

# IMPROVEMENT OF THE CAVITATION EROSION RESISTANCE OF UNS 31803 STAINLESS STEEL BY DUPLEX TREATMENT<sup>1</sup>

D.H Mesa<sup>2</sup>  
Carlos Eduardo Pinedo<sup>3</sup>  
André Paulo Tschiptschin<sup>4</sup>

## Abstract

A Duplex surface treatment consisting of High Temperature Gas Nitriding (HTGN) followed by Low Temperature Plasma Nitriding (LTPN) was carried out in an UNS S31803 duplex stainless steel. The HTGN treatment was intended to produce a relatively thick and hard fully austenitic layer giving mechanical support to the thinner and much harder expanded austenite layer. HTGN was performed at 1200°C for 3 hours, in a 1 atm N<sub>2</sub> atmosphere while LTPN was carried out in a 75% N<sub>2</sub> + 25% H<sub>2</sub> atmosphere, at 400°C for 12 hours. An expanded austenite  $\gamma_N$  layer, 2.3  $\mu\text{m}$  thick, 1500 HV0.025 hard, was formed on top of a 100  $\mu\text{m}$  thick, 330 HV 0.1 hard, fully austenitic layer, containing 0.9 wt% N. For comparison purposes Low Temperature Plasma Nitriding (LTPN) was carried out with UNS S30403 stainless steel specimens obtaining a 4.0  $\mu\text{m}$  thick, 1500 HV 0.025 hard, expanded austenite layer formed on top of a fully austenitic matrix having 190 HV 0.1. The nitrided specimens were tested in a 20 kHz vibratory cavitation erosion testing equipment. Comparison between the duplex treated UNS S31803 steel and the low temperature plasma nitrided UNS S30403 steel, resulted in incubation times almost 9 times greater. The maximum cavitation wear rate of the LTPN UNS S31403 was 5.5 g/m<sup>2</sup>h, 180 times greater than the one measured for the duplex treated UNS S31803 steel. The greater cavitation wear resistance of the duplex treated UNS S31803 steel, compared to the LTPN treated UNS S30403 steel was explained by the greater mechanical support the fully austenitic, 330 HV 0.1 hard, 100  $\mu\text{m}$  layer gives to the expanded austenite layer formed on top of the specimen after LTPN. A strong crystallographic textured surface, inherited from the fully austenitic layer formed during HTGN, with the expanded austenite layer showing {101} crystallographic planes //surface contributed also to improve the cavitation resistance of the duplex treated steel.

**Keywords:** Cavitation-Erosion, Plasma Nitriding, Gas Nitriding, Grain boundary engineering.

<sup>1</sup> Technical contribution to the First International Brazilian Conference on Tribology – TribobR-2010, November, 24<sup>th</sup>-26<sup>th</sup>, 2010, Rio de Janeiro, RJ, Brazil.

<sup>2</sup> Metallurgical and Materials Engineering Department of the University of São Paulo, Av. Prof. Mello Moraes 2463, 05508-900 São Paulo, Brazil / Mechanical Technology Program, Technological University of Pereira, Vereda La Julita, Pereira, Risaralda, Colombia

<sup>3</sup> University of Mogi das Cruzes and Heat Tech - Technology for Heat Treatment and Surface Engineering Ltd, Brazil.

<sup>4</sup> Metallurgical and Materials Engineering Department of the University of São Paulo, Av. Prof. Mello Moraes 2463, 05508-900 São Paulo, Brazil Corresponding author: Phone: +55-11-30915656; fax: +55-11-30915243; e-mail: antschip@usp.br

## 1 INTRODUCTION

High nitrogen austenitic steels have been reported as suitable materials for applications in which erosive damage caused by cavitation is significant, leading to a decrease in the large maintenance costs characteristics of hydraulic systems.<sup>(1-3)</sup> The suitability of high nitrogen austenitic steels for these applications is mainly based on both higher CE resistance compared to conventional nitrogen free austenitic steels and lower cost compared to the CE-resistant cobalt-based alloys. High Temperature Gas Nitriding has been reported as a suitable route to enrich the surface of austenitic and duplex stainless steels in nitrogen.<sup>(4,5)</sup>

