in the matrix, leading to high wear resistance[10].

Nitrided ferritic stainless steels are harder and more wear resistant than austenitic steels. It is well known that plasma nitriding significantly improves the surface properties of austenitic steels; however, little research has focused on the nitriding of ferritic stainless steels[11].

Ferritic stainless steel has long time been used in metallurgical applications due to its lower cost when compared to austenitic steel, as well as its good corrosion resistance. Ferritic stainless steel is weldable, magnetic, highly formable, and highly corrosion resistant under stress and at high temperatures. It is used in the manufacture of nitric acid storage tanks, automobile accessories, domestic utensils, coins, elevator coatings and refrigerated cabinets[12].

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In this study, we use the same plasma nitriding reactor, but with a modified experimental arrangement illustrated in Figure 1, called a cathodic cage[5,13-15], whose principle of operation is based on the hollow-cathode effect in the walls of the all holes.

2. Materials and Methods

The material used in this study was AISI 409 ferritic stainless steel, whose elemental atomic compositions are presented in Table 1.

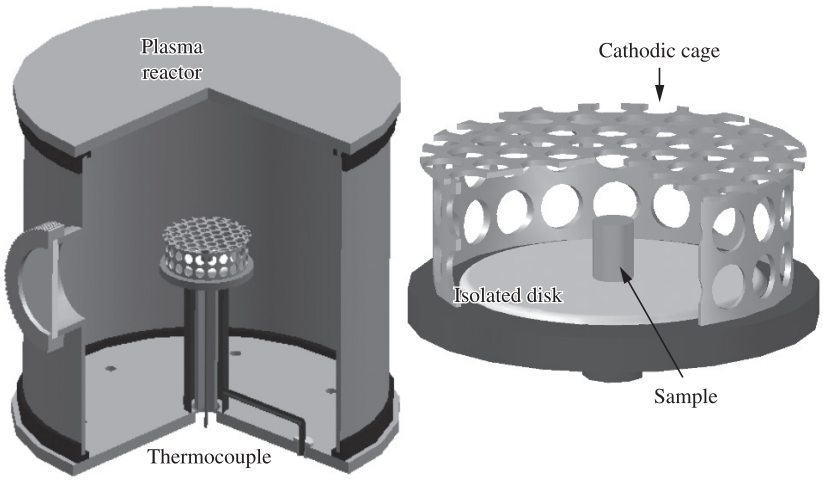

Figure 1. Diagram of the nitriding reactor and view of the cathodic cage containing a sample.

