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PLASMA NITRIDING OF SINTERED AUSTENITIC STAINLESS STEEL 316L WITH NITROGEN PULSED FLOW

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Abstract. *Surface treatments are used in sintered stainless steel with the aim of increasing the hardness of the surface and its wear and corrosion resistance. Previous studies have shown the formation of cracks in layers formed in nitrided samples under some treatment conditions. A promising way to avoid crack formation, which is the aim of this work, is to vary the nitrogen potential, which is achieved by pulsing the nitrogen flow, during plasma nitriding. To reach the objective, samples of sintered stainless steel 316L were plasma nitrided for 4 h e 8 h, with continuous and pulsed nitrogen flows (cycles of 20 minutes, being 2 minutes with nitrogen on and 18 minutes with nitrogen off). After the nitriding, the samples were characterized by scanning electron microscopy, X-ray diffraction and microhardness. In all processing conditions the formation of expanded austenite in the nitrided layers was observed. The sample treated for 8 h in continuous flow, was the only presenting formation of chromium nitrides. The samples nitrided in pulsed flow have shown lower hardness in comparison to the continuous flow, for similar processing times. The sample treated for 8 h with continuous flow showed the highest hardness of all samples. SEM results indicated the lowest occurrence of cracks on the samples nitrided under pulsed flow when compared with the continuous treatment. This behavior is related to the reduction of nitrogen content in the layer, and the consequent reduction of the residual stresses from the formation of expanded austenite.*

Keywords: *plasma nitriding, sintered stainless steel, pulsed nitrogen flow.*

1. INTRODUCTION

The advantages of powder metallurgy, such as resources economy, the production of complex geometry elements and the manufacturing of components with controlled structural properties (Chiaverini, 1992), combined with the high demand of stainless steels provide the wide use of sintered stainless steel parts in automotive, aerospace, electronic, medical and dental areas. Despite its large application, it is common to use surface treatments in stainless steels, aiming to increase the surface hardness, the corrosion and wear resistance, as well as raise the fatigue limit (Carbó, 2008). One of the surface treatments used is plasma nitriding, which consists of promoting a process of nitrogen diffusion into the superficial layer of the material, through generating active species in the treatment atmosphere (Lo *et al.*, 2009).

Studies developed with sintered 316L stainless steel components have shown the formation of cracks in regions adjacent to pores. In the work of Mendes *et al.* (2014), samples of sintered 316L stainless steel were plasma nitrided at 350ºC, 380ºC, 410ºC and 440ºC, and the formation of cracks in regions adjacent to pores was observed for all temperatures in 8 hour treatments. Besides that, the occurrence of cracks was higher with the increase of temperature. The samples treated at 380ºC for 4, 8 and 16 hours have shown cracks, and with the increase in treatment time, the greater the amount of cracks in the nitrided layer. According to the authors, a possible explanation for the occurrence of cracks is the residual stress resulting from the formation of the expanded austenite phase during nitriding.

In addition, other studies show the formation of cracks in nitrided layers in sintered austenitic stainless steels. In the work of Ordoñez *et al.* (2019), sintered yttria-containing 316L stainless steel samples treated by plasma nitriding present cracks within 10 hours of treatment. The presence of cracks after longer treatment times is related to the high compressive stresses developed during the formation of the nitrided layer, which causes plastic deformation in the material, as verified by the author (Bacci *et al.*, 2001).

A study by Stinville et al (2010) investigated the influence of low temperature nitriding on crystallography and fatigue life of 316L steels. Nitriding was carried out at 400°C in treatment times ranging from 20 minutes to 160 hours, and X-ray diffraction analysis showed the formation of expanded austenite, evidenced by the widening and displacement to the left of the austenite peaks, when compared to the non-treated material. It was also verified that these results could indicate a complementary effect of occupation of the octahedral interstices by nitrogen atoms, which modulates the intensity of the peaks (Stinville *et al.*, 2010). The location of the expanded austenite peaks allows to calculate the lattice spaces for different nitriding durations. The results of Stinville *et al.* (2010) show an increase in the lattice parameters up to about 8 hours of nitriding, reaching a value of approximately 0.39 nm, remaining constant after this period. The lattice parameter for the 316L is 0.359 nm and the results showed an expansion of about 9% in the normal direction of the surface. As there is no possibility for the nitrided layer to expand parallel to the surface and as a consequence of the high compression, stresses are induced into the nitrided layer (Stinville *et al.*, 2010). According to the authors, compressive stresses also affect the surface topography. Results showed that after 33 hours of nitriding, the topography of the samples showed damage related to grain boundaries and surface damage may favor the loss of grains by delamination (Stinville *et al.*, 2010). Also, cracks are visible after 1 hour of nitriding.

