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Cathodic Cage Plasma Deposition of DLC Film on D2 Steel Substrate

de Sousa RRM[1], Carvalho Costa TH[2]*, da Costa JAP[3], dos Santos FEP, Nascimento IO[2], Souzab IA[2] and Viana BC[4]

[1]Mechanical Engineering Department, Federal University of Piaui, Teresina, PI, Brazil

[2]Department of Mechanical Engineering - UFRN, C. Universitário, CEP 59072-970, Natal, RN, Brazil

[3]Department of Physics, UERN, Mossoró, RN, Brazil

[4]Department of Physics, Federal University of Piauí, Teresina, PI, Brazil

Research Article

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***For Correspondence**

Carvalho Costa TH, Mechanical Engineering Department, University Center of United Metropolitan Schools, Brazil.

Tel: (84) 99193-6150

E-mail: thercioc@ufrn.edu.br

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ABSTRACT

A diamond-like carbon (DLC) film was deposited on AISI D2 substrates by a cathode cage plasma deposition technique using a plasma nitriding surface treatment/nitriding system, assembled with a graphite cage. The deposition was done at a temperature of 450 °C, in a gas mixture of Ar (25%)+H_2 (75%) with a deposition time of 5 hours under a constant pressure of 2 mbar. The structural analysis using SEM and optical microscopy revealed the existence of material islands arranged as clusters of approximately 20 μm in diameter, while the layer obtained has a thickness of around 4 micrometers. Microhardness tests showed hardness values of around 1300 HV, a figure much higher than that of the substrate (250 HV). With the aid of X-ray diffraction, peaks were identified as Fe_3C (cementite) and carbon, in the diamond phase (DLC). Raman spectroscopy was performed in two regions: in the islands and outside them. In the islands Raman peaks from a highly crystalline structure, identified as DLC, were observed and, around these islands, those from an amorphous region identified as amorphous carbon (a-C) were seen. It was concluded that the plasma deposition process using graphite cathodic cage generated an amorphous carbon coating with crystal islands of DLC on D2 steel substrate.

INTRODUCTION

Diamond-like carbon (DLC) is a carbon structure containing a significant amount of sp^3 bonds. It is considered as a promising material with unique properties such as extremely high hardness, high thermal conductivity, electrical insulation, wear resistance, good optical transparency and chemical inertness[1-4]. Several techniques which include electrochemical [4,5], sputter deposition [2,6], plasma-enhanced chemical vapor deposition [7] have been proposed for the deposition of pure DLC film and films containing metal nanoparticles. A great drawback is that DLC film adhesion to metallic substrates is often poor due to compressive residual stress [6,7] caused by the differences between thermal and other physical properties of the metals and DLC film [8].

The influence of surface polishing of DLC films on their tribological properties has also been investigated [9,10]. Some authors have reported that the wear rate increases with increase in surface roughness, while the friction coefficient is not affected by the surface roughness [11,12]. Other researchers, however, have determined that the friction is higher for rougher surfaces because the scratches are filled with material removed from the coating during wear and the shearing of this material causes a higher friction [13,14].

DLC film can also be synthesized directly on metallic substrates via the PIII&D process due to the formation of a graded transition layer between substrate and film. An implantation stage prior to the deposition of the film is required for this purpose [15,16]. Silicon layers are usually deposited at the metal-film interface when using conventional techniques such as Chemical Vapor Deposition (CVD) [17]. In addition, carbonitriding processes have been performed with the aim of improving the adhesion of the film to the steel substrate [18]. PIII (plasma immersion ion implantation), a non-line-of-sight implantation technique for surface

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modification of materials, has also been successfully used to improve corrosion resistance as well as mechanical and tribological properties of three-dimensional metallic surfaces [19-21].

Plasma nitriding is a well-established process to harden stainless steels and can serve as a pre-treatment to increase adhesion and improve tribological behaviour of the DLC coating. However, the characteristics and phases of the nitrided layer can influence the adhesion and mechanical properties of the system. A porous and brittle nitrided layer is not convenient, and it is necessary to remove it before film deposition [22,23].