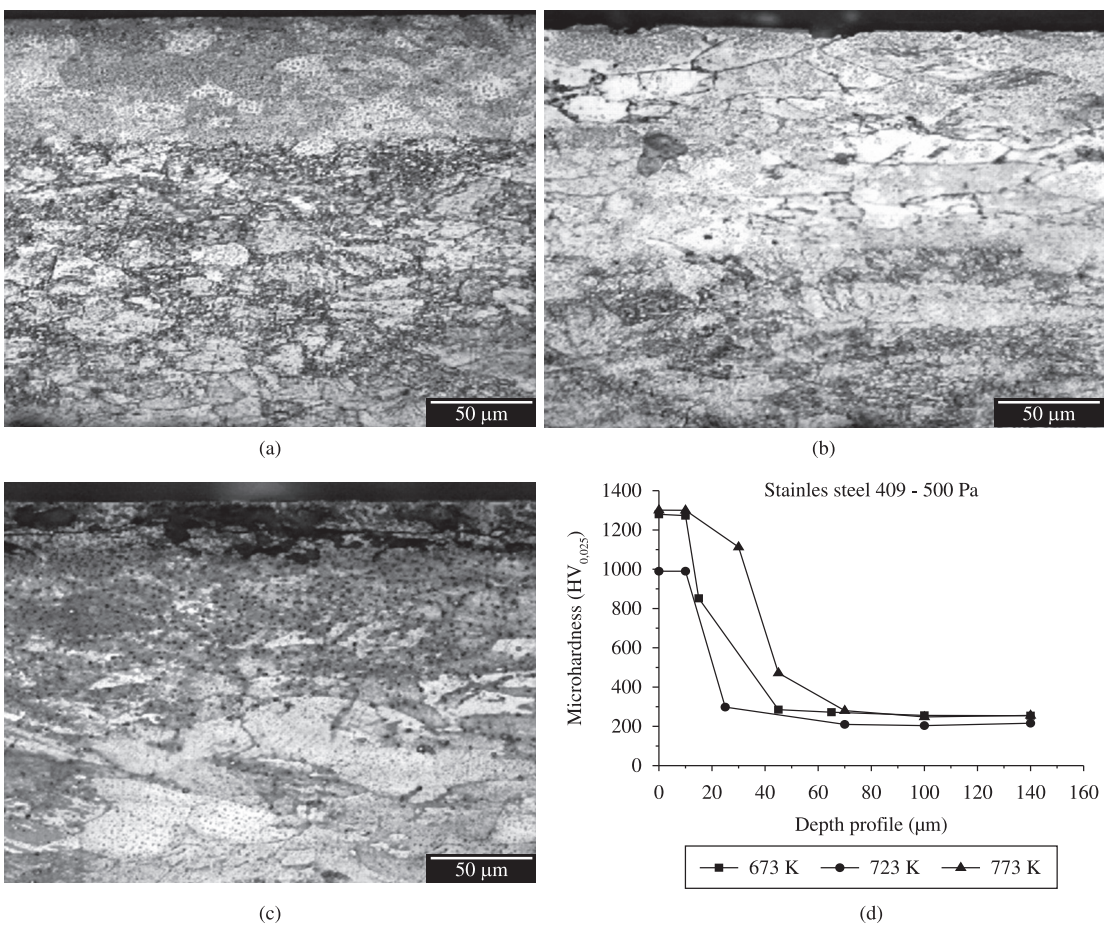

Figure 2. Micrographs of AISI 409 steel nitrided by the cathodic cage technique, with the addition of CH_4, for 5 hours under a pressure of 500 Pa at: a) 673; b) 723; c) 773 K; and d) microhardness profile.

Samples of previously solubilized AISI 409 ferritic stainless steel were machined into cylindrical shapes, sandpapered with 320, 400, 600 and 1200 grit sandpaper, and polished with 1 and 0.3 μm diamond paste using a felt disc. They were then cleaned ultrasonically in an acetone bath and placed in the nitriding chamber.

The nitriding system consisted of a cylindrical stainless steel vacuum chamber (40 cm in diameter and 40 cm in height) equipped with an evacuation system, with gas flux controlled by a mass flow controller, and a power supply (maximum voltage of 1500 V, maximum electrical current of 2 A). This system is similar to the conventional plasma nitriding arrangement, but with the addition of a cathodic cage made of stainless steel plate 316, with dimensions of 0.8 mm thickness, 112 mm diameter, 25 mm height and 8 mm diameter holes distributed uniformly, with a distance of 9.2 mm between holes. The plasma was formed in the cathodic cage, i.e., on the negatively loaded workpiece instead of the sample's surface[13].

Table 1. Elemental composition of AISI 409 ferritic stainless steel (at. %).

