Topic: 21. Thin Films and Surface Treatments

Thermal stability of DLC coating deposited on precipitation hardening stainless steels

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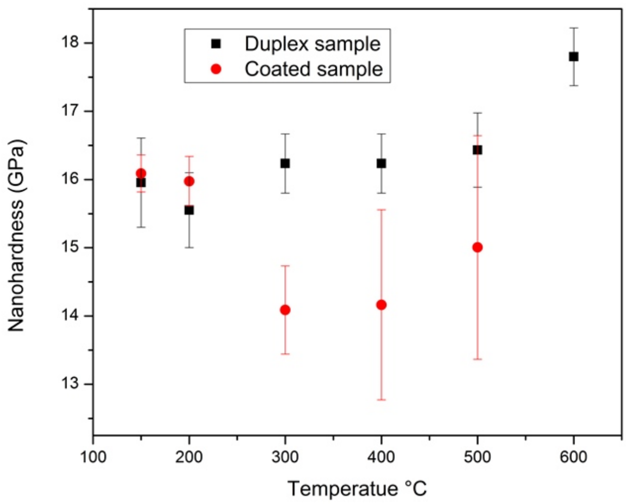
Key words: DLC coating, Duplex treatment, thermal stability, stainless steel.

Graphical summary:



Relationship between nanohardness and annealing temperature of DLC coating on duplex (previously nitrided) and only coated PH steel samples.

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ABSTRACT

The DLC (Diamond Like Carbon) coatings are characterized by good mechanical properties, low friction coefficient and chemical inertness. However, these coatings have problems at high temperature (400 °C) owing to the graphitization which leads to an increase in sp^2 and decrease in sp^3 bonding structure.
In this work, the thermal stability of DLC coatings deposited by PACVD (Plasma-assisted chemical vapor deposition) on nitrided precipitation hardening stainless steel (duplex sample) and without nitriding (coated sample) was studied. The annealing treatments were carried out at 200 °C , 300 °C, 400 °C , 500 °C , 600 °C, 700 °C for 1 hour on coated and duplex samples in vacuum, according to some reports found in the literature. The coatings were characterized by EDS and Raman and hardness was assessed with nanoindentation. The microstructure of the nitrided layer and the coatings was analyzed by OM and SEM. The coatings had about 12 % hydrogen content and the film thickness was about 3 μm. The mean hardness of the duplex sample was 16 GPa without annealing, but it did not decrease and remained approximately constant until 600 °C. However, in the coated sample, the hardness decreased at 300 °C, probably because the sp2 bonds percentage increased in the coating. Moreover, at 600 °C, it was not possible to obtain a value for the nanohardness because the dispersion resulted very large. This could be due to coating detachment in several regions, probably caused by film transformation (graphitization) in these zones. It is possible that in the duplex sample, the nitriding process as previous treatment to the coating deposition improved the thermal behavior of the system. Future analysis will be performed in order to identify the compounds that were formed in the interface of the duplex sample.
Keywords: DLC coating, Duplex treatment, thermal stability, stainless steel.

SUMMARY

Los recubrimientos DLC (Diamond Like Carbon) se caracterizan por sus buenas propiedades mecánicas, bajo coeficiente de fricción e inercia química. Sin embargo, estos recubrimientos tienen problemas a alta temperatura (400 °C) debido a que se produce la grafitización que conduce a un aumento de uniones sp^2 y a una disminución de las uniones sp^3. En este trabajo, se estudió la estabilidad térmica de los recubrimientos DLC depositados por PACVD (Plasma-assisted chemical vapor deposition) sobre acero inoxidable endurecible por precipitación nitrurado (muestra duplex) y sin nitrurar (muestra recubierta). Los tratamientos de recocidos se llevaron a cabo a 200 °C, 300 °C, 400 °C, 500 °C, 600 °C y 700 °C durante una hora en vacío en la muestra duplex y recubierta, de acuerdo a lo reportado en la literatura. Los recubrimientos fueron caracterizados por EDS y Raman y la dureza fue medida con nanoindentación. La microestructura de la capa nitrurada y del recubrimiento fue analizada por OM y SEM. El recubrimiento tuvo un contenido de hidrógeno de aproximadamente el 12 % y su espesor fue de aproximadamente 3 μm. El valor de dureza promedio en la muestra duplex fue de 16 GPa antes del recocido y permaneció aproximadamente constante hasta 600 °C. Sin embargo, en la muestra recubierta, la dureza disminuyó a los 300 °C probablemente porque el porcentaje de uniones sp^2 aumentó en el recubrimiento. Además a 600 °C no fue posible obtener un valor para la nanodureza porque hubo una gran dispersión en los valores. Esto podría deberse a que el recubrimiento se desprendió en algunas regiones probablemente a causa de su grafitización en esas zonas. Es posible que en la muestra duplex, el proceso de nitruración previo al tratamiento de deposición del recubrimiento mejoró el comportamiento térmico del sistema. En el futuro, se realizarán análisis para identificar los compuestos que se forman en la interfase de la muestra duplex.
Key words: recubrimientos DLC, tratamientos duplex, estabilidad térmica, acero inoxidable.

