

Residual stress analysis by different bias voltage of DLC films on AISI 4050 alloy steel

Análise da tensão residual em filmes de DLC sobre a liga de aço AISI 4050 por variação da tensão aplicada

Joao Thiago de Guimaraes Anchieta e Araujo Campos¹, Vagner Eduardo Caetano Marques², Erica Almeida¹, Evaldo José Corat², Danilo Maciel Barquete¹

ABSTRACT

Thin films are one the best choice to improve materials properties. Instead of entire replacement of the material in a component, which may be expensive, a coating process is a good option to achieve required properties precisely where they are required. Generally, coating depends on deposition methods which consist of chemical or physical interactions to form a film on substrate surface. Residual internal stresses are generated during cooling stage after deposition process, due to always present difference in thermal expansion coefficient of film and substrate materials. These stresses produce either failure or performance reduction on component utilization. Raman spectroscopy was used to evaluate these residual stresses. In this work Raman spectrum behavior was analyzed under different residual stress conditions of DLC films deposited on a 4050 steel/ molybdenum alloy steel substrates. The comparative method used at three different bias tensions of -550, -650 and -750 V showed that residual stress increases with increasing bias voltage. The normal compressive load to produce delamination in scratching test decreased from 16 N to 9 N with bias voltage increase from -550 V to -750 V, as expected due to higher interface stresses.

Keywords: Residual stress; Bias voltage; DLC film.

RESUMO

Filmes finos são ótimas escolhas para a melhoria das propriedades de materiais. Ao invés da substituição de um material em um componente onde pode gerar um alto custo, o processo de revestimento é uma boa opção para adquirir as propriedades necessárias. Geralmente, o revestimento depende de métodos de deposição que consiste em interações químicas ou físicas para formar um filme sobre o substrato. A tensão residual ocorre geralmente durante o processo de resfriamento após a deposição devido a diferença de coeficientes de expansão entre os materiais entre o filme e o substrato. Além de causar falhas no material, a tensão residual pode reduzir consideravelmente as propriedades do componente em que ocorre a deposição. Nesse trabalho a espectroscopia Raman foi utilizada para avaliar as propriedades de um filme, especificamente a tensão residual entre o filme e uma liga 4050 de aço/molibdênio. Foi avaliado a tensão residual considerando três diferentes tensões de deposição, tais que -550v, - 650v e -750v. A análise mostrou que a tensão residual aumenta quando há aumento da tensão aplicada para deposição. A carga normal de compressão para delaminação foi reduzida de 16 N para 9N quando há aumento da tensão aplicada, resultado esperado devido ao aumento das tensões residuais entre o filme e o substrato.

Palavras-chave: Tensão residual; Tensão de crescimento; Filme de DLC

¹Universidade Estadual de Santa Cruz – Ilhéus (BA) – Brazil

²Instituto Nacional de Pesquisas Espaciais – São José dos Campos (SP) – Brazil

Correspondence author: Joao Thiago Campos – UESC – Campus Soane Nazaré de Andrade (Salobrinho), Km 16 – BR 415 – CEP 45662-900 Ilhéus (BA) – Brazil
E-mail: joathiangocampos@gmail.com

