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ULTRA-LOW CARBON (ULC) STEEL MODIFIED BY TRIODE PLASMA NITRIDING AND PVD COATING - EFFECTS ON MICRO-STRUCTURE AND PROPERTIES[1]

Carlos Alberto Llanes Leyva[2]
Geralda Cristina Durães de Godoy[2]
Antônio César Bozzi[3]
Ivênio de Oliveira Teixeira[4]

Abstract
Ultra-low carbon (ULC) steels exhibit low yield strength and excellent formability. Plasma Assisted Physical Vapor Deposition (PAPVD) is a potential coating method for enhancing the strength at the surface of these steels. However, when deposited onto low strength alloys PAPVD coatings may undergo premature failure if the substrate plastically deforms under heavy load. Extra load support is usually required for hard coatings to perform satisfactorily. This work describes the characterization of Ti-stabilized ULC steels after surface modification by D.C Triode Plasma Nitriding (DC-TPN) and sequential coating with CrAlN by Electron Beam Plasma Assisted Physical Vapor Deposition (EB-PAPVD). Nitrided steel and duplex system were, respectively, 2.6 times and 3.5 times harder than the untreated Ti-ULC steel. Results indicate that it is feasible to manufacture duplex Ti-ULC steel via PAPVD, as significant improvements in mechanical properties were recorded for both nitrided and duplex-treated steels.
Keywords: Ti-stabilized ultra-low carbon steel; Plasma surface modification; Duplex coating.

AÇOS ULTRA BAIXO CARBONO (UBC) MODIFICADOS POR NITRETAÇÃO A PLASMA TRIODO E RECOBRIMENTO PVD – INFLUÊNCIA NA MICROESTRUTURA E PROPRIEDADES

Resumo
Aços UBC possuem baixa resistência mecânica e excelente conformabilidade. PAPVD é um método de recobrimento com potencial para aumentar a resistência mecânica superficial destes materiais. Entretanto, recobrimentos PAPVD podem sofrer falha prematura se o substrato deformar plasticamente sob carregamento mecânico. Os recobrimentos duros normalmente precisam de suporte adicional de carga. Este trabalho descreve a caracterização de Ti-UBC após modificação superficial por Nitretação a Plasma Triodo D.C (DC-TPN) e recobrimento seqüencial com CrAlN a Plasma por Deposição Física de Vapor com Feixe de Elétrons (EB-PAPVD). Os resultados indicam que é viável a fabricação de sistema dúplex em UBC-Ti via DC-TPN e EB-PAPVD, visto que ganhos significativos nas propriedades mecânicas foram registrados tanto para o sistema nitretado quanto para o sistema dúplex.
Palavras-chave: Aço ultra baixo carbono; Modificação a plasma; Recobrimento duplex.

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[2] *Mechanical Engineer, M. Sc. Metallurgy and Mines Engineering, Dr. Professor, Faculdade UCL, Serra, ES, Brazil - carlosleyva@ucl.br*
[3] *Metallurgy and Mines Engineering, Dr. Professor, PPGEM, Universidade Federal de Minas Gerais (UFMG), Brazil.*
[4] *Metallurgical Engineer, Dr. Professor, DEM, Universidade Federal do Espírito Santo (UFES), Brazil.*
5 *Metallurgical Engineer, M.Sc. Researcher, Usiminas S. A. Minas Gerais, Brazil.*

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1 INTRODUCTION

Over the past few years the range of applications for ultra-low carbon (ULC) steels has spread widely. As a general rule, these steels exhibit low yield strength and excellent formability. For the very same reason, applications for ULC steels are somehow restricted by their low resistance to surface degradation processes as wear. New applications could be developed for ULC steels – e.g. for manufacturing complex shape products - if modification treatments allow enhancing the surface properties. Plasma Assisted Physical Vapor Deposition (PAPVD) could be a potential coating method for enhancing both wear and corrosion resistances of low strength alloys.[1,2] However, when deposited onto low mechanical strength alloys PAPVD coatings may undergo premature failure if the substrate plastically deforms under heavy load. Therefore, an extra load support is often required for hard coatings to perform satisfactorily. Combined treatments involving plasma nitriding and PAPVD coating have been successfully used to improve the load-bearing capacity of hard films.[3] Other plasma thermochemical treatments such as nitriding, carburizing, carbonitriding and post-oxidation have also been employed to improve corrosion and wear resistance of low carbon steels, as well as to increase their surface hardness and fatigue life.[4]
Some research work has been undertaken regarding improvements of surface hardness and corrosion resistance in low carbon steels (AISI 1010 and 1020) which were surface modifiedby PAPVD processes.[4-7] However, to our knowledge, no reference can be found up to this date regarding micro-structure and properties of ULC steelsmodified by sequential treatments comprising plasma nitriding and PAPVD coating (duplex treatment).
This work is focused on thecharacterizationof micro-structure and properties of Ti-stabilized ULC steel before and after surface modification by D.C Triode Plasma Nitriding (DC-TPN) and sequential coating with CrAlN by Electron Beam Plasma-Assisted Physical Vapor Deposition (EB-PAPVD).