On the other hand, Low Temperature Plasma Nitriding has been extensively used as a mean of increasing the wear resistance of austenitic stainless steels, due to formation of a hard expanded austenite layer on top of a fully austenitic microstructure.<sup>(6-10)</sup> The effect of plasma nitriding on the cavitation erosion resistance of steels has been reported by few authors.<sup>(11,12)</sup> The significant improvement in the incubation period of plasma nitrided steels indicates that the hardness of the nitrided layer has a crucial role to play in their performance. However, following the trend observed for hard materials,<sup>(12)</sup> once the hard thin layer cracks or is locally removed from the surface, cavitation damage concentrates on some points on the surface leading to catastrophic cavitation pitting phenomena.

The purpose of this study is to investigate the role of a harder mechanical support to enhance the cavitation wear properties of plasma nitrided layers formed on top of fully austenitic stainless steels.

## 2 EXPERIMENTAL

Before being Low Temperature Plasma Nitrided (LTPN) UNS S31803 specimens (240 HV 0.1) were High Temperature Gas Nitrided (HTGN), at 1200°C in a pure N<sub>2</sub> atmosphere during 3 hours, aiming to obtain a 0.9 wt% N fully austenitic layer.<sup>(13)</sup> Following HTGN, Low Temperature Plasma Nitriding (LTPN) was carried out at 400°C in 75% N<sub>2</sub> + 25% H<sub>2</sub> atmosphere, for 12 hours in an ELTRO PULS DC pulsed plasma reactor.

UNS S30403 austenitic specimens, 190 HV 0.1 hard, were LTPN in the same conditions. Solubilized UNS S31803 duplex stainless steel specimens with hardness of 240 HV 0.1 were also used in the cavitation tests for comparison purposes.

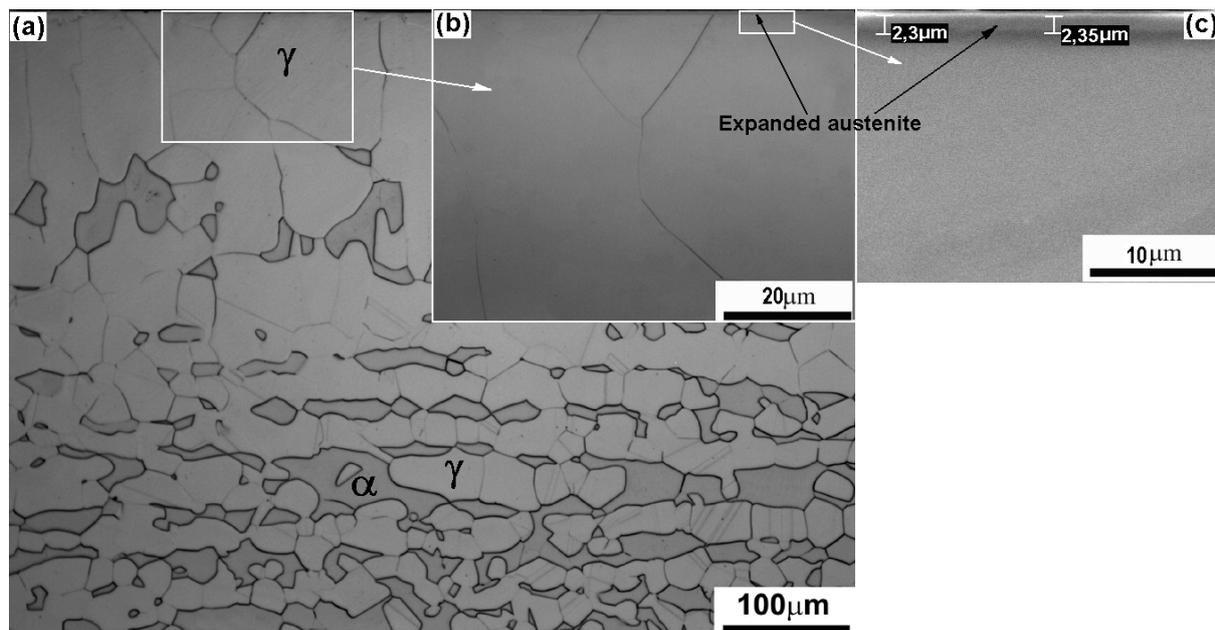
The specimens were tested in a 20 kHz, Telsonic SG 1000, vibratory cavitation apparatus using the indirect method with a 0.5 mm distance from the specimen to the horn, according ASTM G32-92 standard. The amplitude of vibration was 40 µm and temperature was maintained at 20 ± 1 °C. Mass losses were periodically measured in a Shimadzu AUW220D scale, with 0.01 mg readability and wear rates were plotted against testing time.<sup>(14)</sup>