In this work, DLC films are deposited on D2 steel substrates by the cathodic cage technique. The resulting thin film are characterized by optical microscopy, x-ray diffraction (XRD), Raman spectroscopy and scanning electron microscopy (SEM).

EXPERIMENTAL SECTION

Material and Deposition

The material used as substrate in this study is a samples of steel AISI D2, whose chemical composition is shown in **Table 1**, of cylindrical with a diameter of 20 mm and height of 6 mm.

Table 1: Chemical compositions of the alloys (% by weight).

Steel	C	Cr	V	Mo	Si	W	Co	Fe
AISI D2	1,50	12,00	10,48	0,95	0,30	-	-	Balance

Surface using multiple grits of sandpaper. Once the surface has been sanded, stain and finish can be applied evenly to the wooden surface. The sample was sanded with sandpaper of grain size 200, 320, 400, 600, 1000 and 1200, and polished with a felt disk using a diamond slurry of 6, 3 and 1 μm. Finally, it was cleaned in acetone by ultrasound and dried in a hot air jet.

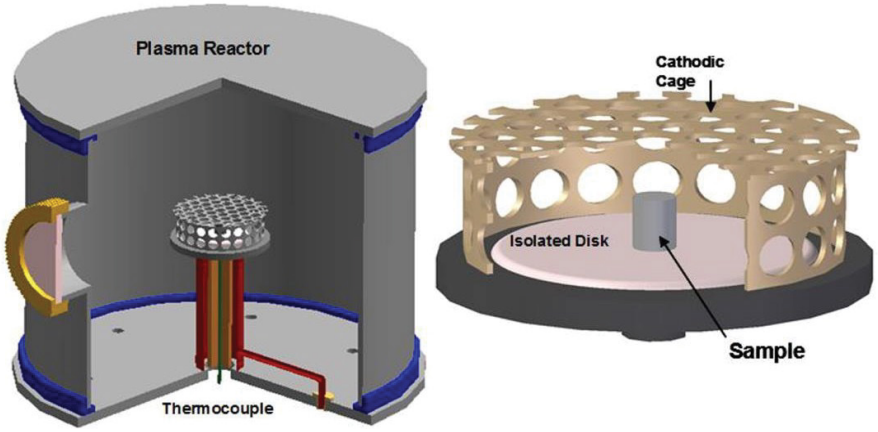

Figure 1: Configuration of the cage used and the way it was placed in the reactor.

In the present work, thin films were produced using the so-called called cathodic cage (CC) method. In cathodic cage deposition we used the same equipment as for the conventional plasma nitriding. The voltage source is continuous and has a maximum voltage and current of 1500 V and 2A, respectively. The cylindrical vacuum chamber with 30 cm in diameter and 40 cm in height was made of austenitic stainless steel. A so- called cathodic cage device made of graphite was added. In this work we used a graphite cage 25 mm in diameter and 35 mm in height, which was mounted on the sample holder of a conventional dc nitration reactor as shown in **Figure 1**. The diameter of the holes on the cage walls is 8 mm and the distance between centers of adjacent holes is 9 mm.

The plasma is formed in the cathodic cage, which acts as the cathode (the chamber wall is the anode) and not directly on the surface of the samples. The substrate, insulated disk and sample holder were placed inside the cage in order to keep them at a floating potential. The sample was treated for 6 hours at a temperature of 450°C, at a pressure of 180 Pa. The gas mixture used was comprised of 12 sccm of H_2 +3 sccm of argon.

The gas mixture was introduced and its flow rate adjusted using a four channel mass flow controller MKS/247D. The treatment pressure was measured by a BARATRON® Model 627D with a multichannel PDR 2000/Mks.

