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Tribological properties of SiNx films on PH stainless steel with and without nitriding as a pre-treatment

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Abstract

In this work, the tribological behavior and adhesion of SiN_x films deposited by PACVD on nitrided and non-nitrided Corrax® PH stainless steel were evaluated.
The films were characterized by FTIR and EDS, hardness was assessed with a nanoindenter and the microstructure was analyzed by Optical Microscopy, SEM and FIB. To evaluate the tribological behavior, fretting and linear sliding tests were performed using WC and alumina balls as counterparts, and the adhesion of the SiN_x films was characterized using the Scratch Test and Rockwell C indentation methods. Erosion tests were conducted in sea water and sand flux. Corrosion behavior was evaluated by the Salt Spray Fog Test.
The film reached a hardness of 2300 HV and a thickness of about 1.4 microns. The duplex coated sample had a better tribological behavior than the simple coated sample, the nitrided layer allowed a graded interlayer which improved the wear resistance. Regarding the film adhesion, the duplex coating had an acceptable adhesion; the nitrided layer reduced the interface stress and enhanced the adhesion. Additionally, the films evidenced good corrosion resistance in a saline environment.

Keywords: duplex, PACVD coating, plasma nitriding, precipitation hardening stainless steel, wear resistance

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1. Introduction

The tribological properties of materials are related to interacting surfaces in relative motion and they are very important to improve the performance of mechanical parts. Precipitation hardening stainless steels are used in mechanical engineering due to their excellent mechanical properties. They can be easily machined in the annealed condition and then hardened with a subsequent aging process (Frandsen et al., 2006). However, in severe service conditions, where a combination of hardness, structural stability, and wear and corrosion resistance is required, surface treatments may be used (Qi et al., 2007).

Some authors have used plasma nitriding with good results (Esfandiari and Dong, 2007; Dong et al., 2008; Li et al., 2008), but also the tribological properties may be improved even further by a combination of two plasma surface treatments, a duplex process like plasma nitriding and a hard coating deposition. Although there are many studies about this topic (Qi et al., 2007; Leskovsek et al., 2009; Chicot et al., 2011) among others, each coating and each substrate requires a specific study (Azzi et al., 2010).

Different types of films such as oxides, nitrides and carbides have low friction coefficients and high wear resistance as well as good chemical and thermal stability, but it is possible that they fail under high concentrated load when deposited on soft steel substrates (Bell et al., 1998).

Plasma nitriding is a diffusion process for surface modification and hardening of steel substrates which generates an interface with a graded compositional and hardness profile. The nitrided layer reduces the difference of hardness between the substrate and the coating, improving in this way the tribological behavior and the load capability of the coating (Guruvenket et al., 2009). However, there is some uncertainty regarding the type of nitriding treatment that imparts the best tribological performance and adhesion of the coating. In general, the nitrided layer is composed by a compound layer on top and a diffusion zone. A porous and rough compound layer reduces the wear resistance and results in low adhesion of the coating, whereas a highly adhesive, homogeneous and dense diffusion layer can improve the sliding wear properties of the film (Zukerman et al., 2007). In order to achieve a good film-nitrided layer combination, several factors such as chemical affinity, roughness (Batista et al., 2003), residual stress and the characteristic of the nitrided layer must be considered (Benkahoul et al., 2009).

In this work, SiN_x films were deposited by Plasma Assisted Chemical Vapor Deposition technique on nitrided and on non-nitrided Corrax® precipitation hardening stainless steel, in order to evaluate the tribological behaviour and the adhesion of the film.

2. Experimental

Corrax® (Uddeholm) precipitation hardening (PH) stainless steel samples of 6 mm in height were sliced from a bar of 24 mm in diameter. The chemical composition in mass percentage of Corrax® PH is 0.03% C, 12% Cr, 1.4% Mo, 0.3% Mn, 0.3% Si, 9.2% Ni, 1.6% Al and Fe as balance.