The microstructure and the worn surfaces of the tested specimens were observed in a Philips XL30TM Scanning Electron Microscope using secondary electrons. EBSD – Electron Back Scattered Diffraction was carried out to analyze the microtexture, the diffraction patterns being collected in areas of 1.5 X 1.5 mm<sup>2</sup> before cavitation-erosion testing. N contents of the nitrided layers were measured by X-Ray Wavelength Dispersive Spectrometry (WDX) according to a procedure reported by Toro and Tschiptschin.<sup>(15)</sup> X-ray diffractometry (XRD) was used to characterize the crystal structure of the surface layers of the UNS S31803 stainless steels.

Hardness of the expanded austenite layers was measured in a Shimadzu NT-M001 microhardness tester using a Vickers indenter and a 25 gf load. Hardness of the substrates was measured using a Zwick microhardness tester with a Vickers indenter and a 100 gf load.

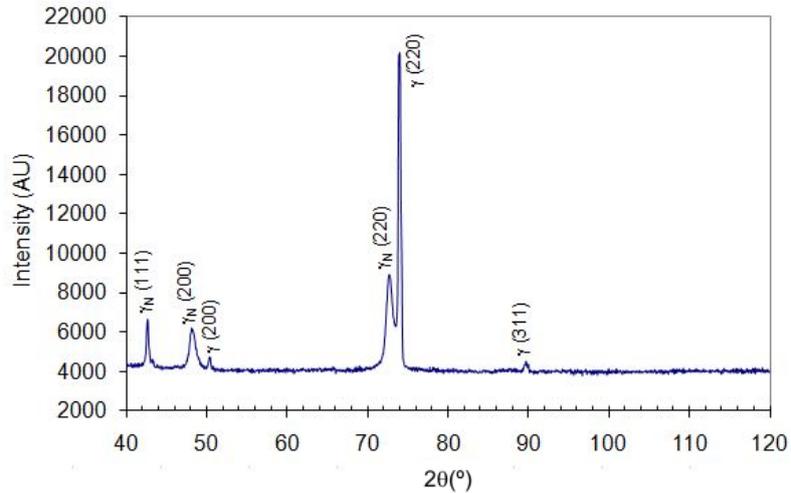
### 3 RESULTS

HTGN of UNS S31803 duplex stainless steel specimens led to formation of a 100  $\mu\text{m}$  thick, 0.9 wt% N fully austenitic layer on top of a duplex structure composed by  $\alpha + \gamma$  grains in the core, as shown in Figure 1a. The average grain size of the fully austenitic HTGN layer was 150  $\mu\text{m}$ .