Characterization of Samples

The phase composition and structural analysis of the deposited films was characterized by Raman spectroscopy and x-ray diffraction. The Raman measurements were performed in a Bruker Vertex 70 spectrometer using a solid-state laser with a wavelength of 785 nm and a CCD detector while the x-ray easurements were performed using Cu Kα (wavelength: 0.154 nm), operated at 40 KV in a XRD instrument (Shimadzu XRD-6000). An optical microscope (Olympus BX60M) was used to observe the morphology of the deposited layer.

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The microhardness was measured with the aid a PANTEC HVS-1000 model with a 200 gf load and a reading time of 15 seconds. For this sample nine measures were made in order to show the homogeneity of the deposited film determining the resulting in an average well as the standard deviation of the measure.

RESULTS AND DISCUSSION

Figure 2 shows the micrograph of the cross section of a D2 steel sample. Through this it was possible to obtain several DLC film thickness measurements along the surface showing an average coating thickness of about 4.68 micrometers.

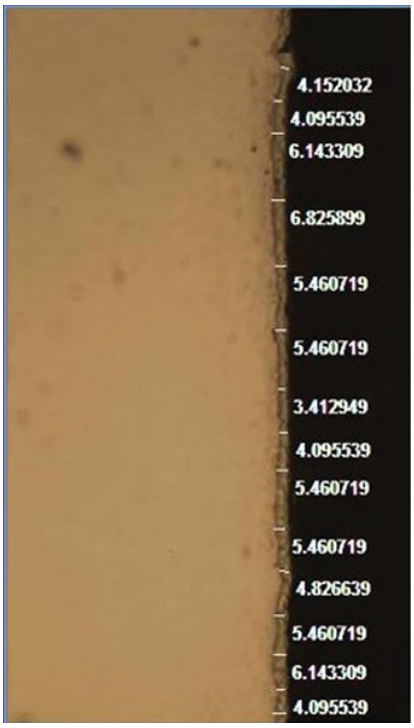

Figure 2: Analysis of optical microscopy of cross-DLC coating profile showing the measurement positions.

The DLC layer shows up a film formed by black islands surrounded by a gray area over the entire surface. This morphology can be best seen in the SEM image presented in **Figure 3**. The islands have a circular geometry with an average diameter of 20 μm and are distributed homogeneous throughout the film. With the aid of SEM images it is possible to observe a film with dark islands of carbonaceous material which can be interpreted as a DLC amorphous carbon matrix deposited on a substrate.

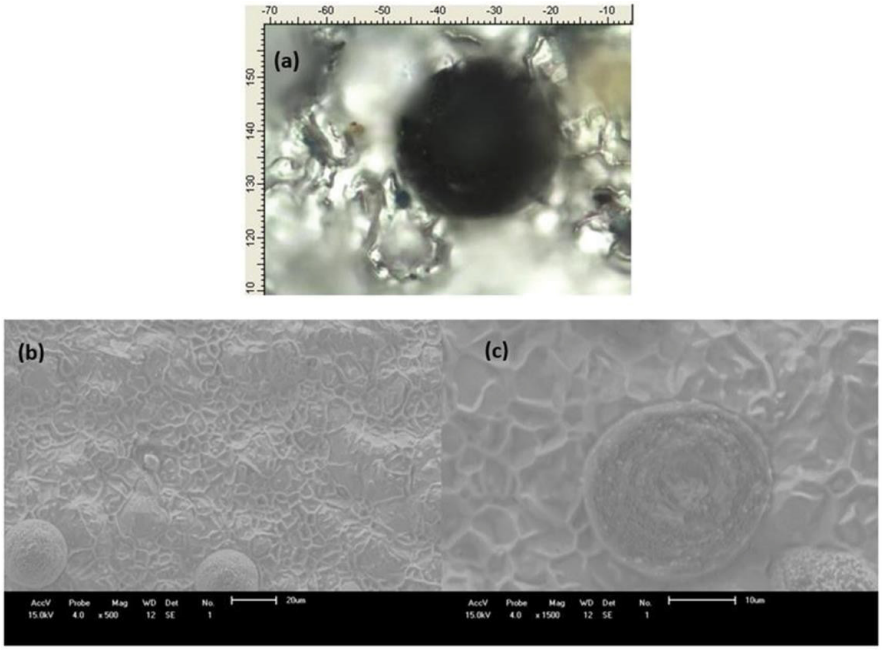

Figure 3: Analysis of (a) optical and (b and c) scanning electron microscopy of the DLC coating.