	C (%)	Cr (%)	Ni (%)	Mo (%)	Mn (%)	Si (%)	N (%)	Cu (%)	Fe (%)
409	0.030	11.25	0.06	0.11	0.74	0.49	-	-	Balance

The samples were pretreated with hydrogen plasma for 30 minutes at 573 K. The treatment conditions were as follows: 5 hours of cathodic cage nitriding using a 95% N_2-5% CH_4 mixture, and 10 hours of conventional plasma carburizing using a 78% H_2 - 20% N_2-2% CH_4 mixture. The two processes were performed at 673, 723, and 773 K. The 20 sccm flow was adjusted by a controller. The treatment was performed under a pressure of 500 Pa, which was measured with a manually adjusted Barocel capacitance manometer. After nitriding and carbonitriding, the samples were annealed, polished and etched with Beraha II reagent. The samples were analyzed by X-ray diffraction (Shimadzu, XRD-6000, operating at 40 KV) using CuK lines and a wavelength of 0.154 nm. The morphology and thickness of the nitrided layer were examined by optical microscopy, and the layer's microhardness profile was determined to confirm its thickness and uniformity.

3. Results and Discussion

Figures 2a,b,c show optical micrographs, while Figure 2d shows the measured microhardness of the AISI

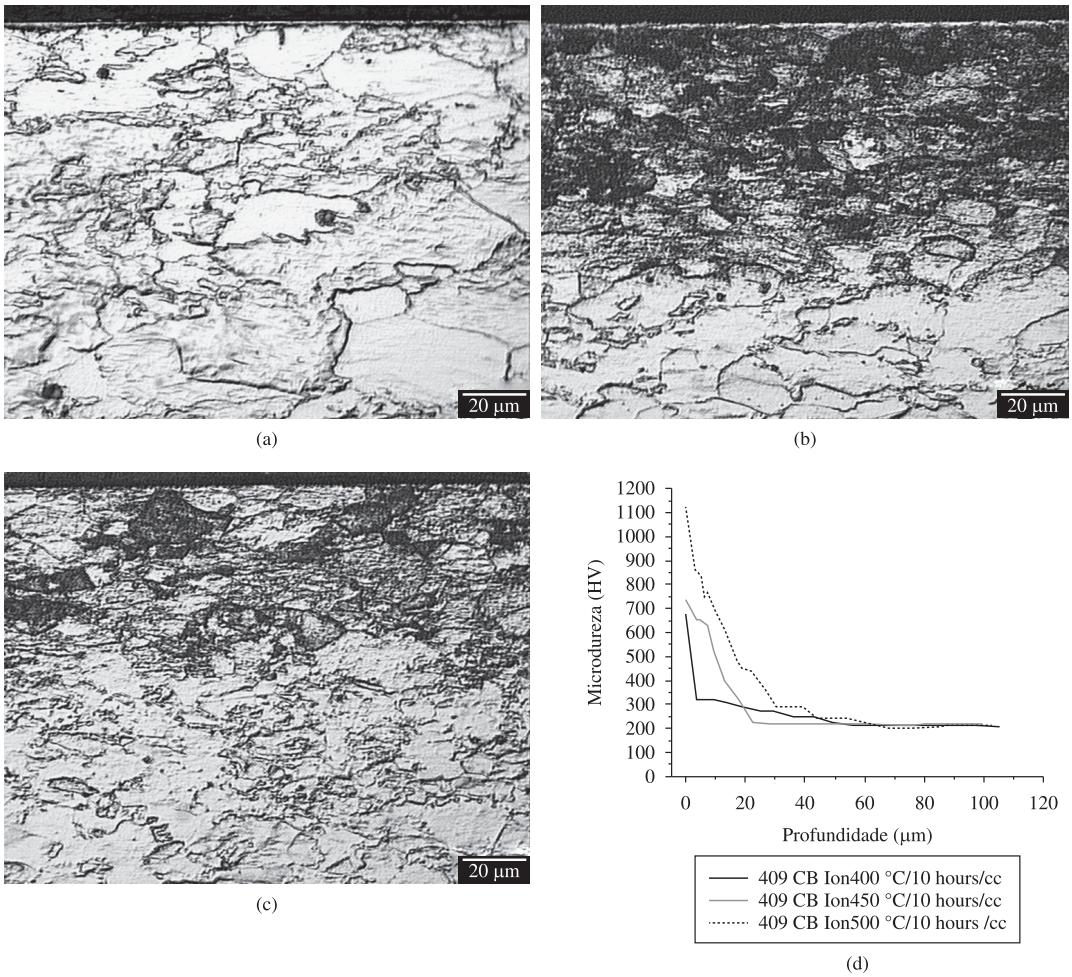

Figure 3. Optical micrographs and microhardness curves of AISI 409 steel plasma carbonitrided for 10 hours under a pressure of 500 Pa at: a) 673; b) 723; c) 773; and d) microhardness profile.