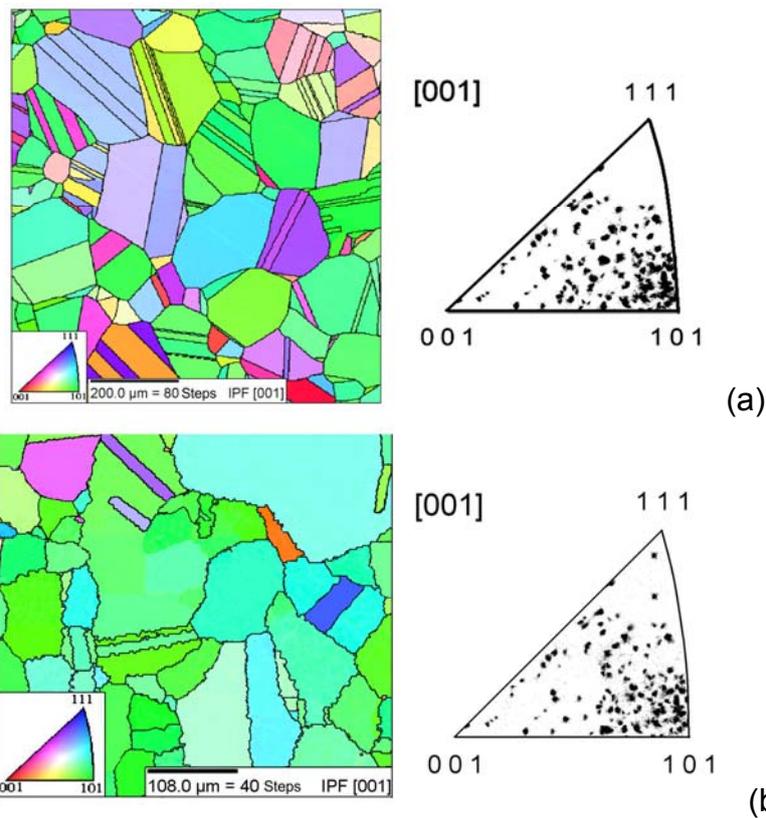
**Figure 1.** Cross section of the duplex treated (HTGN + LTPN) UNS S31803 stainless steel. (a)  $\alpha + \gamma$  microstructure in the core and a 100  $\mu\text{m}$  thick fully austenitic microstructure at the surface (b) fully austenitic layer (c) expanded austenite layer.

Subsequent LTPN treatment resulted in the formation of a 2.3  $\mu\text{m}$  expanded austenite layer, 1500 HV 0.025 hard, on top of the 100  $\mu\text{m}$  fully austenitic layer produced during HTGN. Figure 1 (b) and (c) show detailed micrographs of the UNS S31803 duplex treated (HTGN + LTPN) steel. The N content of the expanded austenite layer, formed on top of the UNS S31803 stainless steel, was measured by WDX giving 19.9 at%. The average grain size of the LTPN layer was also 150  $\mu\text{m}$ . X-ray diffractograms of the duplex treated UNS S31803 stainless steels are presented in Figure 2. Austenite and expanded austenite peaks can be seen in the diffractograms, the austenite peaks corresponding to a lattice parameter of 0.362 nm and the expanded austenite peaks being shifted to the left, corresponding to a lattice parameter of 0.37048 nm.



**Figure 2.** X-Ray diffraction patterns of the (HTGN+LTPN) UNS S31803 specimen.

The EBSD analysis of the HTGN UNS S31803 steel revealed a strong {101} crystallographic planes // surface texture in the fully austenitic layer formed at the surface of the UNS S31803 steel, similar to the results published in previous papers,<sup>(5,13)</sup> as shown in Figure 3 (a).



**Figure 3.** Orientation Image Maps and Inverse Pole Figures (a) surface of the HTGN UNS S31803 steel; (b) surface of the duplex treated (HTGN + LTPN) UNS S31803 steel, where {101} planes // surface predominate.

The expanded austenite layer obtained by LTPN the HTGN UNS S31803 steel also showed a strong {101} planes // surface texture - Figure 3 (b) - inherited from the fully austenitic layer formed on top of the duplex steel during HTGN.