The surface microhardness analysis, presented in **Table 2**, shows a layer with hardness higher than that of the substrate,

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with values in the range 659-1697 HV. Even the lower microhardness value of 659 HV cannot be attributed to the substrate, since the steel ASIDI D2 substrate in the annealed condition has a surface

hardness of about 250 HV. However, an abrupt increase in the hardnesses result, which is certainly related to a markedly tougher stage, it is also noted, thus, we can say that hardnesses around 1600 HV can be related to the presence of DLC. It is noteworthy that the microhardness values are in some cases above those referred to in the literature cited by Mansoureh, 2015 and Eugenia, 2013.

Table 2: Steel sample surface microhardness AISI D2 with and without the DLC film coating.

Carga 200 g/f			
Untreated sample		Treated sample	
Impressão	Dureza (HV)	Impressão	Dureza (HV)
1	236	1	1367
2	237	2	1004
3	265	3	1642
4	284	4	1697
5	220	5	1727
6	264	6	650
7	237	7	1048
8	228	8	1302
9	281	9	1113
Média	250,22 ± 9,4%	Média	1283,33 ± 28,46%

Figure 4a shows the XRD pattern for a sample deposited using graphite cage. Here one can visualize the presence of characteristic peaks for a large amount of iron carbide, as shown in crystallographic chart shown in **Figure 4b**. The presence of peaks corresponding to the carbon at graphite phase at angles of about 32.5° and 57.5° in **Figure 4a** are particularly noteworthy.

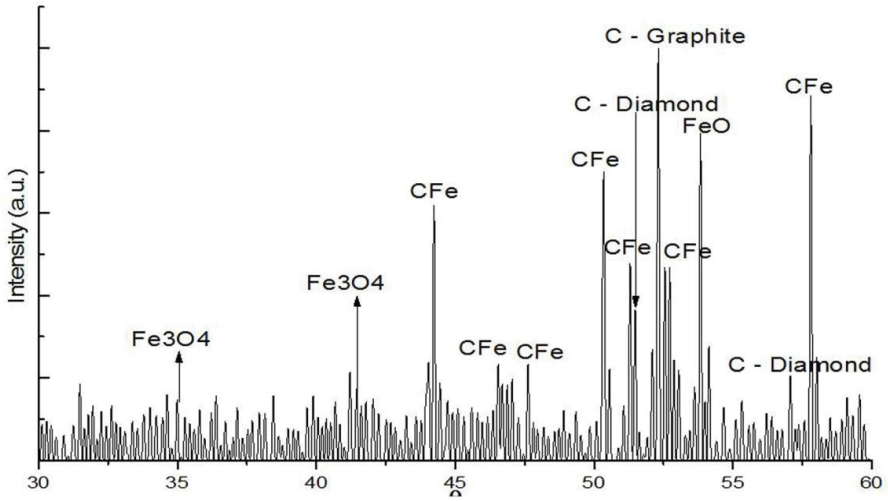

Figure 4: X-ray diffraction patterns for DLC film deposited on the steel AISI D2 surface with graphite cage; (B) crystallographic data for iron carbide Fe_3C.

Crystalline carbonaceous materials, depending on their allotropic form (graphitic or diamonds) exhibit characteristic well differentiated Raman spectra in the region 1000- 2000 cm^{-1} as shown in **Figure 5**. Diamond has a well-defined peak at 1332 cm^{-1}, which does not vary with wavelength. Graphitic materials display the bands D, G, G' and a shoulder D', although the only the G band position is not dependent on the excitation wavelength.