1. Introduction

The DLC coatings are characterized by high hardness, low friction coefficient, good wear resistance and chemical inertia. They are used in different industrial applications such as tool coating or mechanical parts that can reach high temperatures during operation. They are utilized for various sliding situations where they can be exposed to localized heating caused by friction, such as engine components. For these reasons, thermal stability is a very important property for different applications of DLC coatings [1,2].
Some studies have been published about the thermal stability of DLC coatings in which it was reported that the DLC films could not retain their diamond- like properties at high temperature due to the changes in their structure, because of the conversion of sp^3 bonds to sp^2 bonds [1,3].
In order to improve the thermal stability of these coatings, either dopant elements such as Si or N or nanoparticles-dispersed composites have been added [2,4,5].
Another disadvantage of these films is that they present adhesion problems when they are deposited on metallic substrates. Among other reasons, this is due to the fact that the carbon diffuses into the metal delaying the DLC nucleation. Also, the iron has a catalytic effect that leads to the formation of graphite and finally, the thermal expansion coefficients of the coatings and the steels are not compatible, causing poor adhesion and high residual stresses [6].
In order to overcome these problems different interlayers between the substrate and the DLC film (e.g. Si) have been studied. Also diffusion treatments of the substrates, like plasma nitriding, have been tried [6–8].
This work deals with the thermal stability of DLC coatings deposited on a particular stainless steel, the Precipitation hardening type (PH), over nitrided and non nitrided substrate.

2. Experimental

Corrax® PH (Uddeholm) precipitation hardening 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® 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 aged at 530 ºC for 2 hours according to supplier recommendations to increase hardness. Nitriding was carried out for 10 hours in an industrial facility at a temperature of 390 °C using a gas mixture composed of 20 % N_2 and 80 %H_2. The DLC coatings were deposited by the Plasma Assisted Chemical Vapor Deposition technique (PACVD) with an asymmetrical bipolar DC pulsed discharge, using methane as the precursor gas. The process duration was of 2 h and the temperature of 150 °C. Previously, a thin amorphous silicon interlayer was deposited using silane gas as precursor.
The DLC coatings were deposited on only aged PH stainless steel (named coated samples) and on nitrided steel (named duplex samples).
The annealing was carried out at 200 °C, 300°C, 400°C, 500 °C, 600 °C, 700 °C for 1 hour on coated and duplex samples in vacuum following a method already reported in the literature [3]. The nanohardness of the films was measured employing a nano-indenter with 15 mN load before and after the annealing process.
The coatings were characterized by EDS and Raman spectroscopy before and after the thermal process as well. The microstructure of coating was analysed by OM and SEM-FIB. The surface of coatings was observed by OM after annealing.

3. Results and Discussion

The Raman spectra for DLC coating on duplex and coated samples presented two overlapping bands known as the D and G. The D band appeared approximately at 1389 cm^{-1} and the G band, approximately at 1550 cm^{-1}. The intensity ratio of the D and G bands, I_D/I_G, was about 0.8 (Figure 1) which indicate a low percent of sp^3 C-C bonds [9].
Moreover, according to the I_D/I_G ratio and the Full Width at Half Maximum (FWHM) of the D band, it could be inferred that the coating is largely amorphous with a cluster size smaller than 2 nm [9].
The hydrogen content was about 12 % which was estimated from the slope of the fitted line to the base of the original spectrum [9].