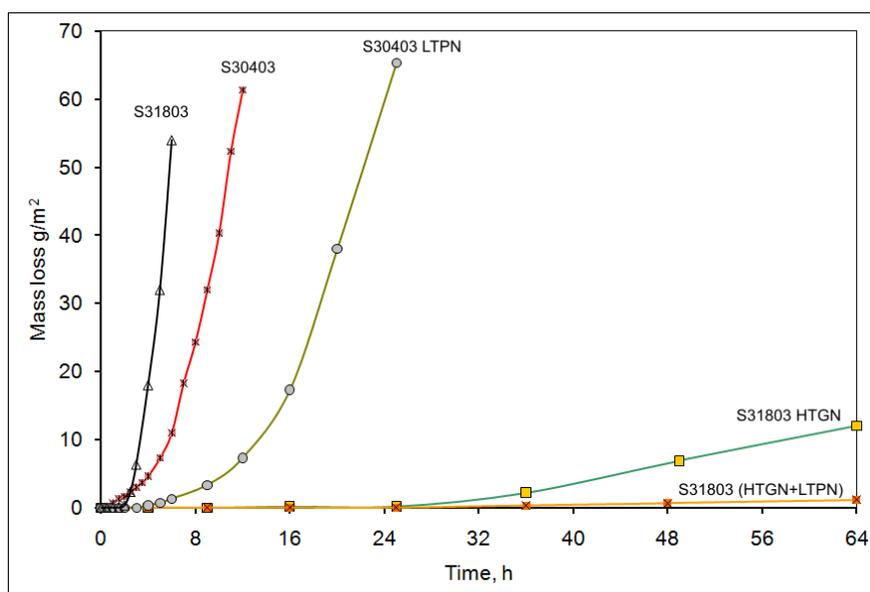
LTPN of UNS S30403 austenitic stainless steel specimens resulted in the formation of a 4 μm thick, 1500 HV 0.025 hard, expanded austenite layer on top of the soft - 190 HV 0.1 -austenitic matrix. The N content of the expanded austenite layer formed on top of the austenitic steel, measured by WDX, was 20.9 at%. EBSD-OIM maps of the expanded austenite layer formed on top of the LTPN UNS S30403 steel showed random texture.

Table 1 summarizes the structural characteristics of the studied specimens.

**Table 1** – Structural characteristics of the studied specimens

Alloy	Surface treatment	N content of the surface	Structure of the surface	Grain size (μm)	Texture measured on the surface	Thickness of the layer (μm)	Vickers Hardness
UNS S31803	Solubilized	0.16 wt%	50% α + 50% γ	Ferrite + Austenite stringers	-	-	240 HV0.1
	HTGN	0.9 wt%	Austenite	150	{101}//surface	100	330 HV0.1
	HTGN + LTPN	19.9 at%	Expanded austenite	150	{101}//surface	2.3	1500 HV 0.025
UNS S30403	Solubilized	0.02 wt%	Austenite	120	random	-	190 HV0.1
	LTPN	20.9 at%	Expanded austenite	120	random	4.0	1500 HV0.025

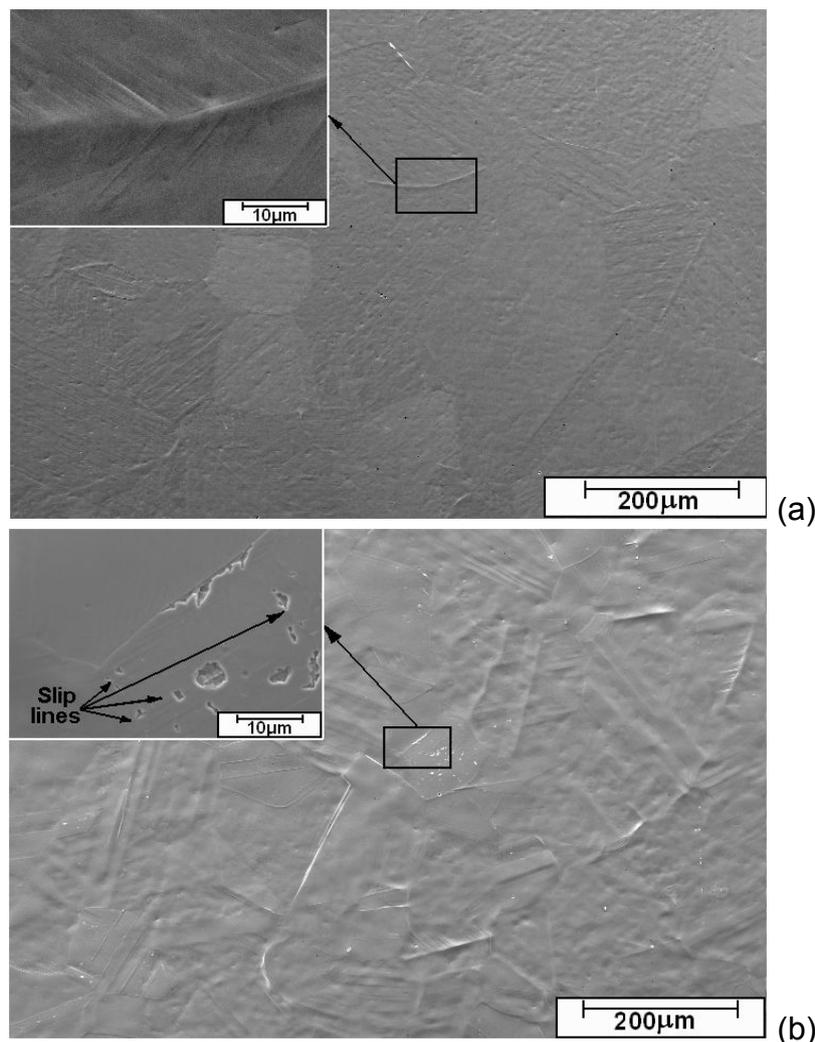
Figure 4 presents the variation of the wear rate with testing time for the untreated UNS S31803 and UNS S30403, the LTPN treated UNS S30403, the HTGN treated UNS S31803 steel and the duplex treated (HTGN + LTPN) UNS S31803 steel.