All samples were hardened according to supplier recommendations by means of an aging process at 530 ºC for 2 hours, to obtain a fine martensitic structure. Before nitriding, they were grounded and polished on one face. Nitriding was carried out for 10 hours in an industrial facility at a temperature of 390 ºC using a gas mixture composed of 20 % N_2 and 80 % H_2. Care was taken to produce only diffusion layers without Cr and Fe precipitation in the nitriding process, by using low temperature (Dong et al., 2008) and low N_2 concentration. The SiN_x coatings were deposited by the Plasma Assisted Chemical Vapor Deposition technique (PACVD) using a DC pulsed discharge at 700 °C with HMDSO and nitrogen as gas precursors. The process was performed in a self made equipment at Facultad Regional Haedo, UTN.

Hardness in the nitrided samples was assessed with a Vickers microindenter, 50 g load. In the coated samples it was measured with a nanoindenter, Berkovich tip and 10 mN load. Microstructure was observed by optical microscopy (OM), and SEM equipped with FIB. The SiNx films were characterized by FTIR spectroscopy and EDS microanalysis. The film thickness was also determined by the Calotest Method.

In order to evaluate the tribological behaviour, two types of the linear reciprocating sliding tests were performed. The first group of tests used a WC ball 5mm in diameter as counterpart, a frequency of 14 Hz, with an amplitude of 50 microns, 30 min duration and 5 N load. These will be called "Small Amplitude Tests" (SA tests) and they were carried out in a self-made machine. The second linear sliding tests were done on a ball-on-disc tribometer, using an alumina ball 4.8 mm in diameter as counterpart, with 5 N load. The frequency was 3.5 Hz, 6 mm track length, and they had 19 min duration. The worn surface or the wear scars were analyzed with SEM, White Light Interferometry and a mechanical profilometer. The adhesion of the SiN_x films was characterized using the methods of Scratch Test and Rockwell C indentation with loads of 20N and 600 N respectively. Erosion resistance was tested against a sea water and sand (AFS GFN of 50) flux during 20 hours at a temperature of 60 °C; the samples rotated in the slurry solution at a mean tangential velocity of 7 m/s. Finally, corrosion behavior was evaluated by the Salt Spray Fog Test according to the ASTM B117 standard.

3. Results and discussion

3.1. Hardness and microstructure

PACVD SiN_x films were deposited on untreated PH stainless steel (named "coated samples") and on nitrided steel ("duplex samples"). Films deposited at low temperature and low energy are known to be amorphous and non-stoichiometric (Choy et al., 2003). In this case the film reached a thickness of 1.40 ± 0.10µm determined by the calotest method.

The EDS spectrum of the film showed Si but also Fe which confirms that the coating is thin (Fig 1a). In the FTIR spectrum, some peaks corresponding to silicon compounds were detected (Fig 1b), the Si-N peak is at 840 cm^{-1}, which was also observed by other authors in SiN_x films (Beshkov et al., 2003); and the silicon oxide peak was found at 900cm^{-1}, this compound could have been formed as a product of the oxygen contamination in the work chamber. These results indicate that the film is actually amorphous hydrogenated silicon oxynitride (a-SiN_xO_x:H), with a typical structure formed by random bondings Si-O and Si-N (Criado et al., 2008).