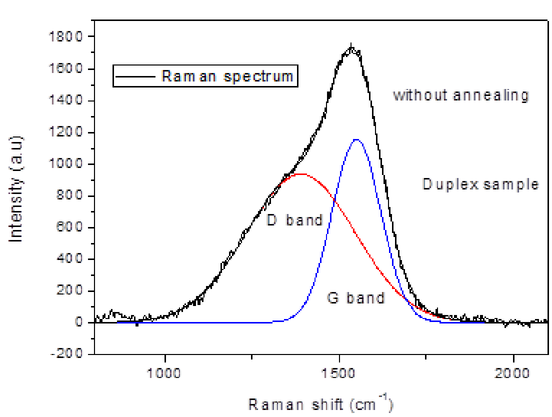

Fig. 1. Raman spectrum of duplex sample without anneling.

In the EDS spectrum (not showed), C and Si were detected as expected. The Si signal corresponds to interlayer.
The coating thickness was about 3 µm with a silicon interlayer of 0.3 µm as it can be observed in the cross-section (Figure 2) which was analysed by SEM/FIB. Prior to the milling process, a platinum protective layer was deposited onto the region of interest in order to prevent the erosion of the surface by the ion beam. The coating presented a well-defined interface with the substrate as well in the duplex so as in the coated samples.
The nitrided layer thickness was about 14 µm, which corresponds to a region of nitrogen in solid solution. It looked white after etching with Vilella reagent in the optical micrograph (Figure 3). Dark regions were not observed, that normally indicate chromium nitrides precipitation and the formation of second phases.

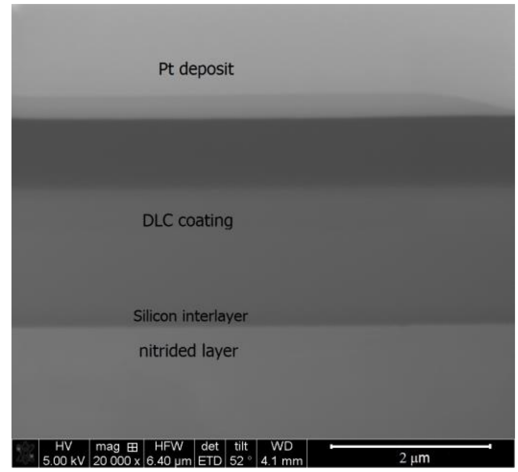

Fig. 2. SEM image of coating on duplex sample

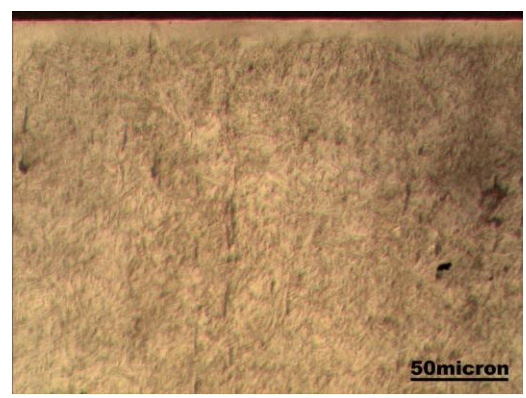

Fig. 3. Optical micrograph of the nitrided layer.

The hardness was about 16 GPa for duplex and coated samples before annealing. The results of nanohardness after the annealing and as-deposited (PACVD, 150 °C) of the duplex sample are presented below (Figure 4). Each point is the average of twenty measurements and the error was determined using the standard deviation.
In this sample, it can be observed that the nanohardness did not decrease; on the contrary, it remained approximately constant until 500 °C, because the variation of the hardness values is within error. At 600 °C, the hardness was slightly higher and this could be because the coating thickness changed after the annealing and the hardness measurement was affected by the nitrided layer (composed hardness) which is transformed at that temperature, where actually nitrides precipitate.
At 700 °C it was not possible to determine an average value due to a big deviation in the individual measurements. Even though it can be pointed out that some hardness values were about 7 GPa which would indicate a transformation (graphitization) of the coating as it was reported by other authors [3].
The results of nanohardness after the annealing and as-deposited (150 °C) of the coated sample are shown below, in Figure 5.