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INTRODUCTION

Generally, the properties of a thin film are measured by the analysis of its surface. For example, chemical reactions begin on surface and proceed into the bulk, like adsorption, corrosion, passivation, weathering, electrode polarization, etc. Mechanical properties also affect the material initially from the surface, like friction, adhesion, wear, lubrication and bonding⁽¹⁾. Thin films are generally produced from carbon containing materials and deposited and fixed on another material, the substrate. The study of thin films depends not only on its composition, but also on substrate properties. Among thin films, diamond and diamond-like carbon are materials with a large set of properties of interest to many applications of high technology. The main difference of diamond and diamond-like carbon is the proportion of sp^2 and sp^3 bounds in the film. Diamond has only sp^3 bounds with a structure derived from face-centered cubic; diamond-like carbon varies sp^2 and sp^3 bounds ratio on a planar trigonal structure. A high concentration of sp^2 bounds characterizes graphite with planar structure⁽²⁾. Furthermore, diamond films may have others elements than carbon, like hydrogen which changes strongly material properties. For example, the Young's modulus of a diamond-like carbon with 5% of hydrogen is almost 900 GPa and less than 300 GPa for a DLC film with more than 20% of hydrogen⁽³⁾. This huge variation depends not only on hydrogen amount but on the relation of sp^2 and sp^3 bounds. Extreme wear resistance and low friction coefficient make diamond-like carbon an important coating option for high performance and high technology products. Its use in high technology applications is wide and constantly growing, replacing polymers, ceramics and metals with better mechanical and chemical responses. However, DLC films deposition process affects substrate mechanical properties, mainly due to residual stresses in the interface DLC-substrate. These stresses are due to the different thermal contraction between coating and substrate during cooling process after DLC film deposition, resulting in residual stresses in the coating-substrate interface. These stresses may causes defects on material or reduction in its mechanical resistance. To improve diamond-like coatings properties it is necessary to develop experimental methods or theoretical models to minimize these residual stresses. Using a suitable method to characterize residual stresses it is possible to evaluate how they affect the materials and their properties, as the residual stresses intensity. While experimental methods permit to identify the behavior of a material based on its properties, mathematical models are important to compare and to understand which variables are affecting these results. This way, the combined use of experimental and theoretical model is important to study residual stress and improve DLC films application. Since residual stress is energy confined in the structure, it is important to use methods for measuring intermolecular behavior as molecular vibrations⁽⁴⁾. Raman spectroscopy characterization method was used due its nondestructive and high sensitivity aspects. DLC films quality and residual stress are evaluated by peak shift, type,

line width and shape of Raman spectrum⁽⁵⁾. DLC films residual stresses are evaluated by peak shift $\Delta\omega_j$ from ω_{j0} – wavenumber at unstressed condition – to ω_j – wavenumber at stressed condition. The residual stress in a Raman spectrum is proportional to the variation of wavenumber by the Equation 1:

$$\sigma = \Delta\omega_j = \omega_j - \omega_{j0} \quad (1)$$

Many authors use the equation deduced for crystalline silicon [100] under biaxial stress to calculate the residual stresses⁽⁶⁾:

$$\sigma \text{ (MPa)} = -250 \cdot \Delta\omega \text{ (cm}^{-1}\text{)} \quad (2)$$

where

$$\sigma = \frac{\sigma_{xx} + \sigma_{yy}}{2} \quad (3)$$

Using Eq. 2 and the condition of no polarization settings for incident scattered light, an average value can be obtained⁽⁶⁾.

The equation may be used for any set of film/ substrate materials. Although the equation was derived for stressed crystalline silicon, the stress factor k changes for each crystalline material and orientation⁽⁵⁾, which results in a new general Eq. 4:

$$\sigma \text{ (MPa)} = k \cdot \Delta\omega \text{ (cm}^{-1}\text{)}$$

In this paper we analyze the behavior of residual stresses on DLC film deposited on steel alloy doped with molybdenum substrate by different bias voltage using Raman spectroscopy and a theoretical model.

METHOD

The method used on this study is a comparative analysis of residual stress in DLC films deposited on AISI 4050 alloy steel, at different bias voltages. This method is divided in three steps:

- DLC film growth process

DLC films were grown on AISI 4050 alloy steel substrates in a PECVD reactor, at three different bias voltages of –550 V, –650 V and –750 V. Each deposition process was performed at the following conditions: duration of 90 min, pressure of 1.5×10^{-1} Torr and constant 3 sccm gas flow. Silicon plasma at 1.5×10^{-1} Torr pressure was applied during the initial 20 minutes of process to enhance film/ substrate adherence.

The substrate is a 4050 steel alloy with 0.5% wt carbon and 0.3% wt molybdenum. Molybdenum alloy steels have excellent strength, good mechanical stability at high temperature, ductility and toughness. The interest on this substrate in this study is due to its good tribological properties, especially friction resistance.

- Raman characterization

The Raman spectrum analysis was used to identify wavenumber shifts to calculate residual stress in the DLC films. It was used a micro-Raman system, model RENISHAW 2000 with wavelength visible excitation of 514.5 nm using argon laser, calibrated with a natural crystalline diamond with peak at 1332 cm^{-1} .

- Tribometer characterization:

Friction resistance evolves many parameters about DLC film and substrate. Residual stresses added to friction forces decrease surface wear resistance of DLC film and substrate system. If the film is under high residual stresses, it may delaminates (release from substrate) during friction loads. With the tribometer test it is possible to analyze the load necessary to delaminate the film and the change of this load for different DLC coatings. Loads up to 20 N were applied to the film, starting from 0 N and gradually increasing until the film is released from substrate. A tribometer, model UMT2-CETR, assess the adherence from the DLC film to the substrate, in atmospheric environment.