409 steel nitrided by the cathodic cage technique with the addition of methane.

The samples nitrided by the cathodic cage technique and by conventional plasma carbonitriding presented a thin composite layer on the ferritic matrix, as shown in Figures 2 and 3, as well as a much thicker diffused layer which varied directly as a function of the treatment temperature. The layer obtained by cathodic cage nitriding with the addition of methane was much thicker than the one obtained by carbonitriding, for samples with the same period of treatment. Figures 3a,b,c show optical micrographs, while Figure 3d shows the measured microhardness of plasma carbonitrided AISI 409 steel. Small amounts of methane were found to prevent the precipitation of chromium nitride, stabilizing the expanded ferrite or α_N phase, and thus increasing the material's corrosion resistance[7]. However, the microhardness decreased with the depht, as can be seen in the curves of the graphs in Figures 2d and 3d, although this decrease occurred more gradually in the samples nitrided in the cathodic cage than in those carbonitrided conventionally, which presented an abrupt drop in microhardness.

Table 2 lists the values of microhardness and composite layer thickness. Cathodic cage nitriding at 673 K did not cause the formation of a composite layer. Hence, the increase in microhardness of this sample was attributed to the formation of a diffusion zone. The dissimilar nitrogen and carbon diffusion rates were attributed to the different bond energies of these elements. Chromium and nitrogen have a

Table 2. Microhardness and thickness of the composite layer of samples nitrided under different conditions.

	Time (hours)	Temperature (K)	Microhardness (HV)	Thickness of composite layer (μm)
Cathodic cage nitriding	5	673	1273	-
	5	723	1000	26
	5	773	1329	46
Plasma carburizing	10	673	700	19
	10	723	750	31
	10	773	1150	55