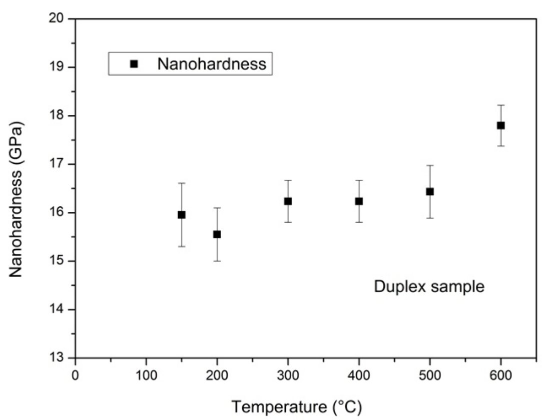

Fig. 4. Relation between nanohardness and annealing temperature of DLC coating (duplex sample).

In the coated sample, the hardness decreased at 300 °C. At 600 °C, it was not possible to obtain a value for the nanohardness because the dispersion resulted very large. This could be due to different factors, in one side the coating detached in several regions and on the other side it is probably that the coating was transformed in some zones because of some hardness values were very low as it was reported in the literature for graphitization in DLC films [3].

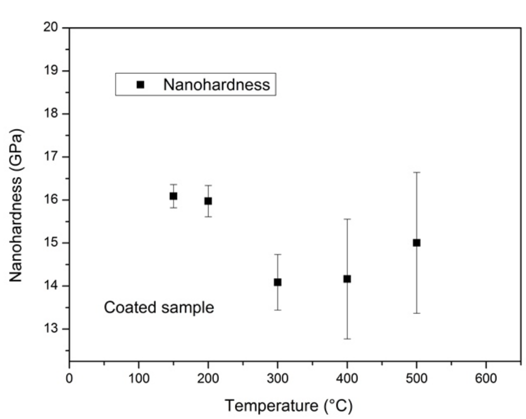

Fig. 5. Relation between nanohardness and annealing temperature of DLC coating (coated sample)

Regarding the film structure, in both samples, the Raman spectra presented similar features for annealing at different temperatures (Figure 6 and 7). In order to compare both figures and show clearly the difference between spectra, the scale is the same on the "y" axis for both figures. As a consequence, in the duplex sample graph (Figure 7), the Raman spectrum corresponding to the annealing temperature of 400 °C does not appear because its background was very high and it is outside the range.

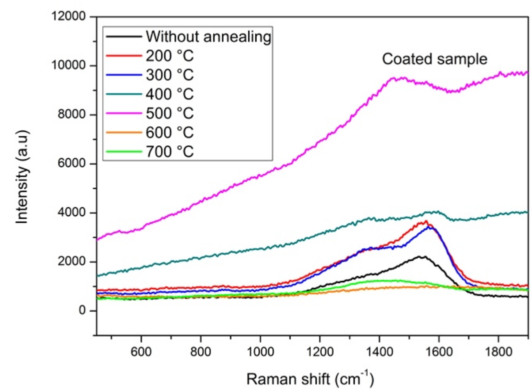

Fig. 6. Raman spectrum of coated sample for annealing at different temperatures.

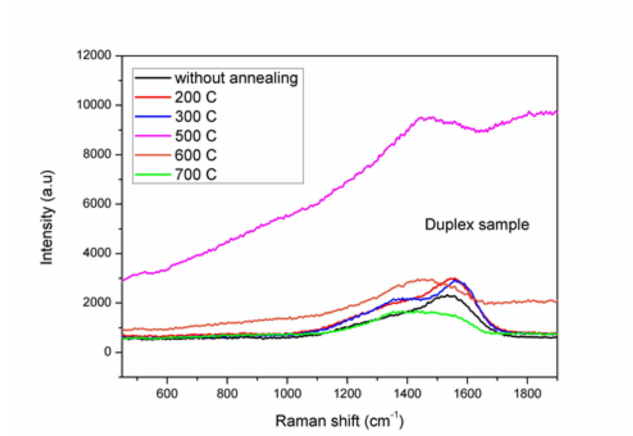

Fig. 7. Raman spectrum of Duplex sample for annealing at different temperatures.