**Figure 4.** Variation of the wear rate as a function of cavitation testing time for the untreated UNS S31803 and UNS S30403 steels and LTPN UNS S30403, HTGN UNS S31803 and duplex treated (HTGN + LTPN) UNS S31803 steels.

The untreated UNS S31803 duplex stainless steel specimens showed the greatest maximum cavitation wear rate  $22.0 \text{ g/m}^2\text{h}$  and the shortest incubation time 1.5 hours. The fully austenitic UNS S30403 showed up to be more cavitation erosion resistant than de duplex stainless steel. The LTPN treated austenitic UNS S30403 steel also showed a low incubation time of 4 hours and a maximum cavitation wear rate of  $5.5 \text{ g/m}^2\text{h}$ . HTGN UNS S31803 steel showed an incubation time of 25 h and a maximum cavitation wear rate of  $0.3 \text{ g/m}^2\text{h}$ . For the duplex treated (LTPN +HTGN) UNS 31803 steel the incubation time was 36 hours and the maximum cavitation wear rate fell down to an almost negligible value of  $0.03 \text{ g/m}^2\text{h}$ .

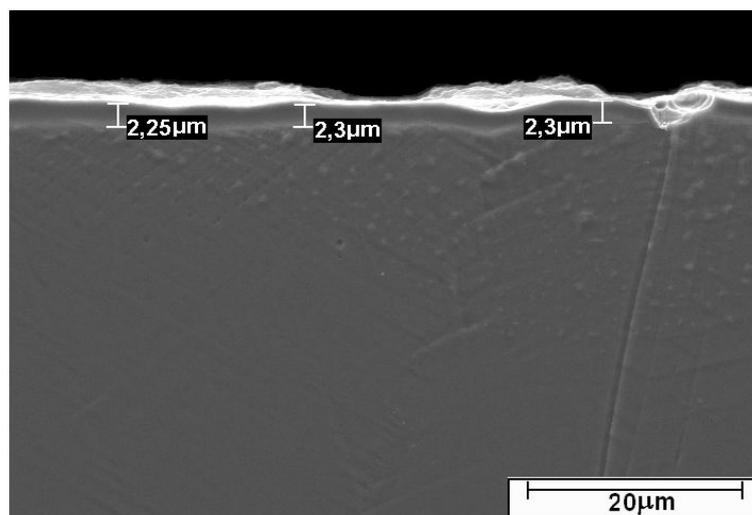
Figures 5 (a) and (b) show SEM photographs of the worn surfaces of the duplex treated (HTGN + LTPN) UNS S31803 steel and of the LTPN treated UNS S30403 specimens, after 4 hours of testing time.



**Figure 5.** Cavitation damage. (a) Duplex treated (HTGN + LTPN) UNS S31803 and (b) LTPN treated UNS S30403 tested in cavitation for 4 h.

