Tribological behavior of DLC films deposited on nitrided and post-oxidized stainless steel by PACVD

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Abstract. In this work, the tribological behavior and adhesion of DLC films deposited by PACVD on AISI 420 martensitic stainless steel was evaluated. Prior to DLC deposition, the samples were nitrided and some of them also post-oxidized. The films were characterized by Raman and EDS, microhardness was assessed with Vickers indenter and the microstructure was analyzed by OM, SEM, FIB. Fretting and linear reciprocating sliding tests were performed using a WC ball as counterpart, and the adhesion of the DLC films was characterized using the Scratch Test and Rockwell C indentation. Corrosion behavior was evaluated by the Salt Spray Fog Test. The film showed a hardness of only about 1500 HV but it was about 15-20 microns thick. The results of the mechanical tests showed that pre-treatments (nitriding and oxidizing) of the substrate did not have a big influence in the tribological behavior of the coating. However, the nitriding treatment before the DLC coating process reduced the interface stress and enhanced the adhesion. Additionally, all the films evidenced good corrosion resistance in a saline environment, better than the AISI 420 itself.

1. Introduction

DLC “Diamond like carbon” coatings are known to be very hard and chemically inert and they also show a low friction coefficient and a high wear resistance. These properties can be useful in a wide range of applications such as drills, seals, bearings, dry cutting operations, medical implants and surgical instruments [1]. However, these films have a problem; they may easy peel off from the substrate in certain situations involving friction. The failure of the film is related to a bad adhesion to the substrates, and other characteristics of the film itself, for instance internal stresses, hardness, surface roughness, topography and elastic modulus [2]. In order to overcome this problem and improve the mechanical and tribological behavior of the films according to various requirements, different interlayer systems have been proposed.

The deposition of interlayers such as titanium, silicon, chromium, CrN or tungsten, have been developed to enhance the adhesion on metal substrates [3,4], compositionally graded coatings have been deposited to minimize the stress concentration and improve the coating adhesion [5], and also duplex process including diffusion treatments previous to the coating have been proposed. Plasma nitriding of a steel substrate is a good possibility because it improves the tribological behavior, increases the load capability of the coating and extends its lifetime [6]. But the characteristics of the nitride interlayer are very important because they can influence not only the adhesion but also the
mechanical behavior of the system, for example, the presence of a compound layer may deteriorate the load bearing capacity in low alloyed steels [7]. Also in stainless steels, a top porous and brittle nitrided layer affects the adhesion and it is necessary to remove it prior to the DLC deposition [6].

Besides, a combination consisting of plasma nitriding followed by a post-oxidizing treatment has been applied in low alloyed steels to achieve superior corrosion resistance; nevertheless there are few studies about this topic in stainless steels [7].

In this work, DLC films were deposited by the Plasma Assisted Chemical Vapor Deposition technique (PACVD) on AISI 420 martensitic stainless steel. Prior to DLC deposition, the samples were nitried and some of them also post-oxidized. Two duplex systems and a single coating are then compared in wear and corrosion situations.

2. Experiment

AISI 420 martensitic stainless steel samples were cut from a plate 1.5 mm in thickness and they were prepared as discs, 22 mm in diameter. The chemical composition in mass percent of AISI 420 is 0.38% C, 13% Cr, 0.44% Mn, 0.72% Si, 0.02% P and Fe as balance. All samples were previously heat treated (quench and tempering) to get the martensitic structure and they reached hardness values around 550 HV (50 g load). Before nitriding, they were grounded and polished in one face.

The nitriding treatment was performed in a standard industrialized DC pulsed process in the firm Rübig (Austria) for 14 hours in with a N$_2$ flow rate of 90 sl/h and H$_2$ flow rate of 30 sl/h at a temperature of 500°C. The mean voltage between electrodes was 550 V in a pulsed mode with a 200µs on-time period and 300 µs off-time period. Oxidizing was carried after nitriding in the same chamber using water steam. The DLC coatings are in fact a:C-H-Si films (silicon containing amorphous hydrogenated carbon) and they were deposited by the Plasma Assisted Chemical Vapor Deposition technique (PACVD) with the same DC pulsed discharge as used for nitriding with HMDSO and acetylene as gas precursors. The deposition rate was 2 µm/h. The process was carried out in a semi industrial facility at the University of Applied Sciences in Wels, Austria.