2 MATERIAL AND METHODS

2.1 Sampled Materials and Plasma Surface Modifications

Sample identification, nomenclature and manufacturing conditions for the different systems under investigation in this work are listed in Table 1.Samples of Ti-stabilized ULC steelwere manufactured under standard industrial conditions by Usiminas S.A, a Brazilian steel company.

Table 1. Sample identification, nomenclature and manufacturing conditions for different systems under investigation

No.	Description and manufacturing conditions	Nomenclature
1	Uncoated, untreated, cold rolled Ti-stabilized ULC steel	ULC
2	Plasma nitrided Ti-ULC steel: D.C Triode Plasma Nitriding at 500ºC for 2 hrs	ULC-TPN
3	Plasma Duplex Ti-ULC steel: Plasma nitrided Ti-ULC steel D.C. triode plasma at 500ºC for 2 hrs followed by EBPAPVD CrAlN coating	Duplex-ULC

Chemical composition of cold rolled ULC steel samples used inthis work are given in Table 2.C, S and N contents were determined by combustion method with Leco –

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CS-444 and Leco TC-136 analyzers. The other elements contents were obtained by optical emission spectroscopy with ARL-3460 analyzer.

Table 2. Chemical composition (in at. %) of as-received, cold rolled, Ti-stabilized ULC steel samples

Elements (at. %)							
C	Mn	Si	P	S	Al	Ti	Nb
0.0025	0.0817	0.0099	0.0096	0.0090	0.0476	0.0639	0.0002
N	B	Cu	Ni	Cr	Mo	Sn	As
0.0015	0.0002	0.0081	0.0131	0.0110	0.0014	0.0003	0.0018
Balance: Approx. 99.74%Fe							

For comparison purposes uncoated, untreated ULC steel samples were investigated in the as-received condition and after being metallographically ground (SiC paper) and polished (MD Dac cloth and DiaproDac 3 µm suspension) to a mirror finish. This procedure was adopted as a pre-treatment to improve the surface finish on samples being subsequently nitrided and coated. Polished ULC steel test discs (38 mm in diameter, 3 mm thick) were treated by D.C. Triode Plasma Nitriding (ULC-TPN), and by a duplex treatment comprising sequential D.C. Triode Plasma Nitriding and PAPVD CrAlN coating to produce a duplex system (Duplex-ULC).
Plasma modification processes were conducted by TECVAC Ltd, U.K. Mirror polished Ti-ULC steel samples were ultrasonically cleaned in a fully automated cleaning line to remove any surface contamination. After cleaning, samples were surface modified by D.C. Triode Plasma Nitriding (DC-TPN) and PAPVD CrAlN coating. D.C. triode plasma nitriding was carried out in a Tecvac IP70L system. For duplex samples, CrAlN coating was deposited by Electron Beam Plasma-Assisted Physical Vapour Deposition (EB-PAPVD) using a Tecvac IP90L twin e-beam system. In order to improve coating adhesion, a thin interlayer of high-purity Cr was deposited prior to CrAlN coating. Before any of the above surface modification processes, samples were subjected to a 5 minutes sputter clean stage in Ar glow discharges. For all plasma processes, bulk temperature of the substrate was continuously monitored using a thermocouple mounted on a dummy sample.

2.2 CharacterizationTechniques and Micro-Abrasive Wear Tests

Vickers micro-hardness (WPM Leipzig, 100 gf, 30 s, 10 replicates) and instrumented indentation hardness (Shimadzu DUHW201S) measurements were performed. Instrumented indentation hardness tests were carried out at two final loads: 300 mN and 1,900 mN. An average of 10 measurements were taken to determine the indentation hardness (HIT), indentation modulus (EIT), Martens or Universal hardness (HM) and contact depth (hc). Samples were also characterized for chemical composition, microstructure and phase composition. X-Ray diffraction analyses were carried out using a Philips PW3020 diffractometer in a Bragg–Brentano configuration ($\theta/2\theta$) and CuKα radiation source (λ = 0.154056 nm, 40kV, 20 mA). The detector (2θ) was scanned from 3° to 120° at a slow rate of 0.02°/s. Phase identification was accomplished by comparison against diffraction standards from the International Center for Diffraction Data (ICDD). Qualitative measurements of coating adhesion were made via Mercedes Test using 120° diamond cone (Rockwell indenter) and 150kgf normal load in a Pantec/RASN-RS Rockwell durometer.
For the duplex system, coating thickness was estimated by the ball crater method (calotest) and calculated from measurements of inner (a) and outer (b) diameters of

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the wear scars.[8-12]Calotests were run in a Phoenix TE66 Micro-Scale Abrasion Tester (Figure 1) using an AISI 52100 steel ball with ϕ25 mm diameter.