Figures 5 (a) and 5 (b) show that at the beginning of the cavitation test traces of plastic deformation appears on the surface preceding cavitation damage. For the duplex treated UNS S31803 steel, cavitation damage initiates at grain boundaries as shown in Figure 5 (a). For the LTPN UNS S30403 steel cavitation damage initiates at slip bands and at grain boundaries Figure 5 (b).

Grain boundary damage observed at the very first stages of cavitation, occurs mainly by formation of grain boundary protrusions. Slip lines could only be seen at the surface of the plasma nitrided specimens after cavitation testing for very long times. The protrusions seen at the eroded surface are very similar to those observed on the surface of HTGN stainless steels and are a consequence of the cavitation damage. After 12 hours of cavitation testing of the UNS S30403 stainless steel, the grain boundaries got severely damaged and the expanded austenite layer was removed from the surface, exposing the substrate to the high pressure shock waves produced by imploding bubbles. Figure 6 shows the cross section of a specimen of UNS S31803 stainless steel tested for 64 h. Despite its lower thickness the plasma nitrided layer of the duplex treated steel is continuous over the grains, losing continuity only at the grain boundary, probably due to grain boundary cracking during the first stages of cavitation damage, as seen in Figure 6.



**Figure 6.** Cross section of the duplex treated UNS S31803 showing that the expanded austenite layer is still preserved after 64 hours of testing.

#### 4 DISCUSSION

Despite the greater chromium, molybdenum and nitrogen contents and the greater hardness of the untreated UNS S31803 duplex stainless steel when compared to the UNS S30403 austenitic stainless steel, the smaller cavitation erosion-resistance of the duplex steel can be attributed to the presence of ferrite, a high stacking fault energy phase, and  $\alpha/\gamma$  interfaces in the microstructure. Austenite usually exhibits very high work-hardening rates (associated with low stacking fault energies), especially the high nitrogen containing austenitic steels, as is the case of HTGN UNS S31803 duplex steel.

On the other hand, the expanded austenite layers formed on top of UNS S30403 steel and of the HTGN UNS S31803 have quite the same hardness, nitrogen content and similar thickness. The greater cavitation wear resistance of the duplex treated UNS S31803 steel, compared to the LTPN treated UNS S30403 steel can thus be explained by the greater mechanical support the HTGN nitride layer gives to the expanded austenite layer formed on top of the specimen after LTPN. In addition, a strongly textured surface, with the expanded austenite layer showing {101} crystallographic planes // surface, a preferred orientation already known to be highly resistant to cavitation erosion in High Nitrogen Austenitic Stainless Steels,<sup>(5,13)</sup> also

contributed to the better cavitation resistance observed for the duplex treated UNS S31803 steel.

Although grain to grain swelling and “damage” have been reported in recently published papers,<sup>(16,17)</sup> it is well established that this phenomena depends on layer thickness and nitrogen contents. The nitrogen content measured in the expanded austenite layers of the studied specimens was around 20 at%. Moreover, expanded austenite layers of the S31803 and S30403 were 2.3  $\mu\text{m}$  and 4.0  $\mu\text{m}$ , respectively. Both layer thickness and nitrogen contents are not large enough to produce significant swelling. Slip lines could only be seen at the surface of the plasma nitrided specimens after cavitation testing for very long times. The protrusions seen at the eroded surface are very similar to those observed on the surface of HTGN stainless steels and are a consequence of the cavitation damage.

Under high loading conditions, arisen during implosion of vapor bubbles, propagation of shock waves and liquid impingement against the surface of the specimen, a thin and hard expanded austenite layer may collapse, mainly due to substrate elastic and plastic deformations, resulting in premature failure of the layer. The performance of the hard expanded austenite layer is limited by the mechanical properties of the substrate material. A mechanical support is needed to avoid the so-called ‘eggshell-effect’, granting good adhesion to the hard expanded austenite layer formed on top of the steel.