A work carried out by Sphair (2017) studied the influence of pulsed nitrogen fluxes on the formation of nitrided layers in 316L austenitic stainless steel samples. Nitriding occurred at 400°C, with periods in the treatment when the nitrogen flow was turned on and periods when it was turned off. The cycles always totalized 20 minutes, and the total treatment times were 0.5 hour, 1 hour, 2 hours and 4 hours. In this study it was observed that cycles with times of 2 and 3 minutes of nitrogen produced thinner layers when compared to treatments of 5 and 10 minutes. The analysis also showed that in all treatment conditions there was an expanded austenite phase formation, and there was no formation of nitrides, which is favorable to the maintenance of corrosion resistance. The work of Sphair (2017) also showed that hardness values in pulsed flow samples tend to be lower when compared to continuous flow, which may suggest that nitrogen enriches the surface quickly and reaches a limit in the phase of expanded austenite (Sphair, 2017). The lower hardness value for pulsed samples may also indicate a lower nitrogen concentration in the expanded austenite layer, despite its rapid absorption, thus causing lower stress levels than in samples that underwent continuous nitrogen flow treatment (Sphair, 2017). It is suggested that with the possibility of controlling the nitrogen concentration in the nitrided layer, it will also be possible to control levels of expansion, hardness and residual stresses.

Thus, the present work aimed to evaluate the influence of nitrogen pulses in the surface treatment of plasma nitriding, as a way to control the formation of cracks in sintered AISI 316L stainless steel components. The characteristics of the nitrided layers regarding phase formation and microhardness were also evaluated.

2. Experimental Procedure

AISI 316L austenitic stainless steel specimens were sintered in the Materials Laboratory (LabMat) of the Federal University of Santa Catarina (UFSC). Edges have been sanded to avoid sharp corners and possibilitate arcs during nitriding. The final samples had a rectangular geometry with dimensions of 18.8mm x 16.35mm x 2.5mm.

Ultrasound cleaning was performed with alcohol for 10 minutes on the samples and then they were nitrided. In all tests, vacuum tests, cleaning with argon and hydrogen, heating and cleaning with hydrogen, and cooling under hydrogen flow were carried out.

The nitriding temperature was 410 ºC, in 8 hour and 4 hour nitriding periods, with continuous flow and pulsed nitrogen flow for each time. In pulsed treatments, the nitrogen flow was turned on and off. The pulses had a total period of twenty minutes each, with two minutes of nitrogen on and eighteen minutes off. The nitriding parameters were 700 volts with a gas mixture formed by 60% N_2 + 20% H_2 + 20% Ar, at times when the nitrogen flow was turned on, and 33.33% H_2 + 66.67% Ar when the flow was off. Treatment pressure was 6.0 Torr and flow 300 cm^3/min.

The samples were placed in pairs in the reactor for nitriding and after the treatments, one of the samples from each test was cut transversely, sanded in 220, 320, 400 and 600 mesh particle sizes and manually polished using 1 µm aqueous alumina solution. The characteristics of the nitrided layers and the occurrence of cracks were analyzed with images obtained by scanning electron microscopy.

For phase detection, X-ray diffraction analyses were performed on all nitrided samples and also on a non-treated sample. The parameters were copper radiation (λ=0,154184 mm), 20 mA and 40kV. The scan rate was 2θ from 30º to 60º, with Bragg-Brentano configuration, speed of 1º/min and angle of incidence of 10º. The following diffraction charts from the "ICDD PDF-2 Release 2003" were used: 00-023-0298 for the identification of the austenite, 01-089-4186 for the identification of the ferrite, 00-011-0065 for the identification of chromium nitrides and 00-026-1136 for the identification of iron oxides.

Surface microhardness measurements were performed with a Shimadzu Micro Hardness Tester HMV2. The applied load was 25 gf and a peak-load contact of 15 s. The results presented are the mean of the measurements.