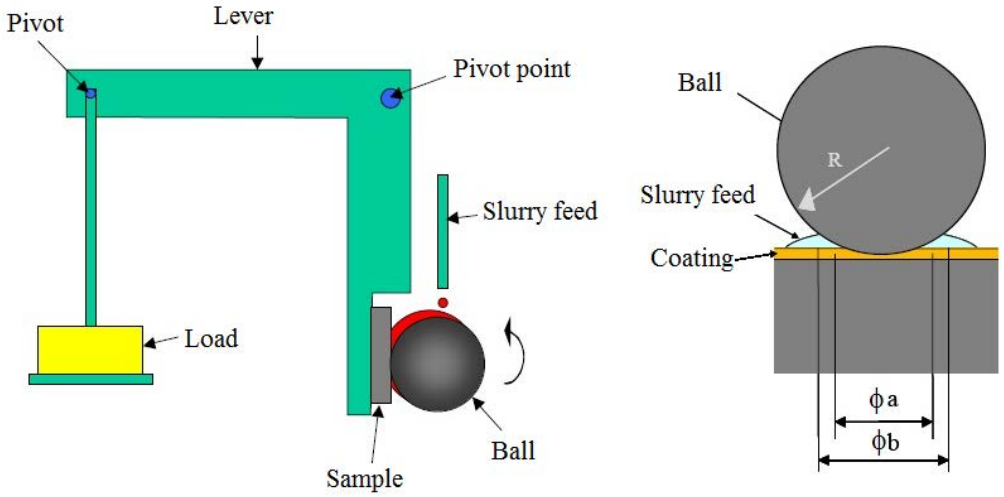

Figure 1. Schematic drawing of the micro-abrasive test apparatus used in this present investigation.[12]

Being R the radius of the ball, the coating thickness (*t*)can bedetermined from the test by measuring the inner(*a*) and outer(*b*) diameters of the wear crater[12]and using Equation 1.

$$t = \left(R^2 - \left(\frac{a}{2}\right)^2\right)^{\frac{1}{2}} - \left(R^2 - \left(\frac{b}{2}\right)^2\right)^{\frac{1}{2}} \quad (1)$$

In this work both diameters (*a*) and (*b*) were measured using an optical microscope equipped with Infinity Analyze Software (Lumenera Corporation) for image analysis.

3 RESULTS AND DISCUSSION

When XRD results and SEM photomicrographs shown in Figure 2 is analyzed in conjunction with Table 2, it is clear that the ULC steel substrate had a single ferrite phase (bcc α-Fe, ICDD 06-0696) with reasonably equiaxial grains. No other phase could be resolved by XRD for this ultra-low alloyed material. The planar spacing measured for (110) α-Fe was $d_{(110)}$ = 2.02736Å and the lattice parameter results $a_{\alpha\text{-Fe}}$ = 2.86712Å, which is only 0.02% larger than the value for ferrite in pure iron ($a_{\alpha\text{-Fe}}$ = 2.8664Å according to ICDD 06-0696).

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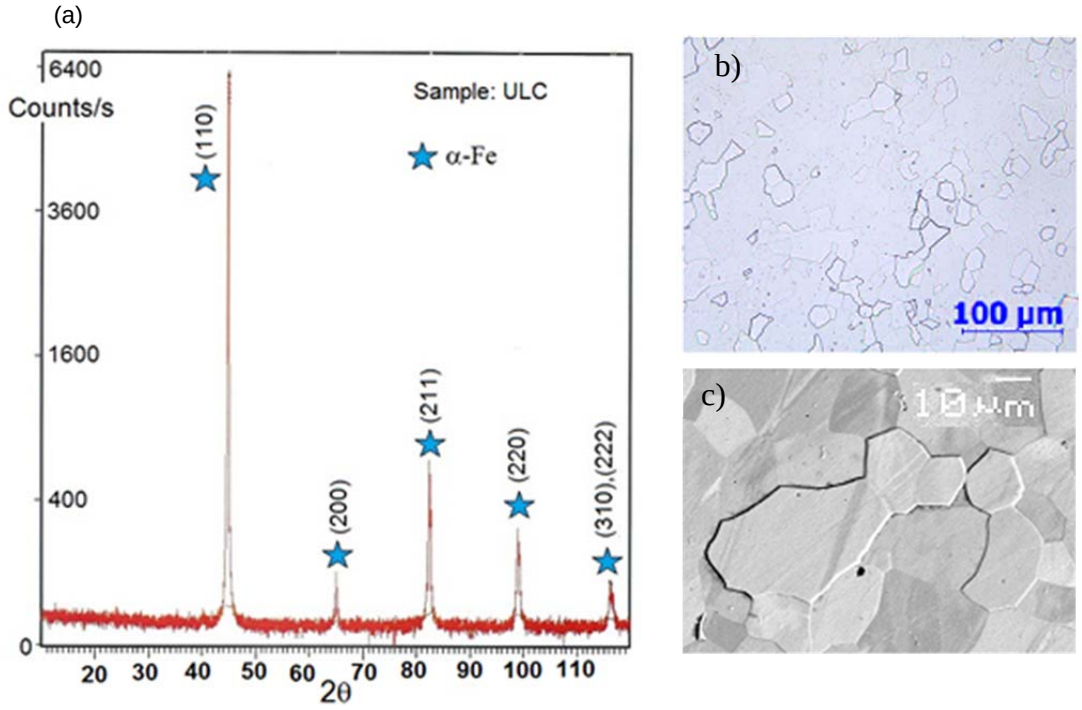