## 5 CONCLUSIONS

- 1) The 4.0  $\mu\text{m}$  thick, 1500 HV0.025 hard, 20.9 at% N expanded austenite layer, formed after Low Temperature Plasma Nitriding UNS S30403 stainless steel, improves the cavitation resistance compared to the untreated condition.
- 2) High Temperature Gas Nitriding (HTGN) UNS S31803 resulted in the formation of a 100  $\mu\text{m}$  thick, 0.9 wt% N, 330 HV0.1 hard, fully austenitic layer increasing even more the cavitation erosion resistance compared to LTPN UNS S30403 and the untreated steels.
- 3) Duplex treated (HTGN + LTPN) UNS S31803 stainless steel with a 2.3  $\mu\text{m}$  thick, 1500 HV 0.025 hard, expanded austenite layer containing 19.9 at% N showed greater cavitation erosion resistance than LTPN treated UNS S30403, with a 4.0  $\mu\text{m}$  thick, 1500 HV 0.025 hard, expanded austenite layer, containing 20.9 at% N. The incubation time for cavitation damage increased 9 times and the maximum cavitation erosion wear rate decreased 180 times.
- 4) The mechanical support the 0.9 wt% N, fully austenitic layer, 100  $\mu\text{m}$  thick, 330 HV 0.1 hard gives to the expanded austenite layer formed on top of the specimen after LTPN is responsible for the better performance of the duplex treated steel.
- 5) A strongly textured surface, with the expanded austenite layer formed on top of the duplex treated UNS S31803 steel, with the {101} crystallographic planes parallel to the surface grants extra cavitation erosion resistance to the duplex treated steel.

## Acknowledgments

The authors would like to acknowledge the support of CAPES and FAPESP, Brazil; Technology University of Pereira, UTP, Colombia; COLCIENCIAS, Colombia and LASPAU

## REFERENCES

- 1 Berns, H. , Duz, V.A., Gavriljuk, V.G., Petrov, Y.N., Tatarsenko, V.A., Zeitsch. für Metallk., 88 (1997) 109.
- 2 Gavriljuk, V. G., Berns, H. in: High Nitrogen Steels-Structure, Properties, Manufacture, Applications, Springer-Verlag (1999) 318.
- 3 Hänninen, H., Romu, J., Ilola, R., Tervo, J. Laitinen Jour. Mater. Proces. Tehn. 117 (2001) 424.
- 4 H. Berns and S. Siebert. ISIJ int., 36 (1996), 927
- 5 Garzón C.M, Dos Santos JF, Thomas H, Tschiptschin AP. Wear, 259 (2005) 145.
- 6 N. Mingolo., A.P. Tschiptschin., C.E. Pinedo, Surf. Coat. Technol., 201 (2006) 4215.
- 7 A. A Recco., ; D. López, ; A.F. Bevilaqua,; F.B. Silva,; A. P.Tschiptschin, Surf.Coat. Technol., 202 (2007) 993
- 8 J. Baranowska., S.E. Franklin., C.G.N. Pelletier, Wear. 259 (2005) 432
- 9 E. Menthe and K.-T. Rie, Surf. Coat. Technol., 116 (1999) 199.
- 10 Y. Sun and T. Bell, Wear 218 (1998) 34.
- 11 C. Godoy, R.D. Mancosu, M.M. Lima, D. Brandão, J. Housden, J.C. Avelar-Batista, Surf. Coat. Tech., 200, ( 2006) 5370
- 12 B.S. Mann, V. Arya, Wear 253 (2002) 650
- 13 D.H. Mesa., C.M Garzón., A.P Tschiptschin, Wear, 99 (2009) 267
- 14 J.F. Dos Santos, C.M Garzón., A.P Tschiptschin. Mater. Sci. Eng. A-Struct., 382 (2004) 378
- 15 A. Toro, A.P. Tschiptschin, Scripta Mater. 63 (2010) 803
- 16 J. Stinville, P. Villechaise, C. Templier, J.P. Rivière, et M. Drouet, Acta Mater. doi:10.1016/j.actamat.2010.01.002, 2010
- 17 J. Stinville, P. Villechaise, C. Templier, J. Rivière, et M. Drouet Surf. Coat. Techn. 204 (2010) 1947