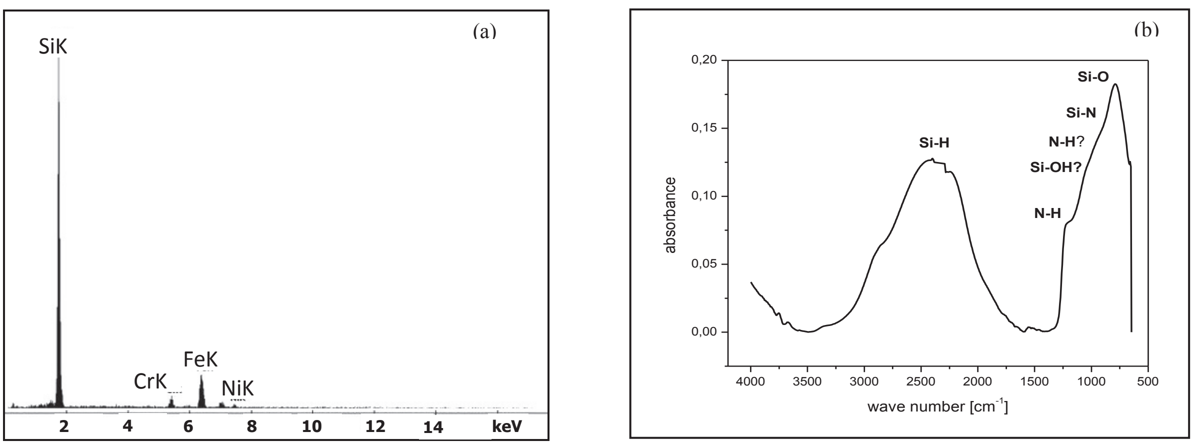

Fig.1. Coated sample: (a) EDS spectrum; (b) FTIR spectrum

In the cross section FIB image (Fig 2a), it can be observed that the thin film has a regular interface with the substrate. In the duplex sample, a nitrided layer 14 microns thick and a bulk martensitic structure can be observed (Fig 2b), but the nitrided layer presented some irregularities and a not well defined interface with the substrate.

The hardness of the precipitation hardening stainless steel was 580 ± 50 $HV_{0.05}$ after aging, and after the nitriding process it reached 1240 ± 60 HV. The hardness of the coating was about 2300 ± 300 HV on the duplex and on the coated sample as well, measured with the Berkovich indenter and converted to Vickers. In both measurements the hardness corresponds to the nitrided layer and to the coating because the indentation depth did not exceed 10% of the modified layer or the film thicknesses (Jedrzejowski et al., 2003).

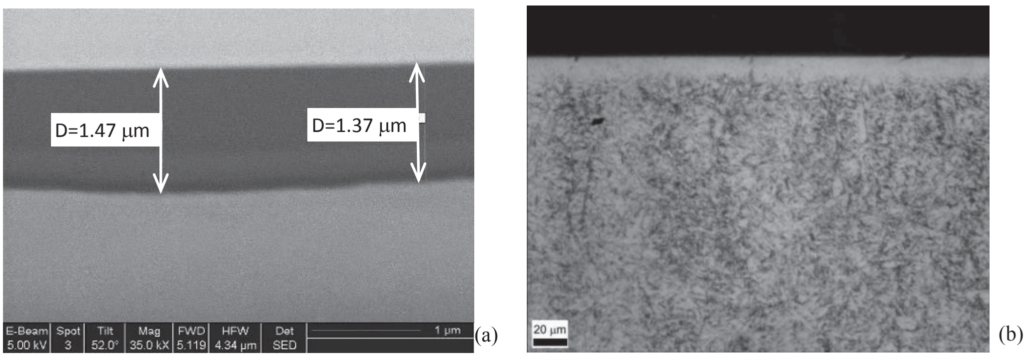

Fig. 2. (a) SEM-FIB view of the film on the coated sample; (b) optical micrograph of duplex sample

3.2. Tribological behaviour

In the SA tests, the damage was greater in the coated sample than in the duplex sample (Fig 3a and b).In the coated sample, the film was clearly broken and was partially detached from the substrate. In the duplex sample only a deformation can be observed with little cracks on the film surface. It is possible that the wear mechanism of the coating had been fatigued due to the low sliding speed during the test and moderately high normal pressure (Hutchings, 1992). Also, oxidation of the formed debris was produced, since the EDS analysis of the wear track detected oxygen (Fig 3c).