Figure 2.ULC steel sample in the as-received condition: (a) XRD results; (b) SEM photomicrograph of polished cross-section after 2% Nital etching at 200 X, SE mode; and (c) SEM photomicrograph of polished cross-section after 2% Nital etching at 1,000 X, BSE mode.

The diffractogram given in Figure 3 indicated that $Fe_{2-3}N$ (ε-hcp, ICDD 73-2102, 76-0090 and 86-0232) and Fe_4N (γ´-fcc, ICDD 86-0231) nitride phases were formed at the surface of the ferritic steel substrate as a consequence of plasma nitriding.

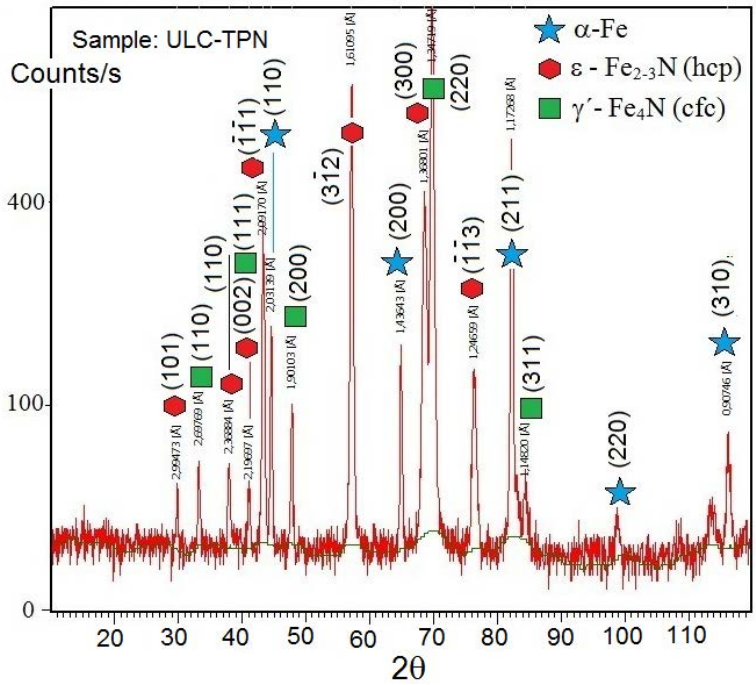

Figure 3. Diffractogram of the ULC-TPN steel sample after plasma nitriding.

These nitrides are relatively iron-rich with less than 35 at.% N. As expected,[13] no nitrogen-richer phases - such as FeN_y ($y > 0.5$), which could have either ZnS-type

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(γ´´) or NaCl-type structure (γ´´´, e.g. ICDD 88-2153) and nitrogen contents equal to or higher than 50 at.% N, or the Fe_3N_4 phasewith even higher N concentration - were found. The planar spacing measured for (110) α-Fe was $d_{(110)}$= 2.03139Å and the lattice parameter results $a_{\alpha\text{-Fe}}$ = 2.8782Å. It is 0.2% larger than the value obtained for ferrite in the untreated ULC steel, indicating presence of N in solid solution in the ferritic substrate close to the sample surface.

During PAPVD coating, the ternary nitride CrAlN film crystallized in a cubic NaCl B1 structure having a (200) texture as preferred orientation (Figure 4a). Diffraction peaks for (111), (220) and other planes were also observed (ICDD 11-0065, 46-1200, 88-2360). The planar spacing measured for (200) in the CrAlN phase was $d_{(200)}$ = 2.06765Å; resulting lattice parameter was a = 4.1353Å. The CrAlN coating could easily be identified at the top of the fracture cross-section shown in the SEM photomicrographs in Figures 4b and 4c. A moderate increase in ferrite grain size may have occurred as a consequence of the temperature-time cycle in the nitriding and coating processes.