3. Results and Discussions

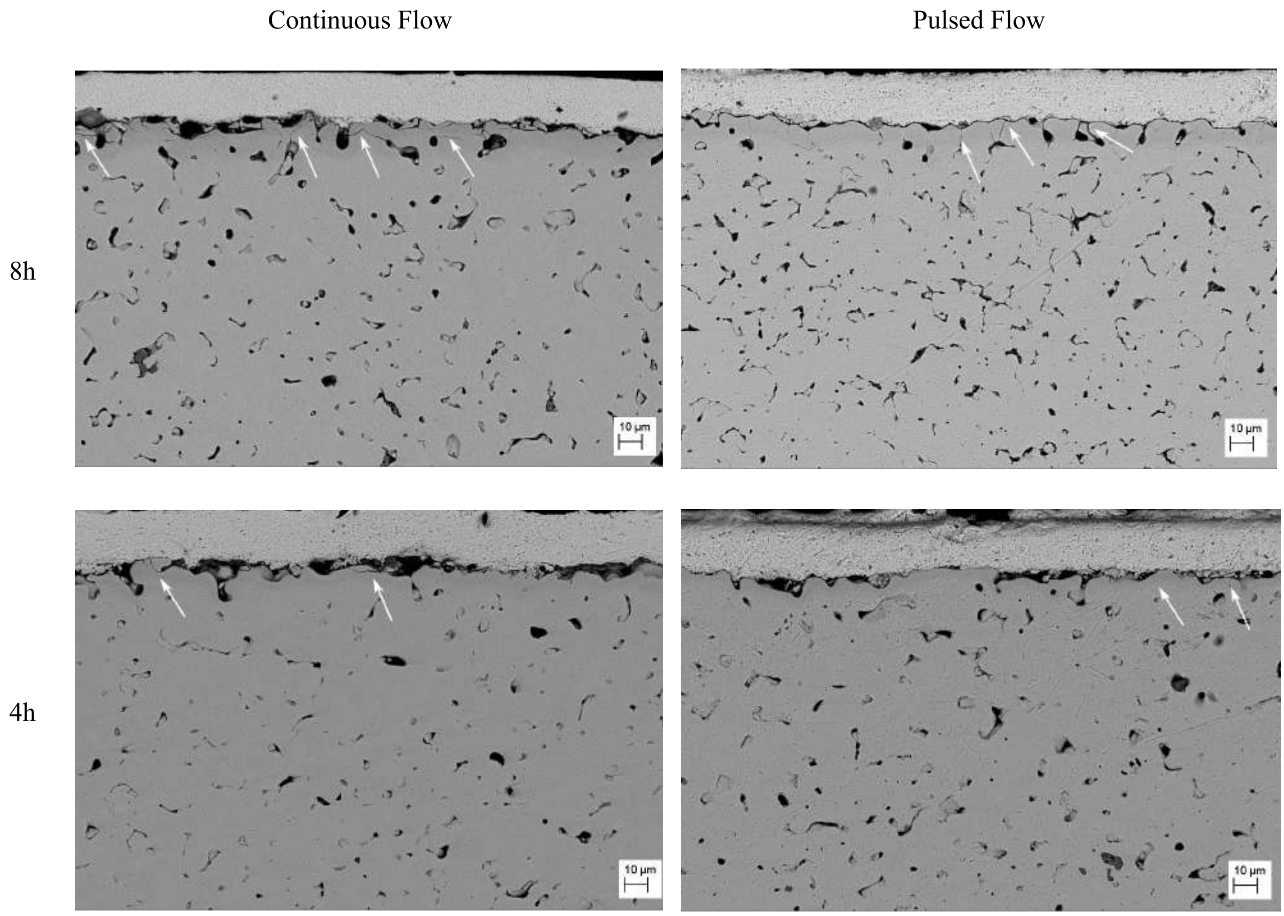
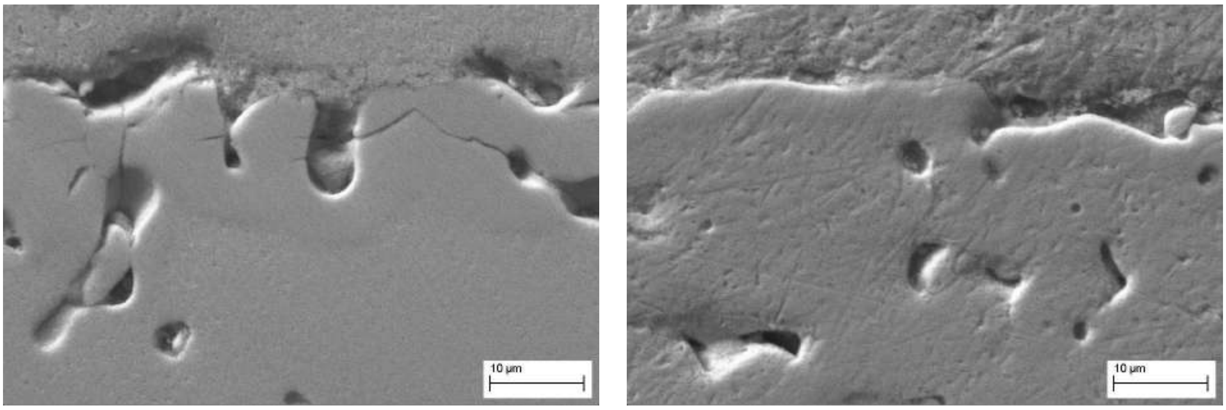