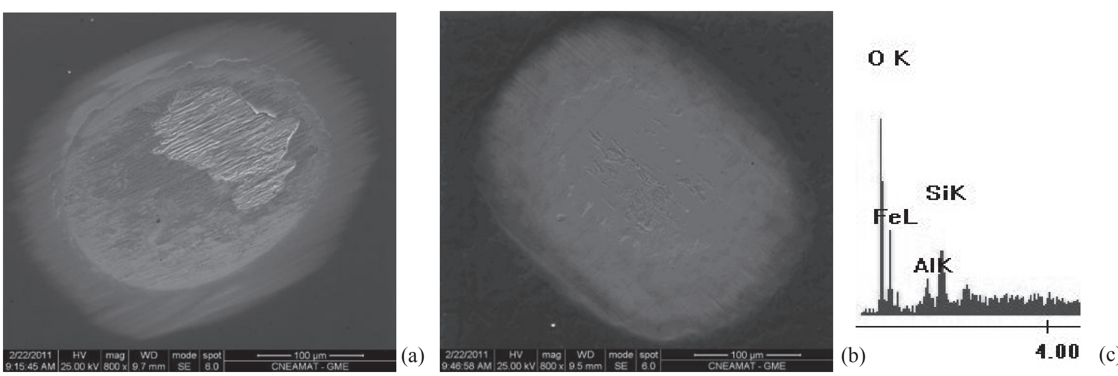

Fig.3. SEM image of the SA wear test track: (a) coated sample; (b) duplex sample; (c) EDS spectrum

The depth of the wear track was greater in the coated sample (3.5 µm) than in the duplex sample (2.5µm) but in both it was greater than the thickness of the film (Fig 4a and b). However, it can be deduced from the wear track profiles that in the duplex sample the hard nitrided layer improved the load capacity of the coating and thus the wear resistance.

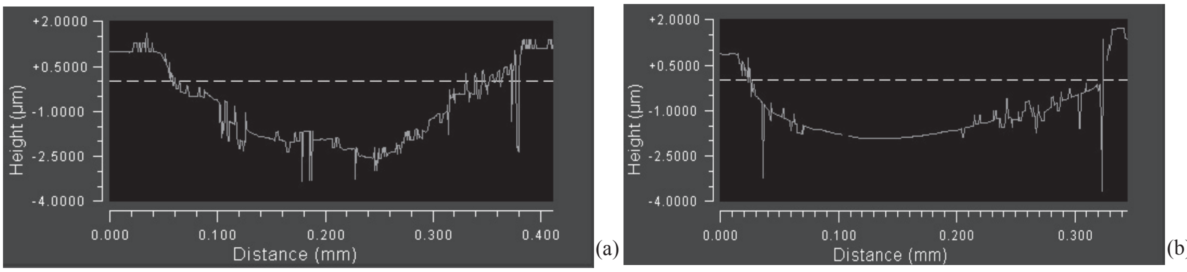

Fig. 4. Depth profile of the fretting wear tracks: (a) coated sample; (b) duplex

In the linear sliding tests 6 mm amplitude, the depth of the track reached 38 microns in the coated sample (Fig 5a), resulting four times deeper than in the duplex sample. With respect to the morphology of wear, it can be noticed that abrasion is the predominant wear mechanism in both samples (Fig 5b and c). But in the coated sample the wear process was far more severe, the abrasive grooves are deeper, and it can also be seen that particles were detached during the test but not removed from the surface, increasing the wear associated damage. This fact has been observed by other authors in silicon films (Ma et al., 2006). It is possible that the coating was fragile and failed after a few minutes testing, and in this case the wear process continued on the substrate material.

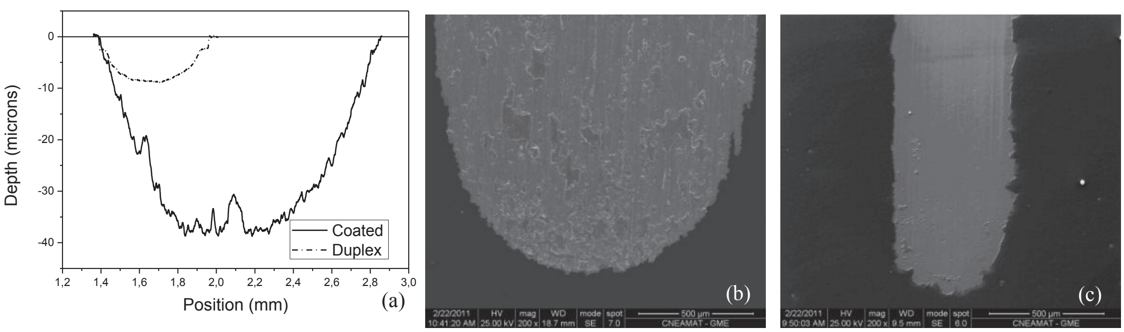

Fig. 5. (a) Depth profile of the linear sliding wear tracks in the two samples; (b) SEM images of part of the wear tracks in the coated sample; (c) in the duplex sample

The tribology results showed that the previously nitrided sample (duplex) had better results in both wear tests, especially when abrasion mechanisms were present, like in the 6 mm sliding test. This could be explained by the fact that compressive subsurface stresses are developed in the duplex sample, which lower the magnitude of tensile and shear stresses because the elastic modules are similar to those of the film.