- Residual stress analysis

Residual stresses are calculated and analyzed as a dependent variable of tension generated during growth process. Comparing the different loads to delaminate the film from substrate and the wave number shift, it is possible to make quantitative and qualitative analysis of residual stress behavior.

DISCUSSION AND RESULTS

In the PECVD process for DLC deposition the a-C:H (amorphous carbon structure) film has been deposited with three different bias voltages of -550 V , -650 V and -750 V . DLC films were then characterized by comparing the amorphous level of D and G peaks ratio:

The low I_D/I_G ratio shows high sp^3 bounds on the DLC structure. The intensity has been measured by two Gaussians curves fitted and a linear background (as shown in Figs. 1 to 3). By increasing bias voltages, the D and G band ratio increases characterizing more amorphous structure.

The Raman spectrum peaks shifts shown on Figs. 1 to 3 are due to residual stresses on DLC film. By changing bias voltage it is possible to analyze the influence of the tension applied on residual stresses. Table 2 shows peak shifts compared to bias voltage applied. The peak shifts due to variations from -550 V to -650 V and -650 V to -750 V indicate the behavior of bias voltage change in residual stresses.

Table 1: Raman analysis of DLC coating

Bias (V)	D band (cm^{-1})	G band (cm^{-1})	I_D/I_G
-550	1301.49	1531.75	0.267
-650	1307.67	1536.39	0.293
-750	1303.03	1541.02	0.311

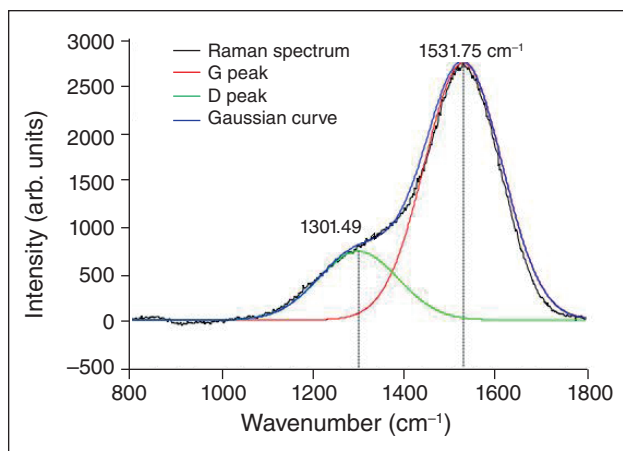


Figure 1: D and G curves of a DLC film deposited at -550 V bias voltage.

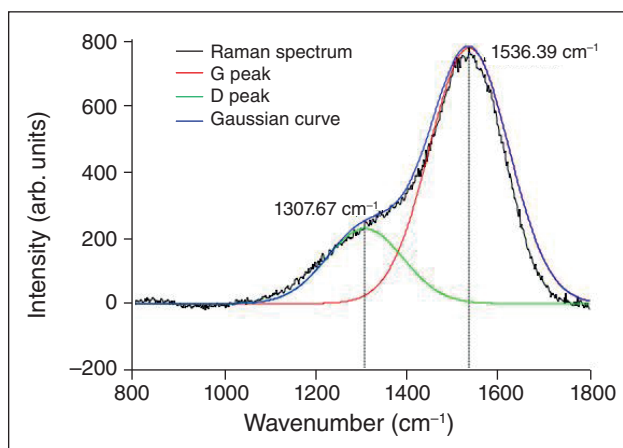


Figure 2: D and G curves of a DLC film deposited at -650 V bias voltage.

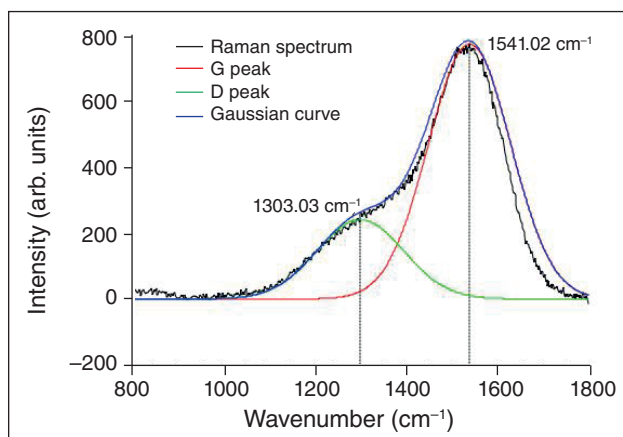


Figure 3: D and G curves of a DLC film deposited at -550 V bias voltage.