Figure 1. Cross-sectional micrograph . SEM images of samples nitrided for 4 hours and 8 hours with continuous and pulsed nitrogen flow.

Figure 1 shows the cross-sectional micrograph of the nitrided samples. In all samples, the pores of the material from the sintering process and the nitrided layer are visible. In samples nitrided for 8 hours with continuous nitrogen flow, the formation of cracks on the surface is observed, as highlighted by the arrows, which are a result of the high level of residual stresses in the nitrided layer (Mendes *et al.*, 2014). In addition to compromising the surface, from a mechanical point of view, cracks promote access of the corrosive agents to the interior of the material, accelerating the corrosion process. Analysis of the samples nitrided for 4 hours with continuous flow also shows the formation of cracks, as in the previous sample. However, after a qualitative analysis, it is possible to see that the occurrence of cracks was lower than in the 8 hour sample.This may be related to the level of residual stresses in the layer, as the exposure to nitrogen in the 4 hour nitriding is considerably lower than in the 8 hour sample. Studies such as the one by Mendes *et al.* (2014) show that, for the same temperature, shorter times of nitriding tend to form nitrided layers with a lower level of compressive residual stresses in the material, which is related to crack propagation. In addition, it is clear that the propagation of cracks occurs in places near to the pores of the sintered material (Figure 2).

In the 8 hour and 4 hour samples it is possible to notice that there was a reduction in the occurrence of cracks compared to the nitrided samples with continuous flow, which, as mentioned, above is a result of the shorter time of exposure to nitrogen and, consequently, lower level of residual stresses in the layer. According to Sphair (2017), in nitriding with pulsed nitrogen flow, it is possible to control not only the thickness of the layer, but also the hardness, the level of expansion and residual stresses. This result is strong evidence of the influence of nitrogen exposure on the residual stress levels of the nitrided material and the influence of nitrogen pulses on layer formation, thus demonstrating a possible control of nitrogen potential and consequent reduction and/or elimination of cracks from nitriding.



a) b)

Figure 2. SEM images of samples nitrided for a) 8 hours with continuous flow and b) 4 hours with pulsed flow.