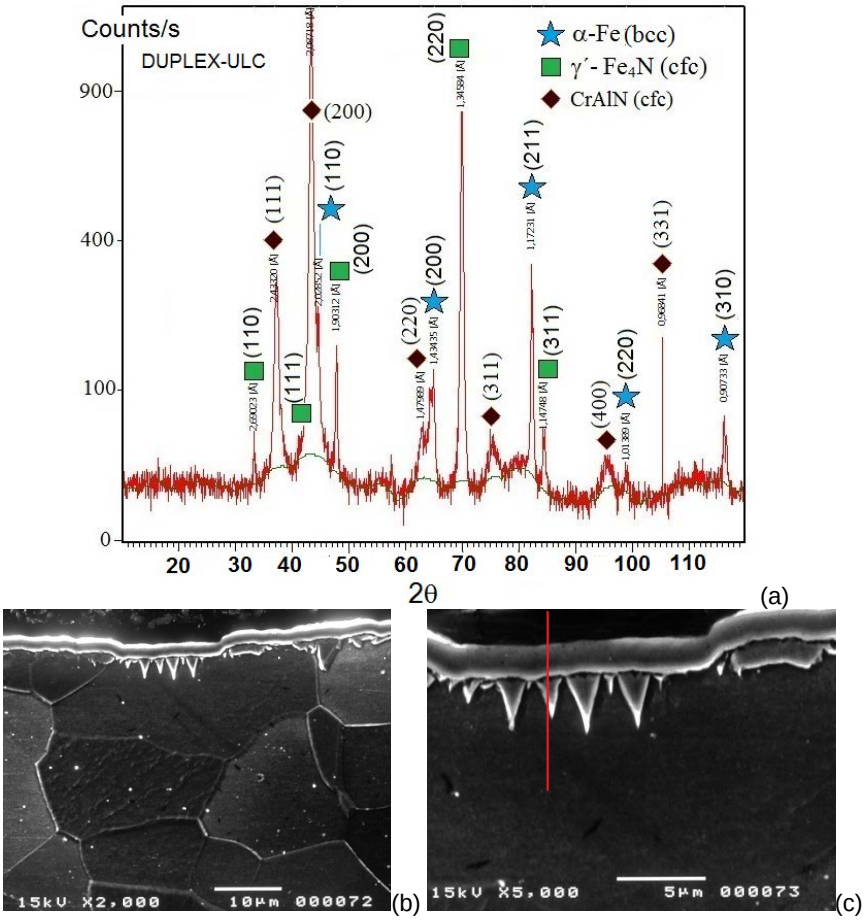

Figure 4. Duplex-ULC: (a) XRD results; (b) SEM photomicrograph, cross-section, 2% Nital etching at 2,000 X, SE mode; (c) SEM photomicrograph, cross-section, 2% Nital etching at 5,000 X, BSE mode.

An interesting fact was that the ε-$Fe_{2\text{-}3}N$ nitride (previously resolved in the nitrided material) could no longer be resolved at the surface of the Duplex-ULC: only the most iron-rich γ´- Fe_4N nitride was found by XRD. This most probably results from two effects occurring during the thermal activated coating deposition process: i) close to the sample surface, N combines preferentially with Cr and Al rather than with Fe; (ii) within the compound layer below the coating, the nitrides decompose from ε-

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$Fe_{2-3}N$ to γ'- Fe_4N. Just underneath the coating, the γ'- Fe_4N nitride phase grew as a succession of relatively wide triangular needles, up to 4 -5 µm long, as shown in Figure 4c). Due to the ε to γ' decomposition and to the progress of nitrogen diffusion in-depth, the lattice parameter of the ferrite reduces in the duplex sample down to $a_{\alpha\text{-}Fe}$ = 2.86876Å for $d_{(110)}$ = 2.02852Å, which is smaller than for the nitrided steel but still 0.06% larger than for the untreated steel.

Below the compound (γ'- Fe_4N) layer a diffusion layer is formed,where very fines nitrides may precipitate and also some N remains in solid solution. This is confirmed by the microhardness HV100 profile with depth below the surface as shown in Figure 5a. The effective hardening depth (considered as reaching 130 HV, about one third harder than the substrate) was 70µm for the nitrided steel. During coating deposition, the N diffusion progresses and the effective hardening depth increases up to 90µm, while the surface hardness decreases from the nitrided system to the duplex system due to εtoγ'decomposition.