In highly ordered graphitic materials (diamond, graphite, etc.) the G band is more evident than D and D' for excitation wavelengths in the visible region. Therefore, the black islands in the film have a greater crystallinity. This may be understood as crystalline forms of carbon, graphite, graphene or carbon nanotube. The gray part has a characteristic spectrum of amorphous carbon (at the top of the figure is shown the zoom of amorphous carbon region) and of cementite (Fe_3C) .The high frequency band located around 1560 cm^{-1} (G band) is related to graphite carbon bonds of sp^2 type. The frequency around 1350 cm^{-1} (D band) is related to sp^3 type bonds. One can also observe a predominant enlargement of the D and G bands in the spectrum which is characteristic of amorphous carbon bonds, in the gray regions. However, in the black region of the sample, we observed a higher intensity of bands associated with carbon, with peaks with less FWHM, showing a greater crystallization of the deposited film. Thus we can confirm the indication suggested by XRD of the presence of DLC on a thin carbon film and cementite deposited on a D2 steel substrate, since micro-Raman spectroscopy is an effective means to analyze derived carbon structures and characteristics of the bonds C-C in DLC structures.

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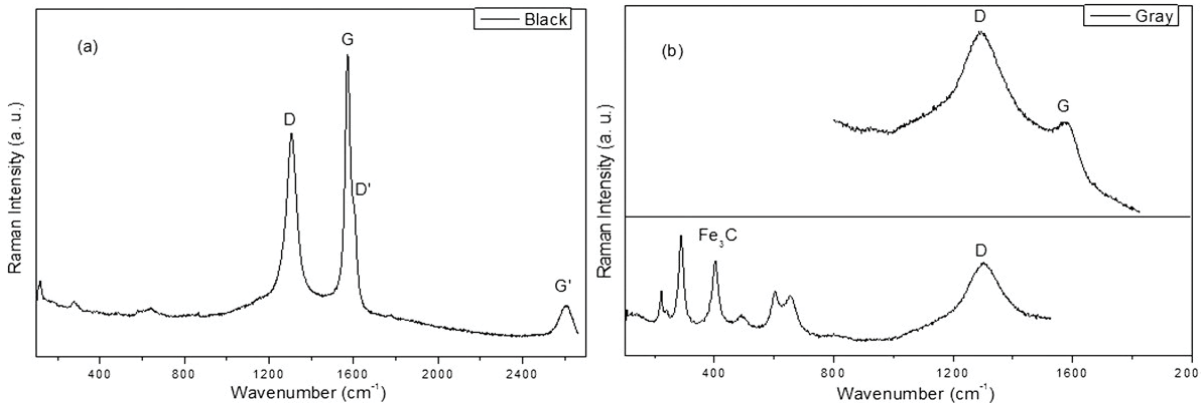

Figure 5: Mmicro-Raman spectroscopy analysis of the dark and gray regions of the film deposited in D2 steel, using a laser of 785 nm.

The relationship between the intensities of the bands D and G (ID/IG) is a qualitative way to measure the crystallite size. The crystallite size is inversely proportional to the ratio ID/IG. (LG Cançado, K. Takai, T. Enoki, Endo M. YA Kim et al, Appl. Phys. Lett. 88, 163106 (2006). Therefore an significant increase in crystallite size in the black region related to increase of carbon crystallization in this region, is observed.

With the aid of the tests discussed above it may be said that an amorphous carbon layer of DLC sites was formed.

CONCLUSIONS

DLC film was deposited on D2 steel substrates using deposition technique by plasma CVD in a cathodic graphite cage at constant temperature and pressure for 6 hours. The coating showed DLC sites of circular geometry with 20 μm in diameter with high degree of crystallinity surrounded by amorphous carbon. From the results presented here it is concluded that the cathodic cage plasma film deposition technique using a cathodic cage of graphite is a promising technique for the manufacture of DLC coatings.

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