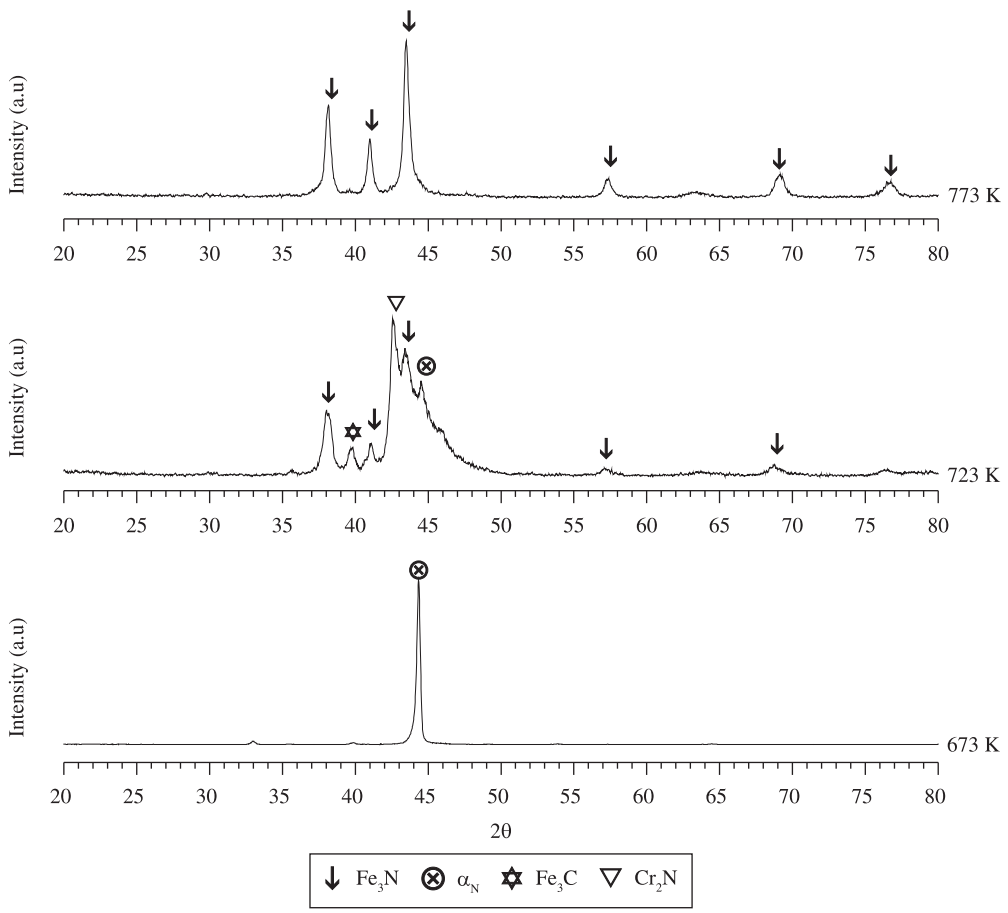

Figure 4. X-ray diffractograms of samples nitrided by the cathodic cage technique, with the addition of CH_4, under a pressure of 500 Pa at 673, 723 and 773 K.