3.3. Adhesion

In the Scratch Test, a failure event of the coating occurred in both samples, (Fig 6a and b), but the main failure modes were different. In the coated sample, spallation and buckling failures arose due to the compressive stresses generated ahead of the indenter movement. The buckling failure mode is common for hard coatings on a softer substrate where the plastic deformation of the substrate leads to interfacial defects and detachment which initiates the failure (Bull, 1997). In the duplex sample (Fig 6b) the affected area is smaller than in the coated sample.

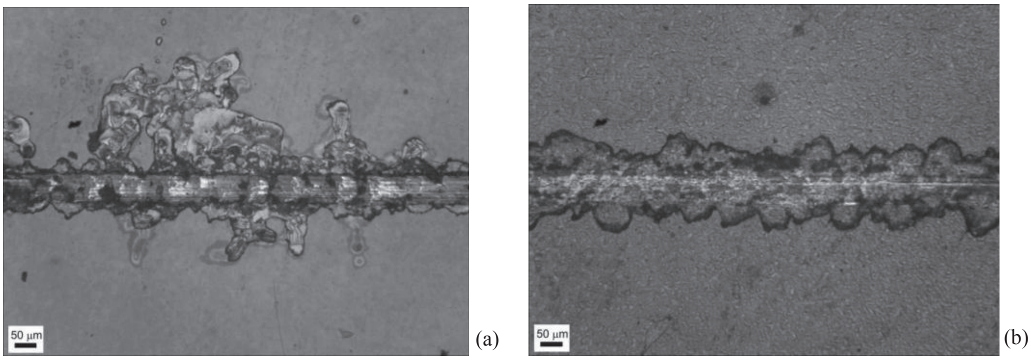

Fig. 6. Optical micrographs 400x of the scratch test tracks: (a) coated sample; (b) duplex

In the Rockwell C indentation test, the coated sample can be classified into adhesion HF 6 according to the VDI 3198 standard (Fig 7a); a large part of the coating material surrounding the indentation was detached and this behavior is “unacceptable”. The duplex sample can be classified into HF3 “acceptable” according to the VDI standard although radial cracks can be observed in the coating around the indentation, and it is fractured at about 1100 microns radius from the edge of the indentation but without film detachment (Fig 7b).

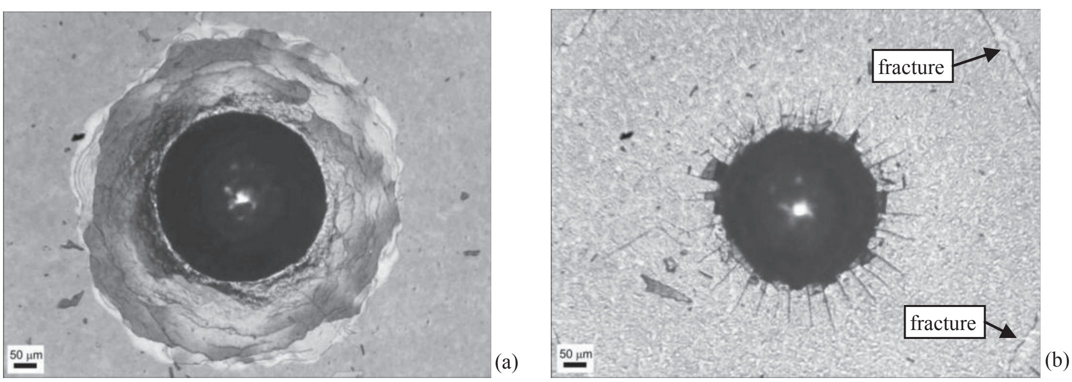

Fig. 7. Optical micrographs 100x of the samples after Rockwell C indentation: (a) coated sample; (b) duplex