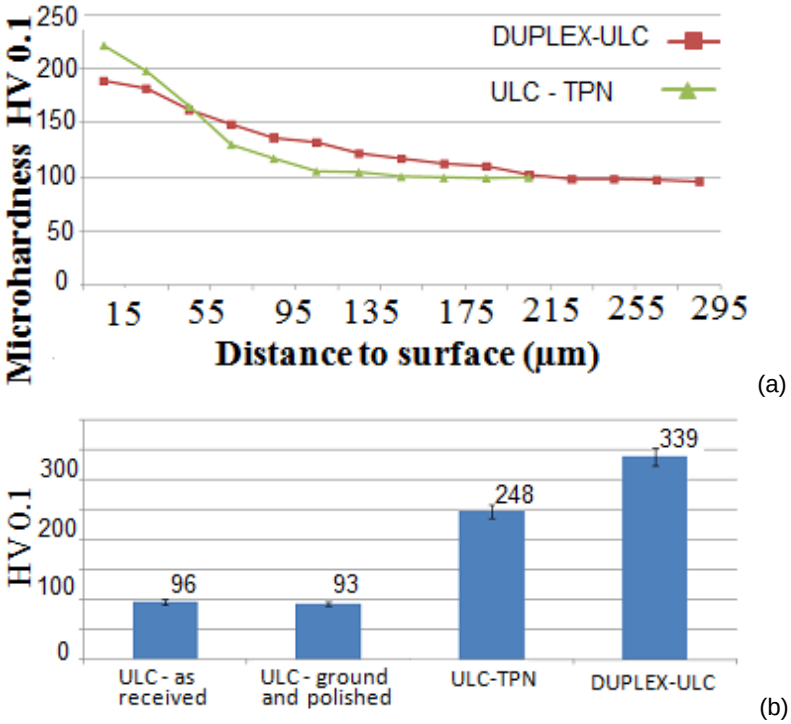

Figure 5.(a) Microhardness HV100 profile with depth below the surface; (b) Top Vickers micro-hardness results.

The effect of plasma nitriding and sequential coating on the Vickers micro-hardness measured on top of the sample surface is also shown in Figure 5b. When compared to untreated ULC steel, nitrided steel is 2.6 times harder and Duplex-ULC is 3.5 times harder. Additional results from instrumented ultra micro-hardness tests using a Berkovich indenter are presented in Figure 6. Progressive hardening of ULC steel by plasma nitriding and sequential CrAlN coating was confirmed by both HIT and HM hardness values, especially for the low final load (300 mN) at which penetration (*hc*) was greatly reduced. Under this low load, the effect of coating was further highlighted.

In order to retard coating failure and wear damage, it is vital to reduce plastic deformation of the substrate. For abrasive wear mainly caused by plastic deformation, surface hardness is the main parameter that will influence the wear response. In general terms, the harder the surface, the higher is the resistance to

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abrasive wear. On that basis, combined treatments involving plasma nitriding and PAPVD coating could be quoted for improving the surface hardness and therefore the abrasive wear resistance of low strength alloys, as ULC steel and others.