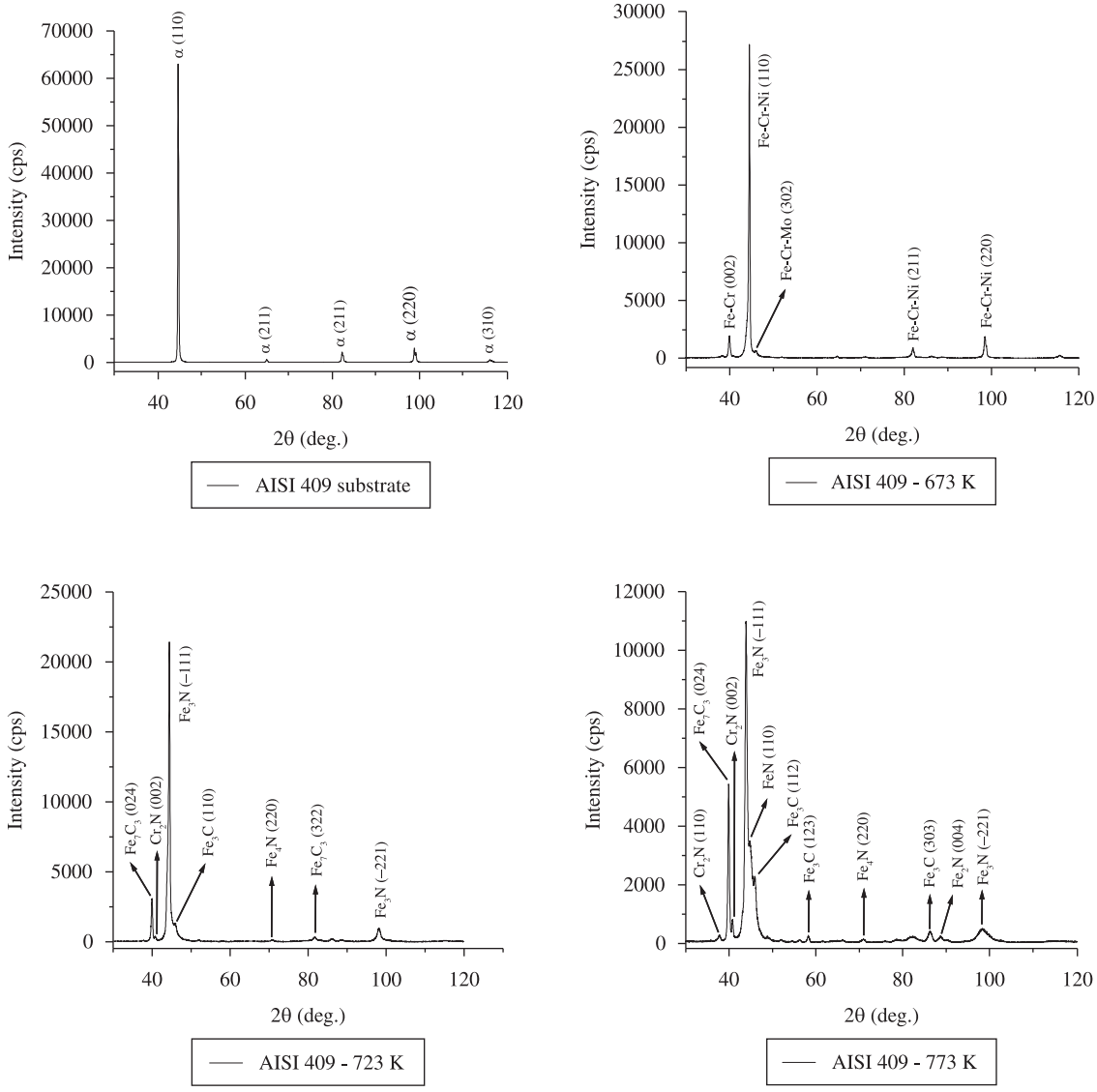

Figure 5. X-ray diffractograms of samples carbonitrided under a pressure of 500 Pa at 673, 723 and 773 K.

strong electronic affinity and easily bond to each other. On the other hand, carbon can diffuse freely through the surface, while nitrogen is more likely to bind to chromium (which will hinder the diffusion of nitrogen)[16]. The values presented here confirm the greater microhardness and thinner layer of the samples treated by cathodic cage nitriding than those of the carbonitrided samples.

In Figure 4, the X-ray diffractograms of the samples nitrided in the cathodic cage with added methane indicate the formation iron nitride, chromium nitride, iron carbide and expanded ferrite, α_N, a term used for comparison to expanded austenite, which is due to expansion of the crystalline network. The presence of iron carbide is due to the higher carbon content in ferritic stainless steel than in austenitic steel. Expanded ferrite is responsible for the high hardness of nitrided ferritic steel. Note, in Figure 4, that the peak intensity of the expanded ferrite decreases with increasing temperature, similar to what occurs with expanded austenite in austenitic stainless steel[17]. Precipitation of chromium nitride begins starting from 723 K, when the peak intensity of expanded ferrite decreases. The presence of chromium nitride is less intense in plasma nitriding without the addition of methane, as well as in plasma carbonitriding.

Figure 5 compares diffractograms of AISI 409 steel samples plasma carbonitrided at 673, 723 and 773 K against the diffractogram of a non-treated sample. Note the greater presence of chromium nitride and the predominance carbides in comparison to the material subjected to cathodic cage nitriding. This finding confirms that cathodic cage nitriding with the addition of small amounts of methane inhibits the precipitation of chromium nitride, thus reducing the loss of corrosion resistance as the nitriding temperature increases.

4. Conclusions

The addition of small amounts of methane to the nitriding atmosphere during cathodic cage plasma nitriding

produces notable changes in the properties of ferritic stainless steel. This nitriding method produces thinner layers that are harder than those obtained by conventional plasma carbonitriding. Moreover, when compared to conventional plasma carbonitriding, cathodic cage nitriding with methane reduces the formation of carbides and inhibits chromium nitride precipitation, increasing the material's corrosion resistance. The increase in hardness may be due to the decrease in chromium nitride precipitation and the resulting stabilization of expanded ferrite.

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