3.4. Erosion and corrosion behavior

In the erosion tests, the coated sample lost more mass than the duplex sample (both in relation to a control untreated sample) (Fig 8a). The erosion damage and the observed plastic deformation in the coated sample were more severe than in the duplex sample (Fig 8b and c). This can be explained by the fact that the erosion resistance is a complex process that depends on many factors and one of them is residual stress (Batista et al., 2003). With the plasma nitriding a graded interlayer is generated, which increases the hardness and reduces the stresses (Zukerman et al., 2007).

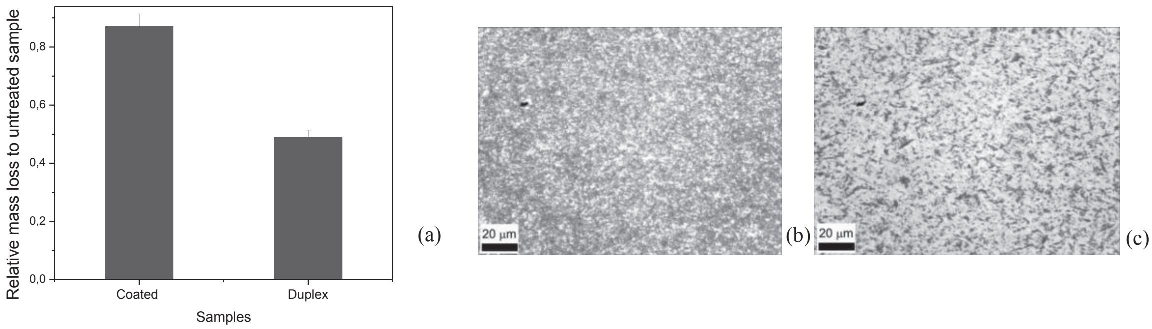

Fig. 8. (a) Quantitative erosion results; (b) OM of eroded surfaces in the coated sample; (c) duplex sample

After 100 hours exposure in the salt spray chamber, the coated samples were clean of corrosion products. (Fig 9). Only on the duplex sample a small corrosion area can be observed near the edges. Anyway local corrosion did not occur since pits were not detected on any sample.

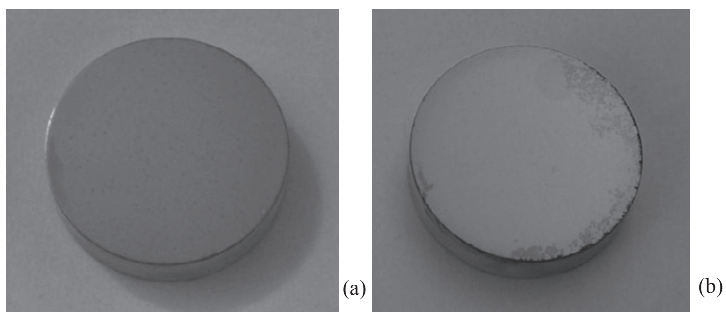

Fig. 9. Surface of coated samples aspect after the salt spray fog test; (a) coated sample; (b) duplex

4. Conclusions

The results of the mechanical tests showed that the deposition of a SiNx hard coating directly on the precipitation hardening stainless steel is not convenient. The nitrided layer proved to be a good interface that increased the substrate hardness and improved the wear resistance. The previously nitrided sample (duplex) had better results in all wear tests, especially when abrasion mechanisms were present. Finally, both films deposited on samples with and without nitriding pre treatment showed an outstanding corrosion resistance in saline environment.

The adhesion quality was also better in the duplex sample than that in the one without any pretreatment, but it was only “acceptable”, it would still be necessary that some parameters of the process be changed to reach even better results, like HF1 in the VDI3198 standard. For example; with the aim of increasing the film flexibility to copy the substrate topography, some kind of surface activation before the coating process should be carried out, which could improve the chemical affinity. Another possibility would be the deposition of a thin Si or SiO_2 interlayer to allow the film growing and nucleation in a way that improves adhesion.

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