Microhardness was assessed with a Vickers indenter, 50g load. Microstructure was observed by optical microscopy, scanning electron microscopy (SEM), focused ion beam (FIB). The DLC films were characterized by Raman spectroscopy and energy dispersive spectroscopy (EDS) microanalysis. X-ray diffraction analyses were performed in a PANalytical diffractometer with Cu-Kα radiation and graphite monochromator. Diffraction patterns were collected in the Bragg-Brentano configuration. Fretting and linear reciprocating sliding tests were performed in a self-made machine using a WC ball 5mm in diameter as counterpart and a frequency of 11.7 Hz. Fretting tests were performed with a track length of 84 microns, a duration of 30 min and at a load of 8.49 N. Reciprocating sliding tests were carried out with a track length of 953 microns, a duration of 90 min and using loads of 4.42 N and 12 N. The worn surface or wear scars were analyzed with SEM, White Light Interferometry and a mechanical profilometer. The adhesion of the DLC films was characterized using the methods of Scratch Test and Rockwell C indentation with loads of 2 kg and 150 kg respectively. Finally, corrosion behavior was evaluated by CuSO$_4$ spot and the Salt Spray Fog Test (ASTM B117).

3. Results

3.1. Coating

The samples were named: DLC, N+DLC and N+O+DLC, where “N” and “O” mean Nitriding and Oxidizing, respectively. The EDS spectrum of the film showed Si, C and O, as expected (figure 1), and the Raman spectrum of the film showed only a peak around 1500 cm$^{-1}$ of amorphous carbon [8], containing hydrogen but without graphitization (figure 1). A thin amorphous silicon interlayer was deposited to improve the film adhesion.
3.2. Microstructure and hardness

The hardness of the DLC films reached 1500 HV\textsubscript{0.05}. This is considered a “soft a-C: film”, it results from a high hydrogen content and it is known to have also a low elastic modulus, 80-90 MPa. Its thickness varies between 15 and 20 microns (figure 3) and in the case of the N+O+DLC sample, it has an irregular interface with the previous layer, a thin and porous oxide layer of 3 microns which can be observed in the FIB image, in a place where the film was detached (figure 4). It can be noticed that the oxidized surface has imperfections which could affect adhesion. It is composed of magnetite (Fe\textsubscript{3}O\textsubscript{4}) and hematite (Fe\textsubscript{2}O\textsubscript{3}) phases according to the XRD analysis (figure 5). The first phase (magnetite) is known to be compact and homogeneous but the second (hematite) is porous and brittle and it could affect the surface roughness and the adhesion \[9\].

Underneath the oxide layer, a nitrided diffusion zone of about 90 microns in thickness could be detected by optical microscopy (OM) and it is showed in figure 6. The XRD pattern reveals that it is composed of \(\alpha\) Fe (martensite) and the nitrides Fe\textsubscript{4}N and CrN, which were formed because nitriding was carried out at high temperature. Only the \(\alpha\) peaks were identified in the XRD diffractogram of the DLC sample (figure 5) because the film is amorphous and transparent to x ray radiation.

3.3. Fretting test

In the fretting tests, no big difference regarding the different pretreatment could be observed according to the calculated volume loss from the wear scar analysis (table 1 and figure 7). It could also be demonstrated that the film deformed plastically without breaking in all cases, and in general the tribological behavior of the film was far better than in the untreated samples, as it can be observed comparing figure 7 and 8.

**Figure 1.** EDS spectrum N+O+DLC sample.  
**Figure 2.** Raman spectrum DLC sample.  
**Figure 3.** SEM image of the DLC film.  
**Figure 4.** SEM-FIB view of the oxide layer.
3.4. Reciprocating sliding tests
In both wear tests using 4.42 N and 12 N loads, the depth of the wear tracks was lower in the treated samples than in the untreated samples (figure 9). However, there is not a big difference between the different pretreatments. The thick DLC film resulted mechanically resistant and underwent the test with the highest load without breaking, regardless of the substrate or the prior surface pre-treatment.

Figure 5. XRD diffractograms of the three samples. Figure 6. OM micrograph of N+DLC sample.

| Samples          | Relative Wear volume loss | Wear scar depth | Roughness |
|------------------|---------------------------|-----------------|-----------|
| DLC+O+N          | 0.39                      | 1.46 ± 0.03     | 0.2551    |
| DLC+N            | 0.40                      | 1.53 ± 0.02     | 0.064     |
| DLC              | 0.41                      | 1.54 ± 0.03     | 0.028     |
| Untreated        | 1.00                      | 2.34 ± 0.02     | 0.0043    |

Table 1. Quantitative wear results.