Continuous Flow Pulsed Flow

8h

4h

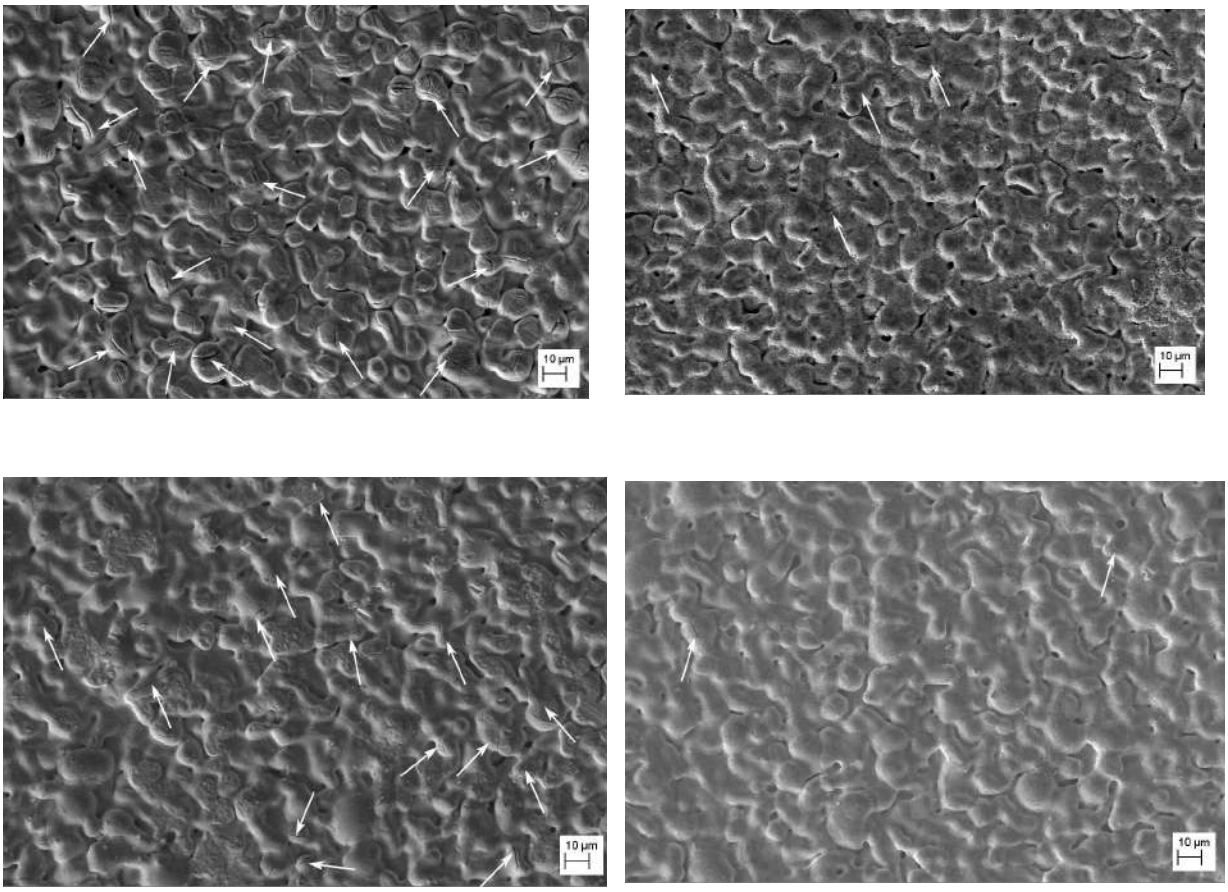


Figure 3. Top of the samples micrograph . SEM images of samples nitrided for 4 hours and 8 hours with continuous and pulsed nitrogen flow.

Figure 3 shows also the microscopy of the top of the samples nitrided for 8 hours and 4 hours with pulsed nitrogen flow, with indications for the cracks that occurred in the material. For the evaluation of the top of the nitrided layers the SEM was performed directly on the material after nitriding. Despite not evaluating in depth the layer formed in the material, this view helps in an overview of the nitrided layer. In Figure 3, cracks are visible in all treatment conditions. In the 8 hour condition with continuous flow, it is verified that the formation of cracks extends over a large part of the surface, as well as in the 4 hour condition with continuous flow. According to proposed crack propagation mechanisms (Stinville *et al.*, 2010), pores are stress concentrators and provide propagation in their surroundings. This is visible in Figure 2, with propagation at the pore contours. Again, a reduction in the occurrence of cracks in the 4 hour sample compared to the 8 hour nitrided sample is observable. This may demonstrate the possibility of using pulsed nitrogen flow to control residual stresses and crack incidence in sintered austenitic stainless steel materials.