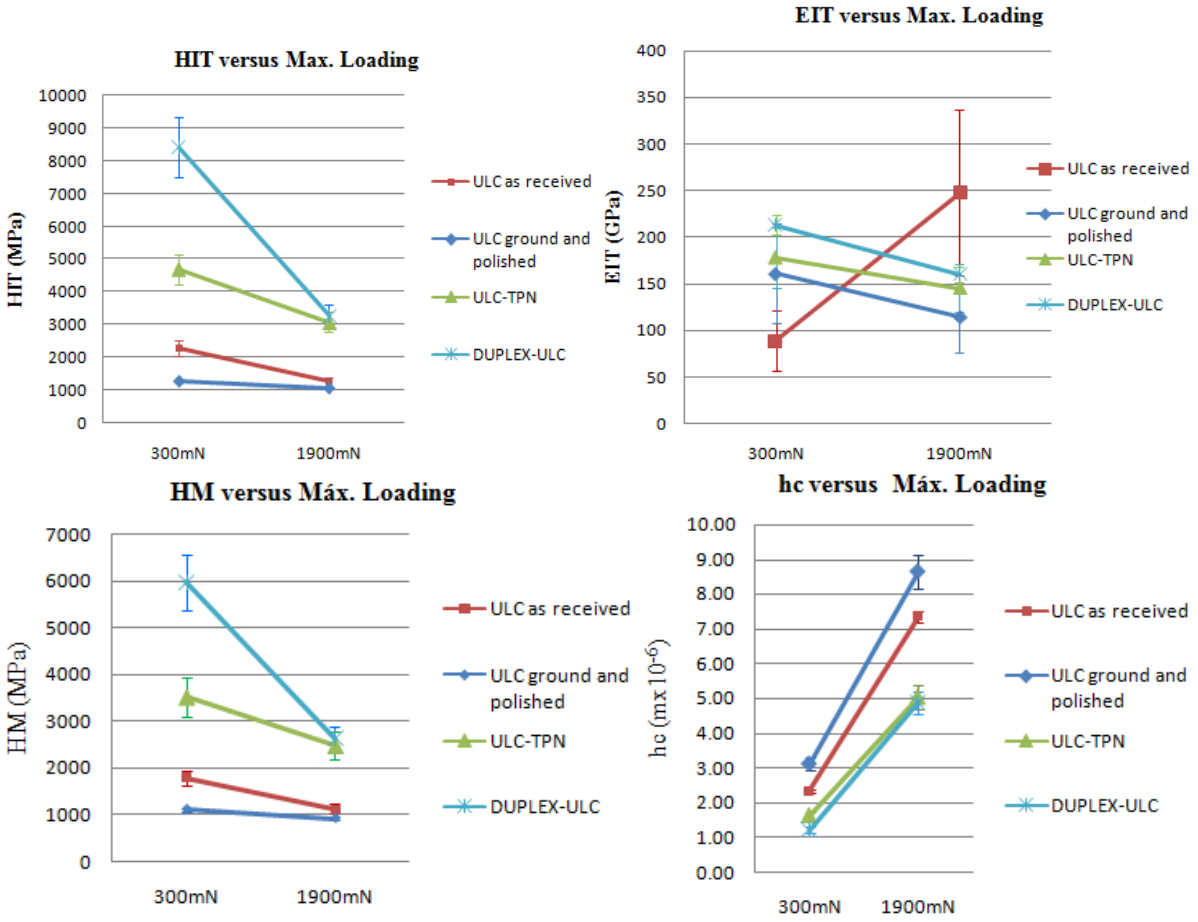

Figure 6. Results from instrumented ultra micro-hardness tests carried out using a Berkovich indenter: (a) HIT (Indentation hardness); (b) EIT (Indentation modulus); (c) HM (Martens or Universal hardness); (d) hc (contact depth).

It can also be seen from Figure 6 that the effects of plasma modifications on the elastic modulus of the ULC steel were rather inconclusive. If the mean values over 10 replicates are considered, it could be inferred that plasma nitriding and coating progressively increased the indentation elastic modulus, EIT, when compared to ground and polished ULC steel. However, the standard deviations of the EIT values were large, hindering a conclusive statement. For the as-received ULC steel the EIT values were even erratic. Several factors could have played a part in instrumented indentation measurements carried out in this sample, including its high values for surface roughness parameters and the eventual effect of an oxide layer at the surface. It has already been reported in the literature that EIT values measured from instrumented indentation tests do not always agree with those resulting from tensile tests.[14,15] EIT is usually load dependent and is often affected by measuring method (unloading or reloading curve), grain orientation and size (especially for low loads), local defects (porosity, micro-cracks etc.), problems in computing contact area (especially for soft materials) and the mechanics of systems comprising hard coatings on soft substrates etc.

The surface roughness of the samples measured by stylus profilometry is illustrated in Figure 7 (note that different scales were used from Figure 7a to 7d). The numerical

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values for the amplitude and statistical parameters of the initial surface roughness are shown in Table 3.

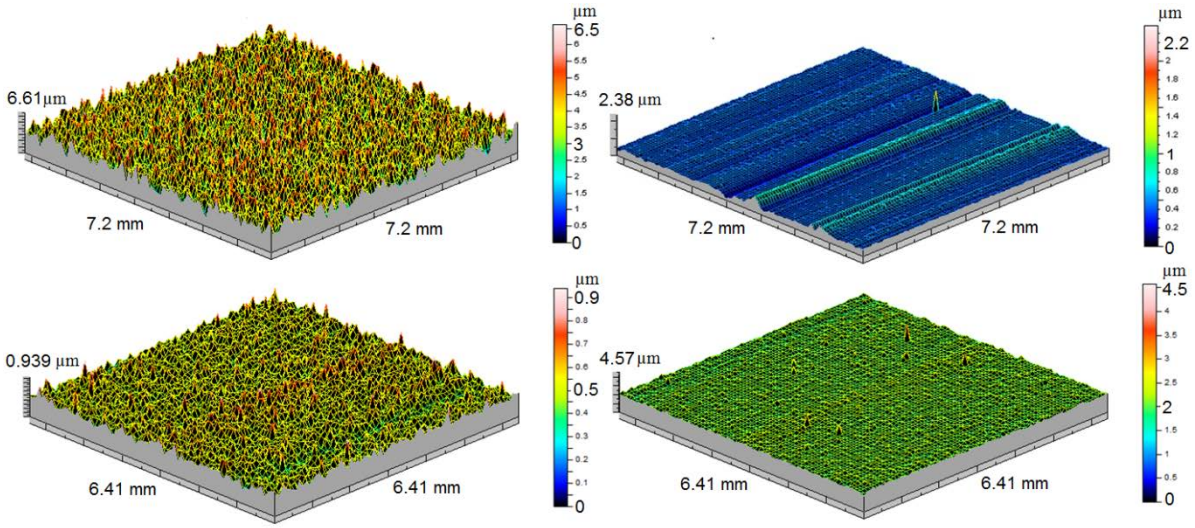

Figure 7. Surface topography of samples, obtained by surface profilometry: (a) as-received ULC steel; (b) metallographically ground and polished ULC steel; (c) plasma nitrided ULC-TPN steel; and (d) Duplex-ULC steel.