Figure 7. WLI 3D plot of the fretting wear scar in an untreated sample. Figure 8. WLI 3D plot of the wear scar in a DLC coated sample.
3.5. Adhesion

The adhesion quality of the DLC pretreated samples is better than that of the sample without any pretreatment. In this case a significant spalling and delamination at the vicinity of the indentation can be observed (figure 10). In the N+O+DLC sample, a part of the coating surrounding the indentation was detached, indicating that the presence of hematite deteriorated the adhesion strength as it was also observed by other authors [10]. The best behavior was achieved in the sample which had only the nitriding treatment prior to the DLC coating. This diffusion modified layer, even with nitrides precipitations, resulted in a good interlayer to reduce the internal stress between the DLC film and the steel substrate [6].

In the scratch test the same results were obtained, the N+DLC sample had better adhesion than the other samples tested with 20 N load. In the untreated sample small areas of apparent delamination could be observed along the edge of the track. In the N+O+DLC, the high roughness could have influenced in the film adhesion.

![Figure 10. Optical micrographs 100x of samples after Rockwell C indentation.](image)

3.6. Corrosion behavior

All treated samples did not show sensitization after 6 min of CuSO₄. The untreated sample did not pass this test, and copper deposited immediately, showing the absence of passivity.

After 100 hours exposure in the salt spray chamber, the coated samples were clean with no sign of general or local corrosion (figure 11). The untreated sample had some pits and beginning of general corrosion.

4. Conclusions

The results of the mechanical tests show that the different pretreatments of the steel substrates do not have a big influence in the tribological behavior of the samples in the evaluated conditions; since the DLC films are thick enough and they have a good mechanical resistance. They underwent the fretting...
and reciprocating wear test with a good performance. However, the adhesion quality of the DLC film over the nitrided sample without oxidation (N+DLC) was better than in the post-oxidized one (N+O+DLC) and the sample without any pre-treatment. The nitride layer provided a graded interface between the DLC coating and substrate; which reduced the internal stress and enhanced the adhesion. On the contrary, the oxide layer consisting of hematite and magnetite did not promote a good adhesion considering nitrided stainless steel as a substrate.

The films also evidenced a good corrosion resistance in a saline environment, far better than the AISI 420 stainless steel itself, without any treatment but quench and tempering.

![Figure 11. Surface of coated samples aspect after the salt spray fog test.](image)

**Acknowledgements**

The authors would like to thank to Mg. Eng. Agustina Guitar and the Saarland University (Germany) for the SEM-FIB analysis; to Dr. Adriana Márquez (INFIP-UBA) for the use of the Scratch Tester, to Dr. E. B: Halac (CNEA) for the Raman measurements and to Dr. Mariela Desimone (INTEMA) for XRD measurements. Also to the Materials Department of CNEA-CAC (Argentina) for the use of SEM and EDS, to the firm Rübig (Austria) for performing the diffusion treatments. Finally to UTN and ANPCyT (Argentina) for the Doctoral Fellowship of Eugenia Dalibon.

**References**

[1] Li K Y, Zhou Z F, Bello I, Lee C S and Lee S T 2005 Wear 258 1577
[2] Wu X, Ohana T, Nakamura T and Tanaka A 2010 Wear 268 329
[3] Glozman O, Halperin G, Etsion I, Berner A, Shectman D, Lee G H and Hoffman A 1999 Diamond and Related Materials 8 859
[4] Trava-Airoldi V J, Bonetti L F, Capote G, Fernandes J A, Blando E, Hübler R, Radi P A, Santos L V and Corat E J 2007 Thin Solid Films 516 272
[5] Choy K L and Felix E 2000 Materials Science and Engineering A278 162
[6] Chicot D, Puchi-Cabrera E S, Decoopman X, Roudet F, Lesage J and Staia M H 2011 Diamond & Related Materials 20 1344
[7] Forsich C, Heim D and Mueller T 2008 Surface & Coatings Technology 203 521
[8] Baba K, Hatada R, Flage S and Ensinger W 2009 Surface & Coatings Technology 203 2747
[9] Rovani A C, Fischer R R, Cemin F, Echeverrigaray F G, Basso R L O, Amorim C L G, Soares G V, Baumvol I J R and Figueroa C A 2010 Scripta Materialia 62 863
[10] Esfahani A, Soht M H, Rassizadehghani J and Mahboubi F 2008 Vacuum 82 346