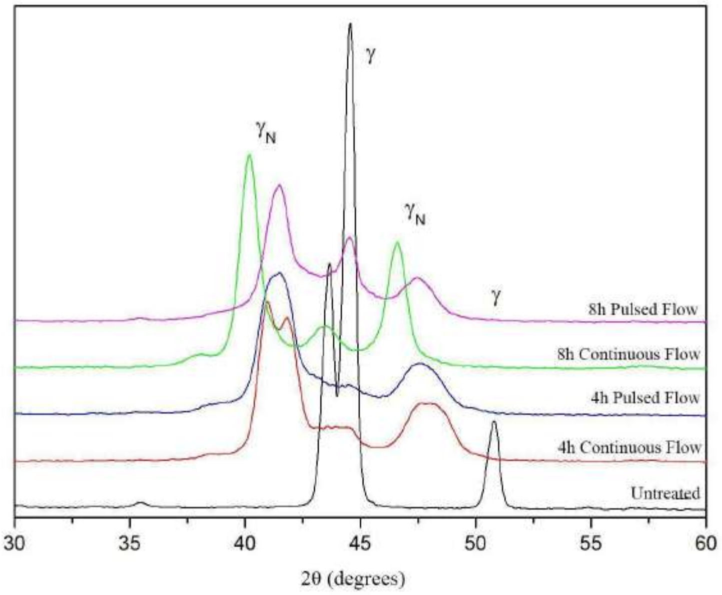


Figure 4. X-ray diffraction of nitrided and untreated samples.

Figure 4 shows the X-ray diffractions for the 2θ range from 30° to 60° with an incidence angle of 10° of the untreated sample and also of the samples nitrided for 8 hours and 4 hours with continuous and pulsed flow of nitrogen. Analyzing the position of the peaks present in the diffractogram, it is possible to identify the presence of austenite in the untreated sample, characteristic of 316L stainless steel, in the peaks at 44.59º and 50.82º, locations that are in agreement with Mendes *et al.*(2014) results. The formation of the expanded austenite phase (γN) can be identified in diffractograms observing a displacement of the austenite peaks to the left and also an enlargement of the peaks in relation to the material in the supply state, which may be a result of the deformation of the crystalline reticulate during nitrogen diffusion in nitriding, in addition to the presence of residual stresses, crystalline defects in the layer and nitrogen concentration gradients (Borgioli *et al.*, 2005). In the diffractogram of all nitrided samples, the formation of expanded austenite can be seen, visible by the shift of the peaks to the left, indicating the phase change that occurred during nitriding. The peaks at angles between the expanded austenite peaks can also indicate the presence of austenite in the untreated material, not having been completely changed to the S phase.

Table 1. Vickers microhardness

Sample	Mean Value (HV0.025)	Standard Deviation
8h - Continuous Flow	973.8	57.3
8h - Pulsed Flow	698	78.3
4h - Continuous Flow	621.2	93.8
4h - Pulsed Flow	593.8	72.0

Table 1 presents the microhardness results. The hardness values of pulsed samples were lower compared to continuous samples. The greatest difference is observed in samples nitrided for 8 hours, in which the sample with continuous flow had a hardness value 1.39 times higher compared to the pulsed sample. The hardness of the sample nitrided for 4 hours with continuous flow was 1.05 times greater than the sample for 4 hours with pulsed flow. This result is consistent with previous studies, since the time of exposure to nitrogen was shorter in pulsed parts, which reduces its concentration in the layer. The reduction in hardness not being so prominent in pulsed samples combined with a considerable reduction in the occurrence of cracks may indicate the possible application of pulsed nitrogen fluxes as a way to control cracks in sintered stainless steels.

4. Conclusion

From the analysis of the results, it was possible to evaluate the influence of nitrogen pulses on nitriding of 4 hours and 8 hours of sintered austenitic stainless steel 316L.

All processing conditions produced superficial layers of expanded austenite, and nitriding with longer treatment times caused peaks with higher intensities of this phase in the X-ray diffractions, which may indicate greater thicknesses of expanded austenite.

The samples nitrided with pulsed flow of nitrogen showed a lower occurrence of cracks when compared to samples nitrided with continuous flow, being evidenced by the reduction of cracks in the samples of 4 hours and 8 hours nitrided with pulsed flow.

The hardness of the continuous flow nitrided samples showed results consistent with previous studies, in which the 4 hour samples had a lower hardness compared to the 8 hour sample. Pulsed flow samples had lower hardness compared to continuous flow. This may indicate a reduction in the nitrogen potential in the layer and a consequent reduction in residual compressive stresses arising from the formation of expanded austenite.

Thus, the use of pulsed nitrogen fluxes can be a possible tool to control nitrogen concentration and compressive residual stresses arising from the expansion of austenite during nitriding, and a mechanism to eliminate cracks.

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