Without annealing the Raman spectrum presented two overlapping bands known as the D and G bands which were well positioned, indicating a good quality film as it was mentioned above (Figure 2).
With annealing at 200 °C, a slight D peak position shift can be observed, and at 300 °C, it can be said that the film starts to transform (sp^3 to sp^2).
At 400 °C, a very strong fluorescence appears indicating a degradation of the diamond-like structural properties of the films.
At 500 °C, there is no DLC coating structure at all and the graphite-like component increases. A small band in the region of 500 cm^{-1} can also be detected which could correspond to the silicon interlayer.
At 600 °C, this transformation effect is more evident and the graphite band appears displaced. At 700 °C, the graphite band is even more evident.
In the duplex sample a change on the surface could be observed after the annealing process at 600 °C (Figure 8). Large cracks could be detected but there was not detachment of the coating.

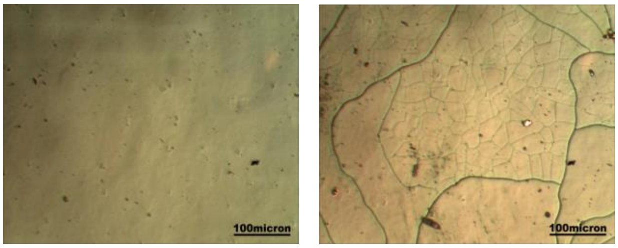

Fig. 8. Optical micrograph of duplex sample, with annealing at 400 °C (left) and at 600 °C (right).

In the coated sample, different features could be detected. The transformation of the coating was observable earlier at 400 °C (Figure 9), where part of the coating was detached. After annealing at 600 °C, the transformation was completed and also cracks appeared on the surface

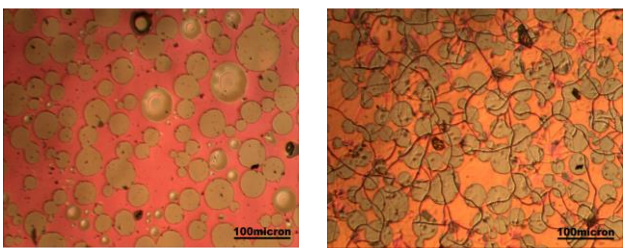

Fig. 9. Optical micrograph of coated sample, with annealing at 400 °C (left) and at 600 °C (right).

According to the results of hardness and the surface images, it could be concluded that in the duplex sample the transformation of the DLC coating was produced at a higher temperature (about 600 °C) than in the coated sample.

Taken into account the Raman spectrum, in the duplex sample some changes were observed but probably the rate of graphitization in the coating was lower than in the coated sample and consequently the effect of the transformation was less noticeable.

The adhesion was better in the duplex sample than in the coated sample. This could be due to the difference between the elastic moduli. This difference is smaller between the coating and the nitrided layer than between the coating and the stainless steel. Consequently the stress gradient is lower, and the coating was not detached in the duplex sample.

On the other hand, during the annealing, thermal stresses are induced. Probably, these stresses were higher in the coated sample than in the duplex sample because of the presence of the silicon layer (with thermal coefficient similar to DLC) and the precipitation of second phases such as Cr nitrides [10] that modify the thermal coefficient compared to stainless steel without any treatment. Consequently decreases the gradient of thermal expansion coefficient between the substrate and film.

4. Conclusions

The DLC coating deposited over nitrided PH steel presented better thermal stability than the same coating over stainless steel without treatment. In the duplex sample, the hardness did not decrease, the morphology of the surface did not change until 600 ºC and the coating did not detach. This could be due to the facts: i) the duplex samples had better adhesion, ii) the similarity of the thermal coefficients of the nitrided layer and the DLC coating during the thermal treatment.

Gratefulnesses

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