Table 3. Surface parameters of samples,as measured by stylus profilometry

Surface parameter (Gaussian filter, cut-off 0.8mm)			As-received ULC	Ground and polished ULC	Plasma nitrided ULC-TPN	Duplex-ULC
Amplitude parameters	S_a µm	Arithmetic average deviation	0.712	0.062	0.060	0.066
	S_q µm	Root mean square (RMS)	0.889	0.097	0.077	0.094
	S_p µm	Highest peak	3.20	1.94	0.433	2.48
	S_v µm	Deepest valley	3.42	0.44	0.51	2.10
	S_tµm	Max. total height	6.61	2.38	0.94	4.57
	S_zµm	Mean peak-to-valley height, 10 points	6.43	1.35	0.759	2.89
Statistic parameter	S_{ku}	Kurtosis	2.90	7.39	3.76	47.91
	S_{sk}	Skewness	-0.068	1.350	0.456	1.991

The surface roughness of the as-received ULC steel was significantly reduced by metallographic grinding and polishing. Plasma nitriding did not essentially alter the previous surface topography, as evidenced by the ULC-TPN sample. Sequential coating of the plasma nitrided steel (Duplex-ULC) increased the maximum peak and valley heights (as localized non-uniformities) but did not change both *Sa* and *Sq* parameters of the surface.

The measured inner and outer diameters of the wear scars resulting from calotest - as well as the calculated coating thickness - are resumed in Table 4. Three replicates were tested for each system.

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Table 4. Dimensions of the calotest wear scars after 1,350 rev, and calculated coating thickness

Sample	Mean inner diameter of the wear crater, *a* (x10^{-2} m)	Mean outer diameter of the wear crater, *b* (x10^{-2} m)	Average coating thickness *t* (x10^{-6} m)	Standard deviation of *t* (10^{-6} m)
Duplex-ULC	1,482.9 ± 13.7	1,582.0 ± 12.7	3.1	0.02

Coating thickness calculated from ball cratering (i.e. from measurements of inner and outer diameters of wear scars, using Equation 1)was found to be around the maximum value of 3µm. This value was in good agreement with measurements taken at sample cross-sections when examined by SEM.
Figure 8 showsthe micrograph resulting from qualitative Rockwell adhesion test for Duplex-ULC. No cracking was observed, indicating good adhesion of the coating to the nitrided substrate in the duplex system.

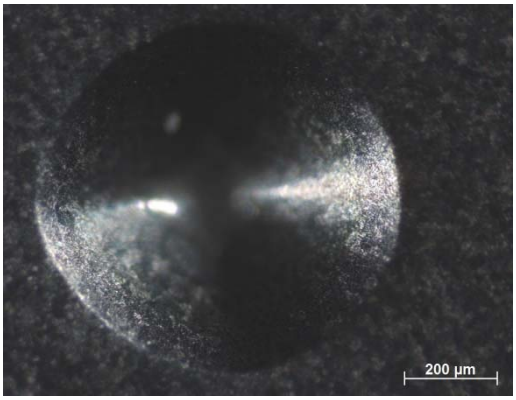

Figure 8. Duplex-ULC: micrograph from qualitative Rockwell adhesion test.

4 CONCLUSIONS

When compared to untreated ULC steel, nitrided steel ULC-TPN was 2.6 times harder and Duplex-ULC was 3.5 times harder ($HV_{0.1}$). Top micro hardness registered an increase from 100HV (100 gf, 30 s) in the ULC steel to up to 340HV in the Duplex system. Instrumented hardness tests confirmed this result.
Coating thickness resulted 3µm max. asdetermined from measurements of inner and outer diameters of wear scars produced by calotests.
The surface modification via plasma nitriding and sequential CrAlN coating produced significant surface hardening, even for a soft substrate as the ULC steel. Surface hardening processes led to chemical and microestrutural changes at the surface as previously described. It is feasible to manufacture duplex ULC steel by PAPVD, with expected improvement in wear resistance for both the nitrided and duplex-treated ULC steels.
Duplex treatment is a promising method to enhance the wear resistance of ULC steels and other low strength alloys. The development of a manufacturing route via plasma nitriding and sequential CrAlN coating may enlarge the range of applicability of ULC steels.

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