Table 2: Measured data of DLC Raman peak shifts by different bias (V)

	Characteristic peak of diamond-like carbon					
	D peak			G peak		
	1 st peak (cm^{-1})	2 nd peak (cm^{-1})	$\Delta\omega$	1 st peak (cm^{-1})	2 nd peak (cm^{-1})	$\Delta\omega$
-550 V and -650 V	1301.49	1307.67	6.18	1531.75	1536.39	4.64
-650V and -750V	1307.67	1303.03	-4.64	1536.39	1541.02	4.63

Table 2 shows $\Delta\omega$ comparing the peaks of D and G band. Using Eq. 4 and k factor as -250 for a silicon surface between diamond-like carbon and substrate, it is possible to calculate the residual stress for each diamond-like film.

According to Raman spectrum analysis, residual stresses increased with increasing bias voltage. This relation is useful to identify the parameters that influence residual stresses in coatings and in its substrates surfaces. The D peak has a different behavior when comparing -650 V and -750 V. The peak variation has a negative value which due to compressive residual stresses, different from -550 V and -650 V variation, which is positive and represents tensile residual stress. Even though the peak shifts of G band is almost the same for bias voltage changes from -550 V to -650 V and from -650 V to -750 V (4.64 cm^{-1}), the peak shift of D band decreases, resulting in a negative value as shown in table 2 for bias voltage change from -650 V to -750 V. This negative shift may be explained as the good crystalline structure ordering with higher ratios of sp^2 bounds. This decreases the D band which represents the disorder of the crystalline structure in a sp^2 and sp^3 mix of a-C and Ta-C amorphous carbon.

Comparing the tribometer results of each DLC film, diamond-like carbon coating with high residual stress tend to delaminate with smaller applied loads than others with low residual stresses. As shown in Figs. 4 to 6, the film deposited at the highest bias voltage (-750 V) delaminated at 9 N load, while the lowest bias voltage resulted on delamination at 12 N load. This relationship may be observed on the Table 4.

Comparing results from Raman spectrum peak shift and the tribometer results, higher bias voltage increases residual stresses in the DLC film, even it does not change its amorphous carbon

Table 3: Residual stress analysis of DLC coating

ΔV (V)	$\Delta\omega$ (cm^{-1})	Residual Stress (GPa)
-550 and -650	4.64	-1160
-650 and -750	4.63	-1157.5

Table 4: Delamination load - tribometer results

Bias voltage (V)	Delamination force (N)	Time (s)
-550	16	40.9
-650	12	43.0
-750	9	31.5

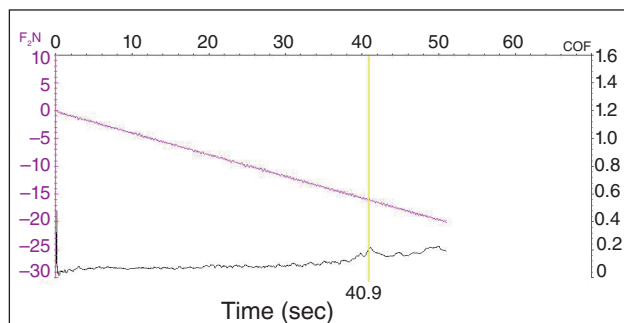


Figure 4: Tension point of film delamination for deposition at -550 V bias voltage.

properties considerably. Using optical microscopy images, it is possible to see the delamination process under different applied loads. The film is removed from a substrate surface by a load applied on the film, which brakes and delaminates it from the substrate, pushing it away from surface.

Figure 7 shows the path done by the tribometer with 5 N load. Under load, the tip may scratch the film or, if it exceeds film/substrate adhesion, may produce delamination. In this example, the film has not delaminated and a scratch is done in the diamond-like carbon film.

Figure 8 shows a film delamination in the load scratch test. The difference of colors shows clearly that film is removed from substrate surface. The scratched path is present but the film has also broken.

Figure 9 shows the delamination of the DLC film on AISI 4045 steel under 15 N normal compressive load. Film has been removed from surface and scratching lines on substrate are shown.

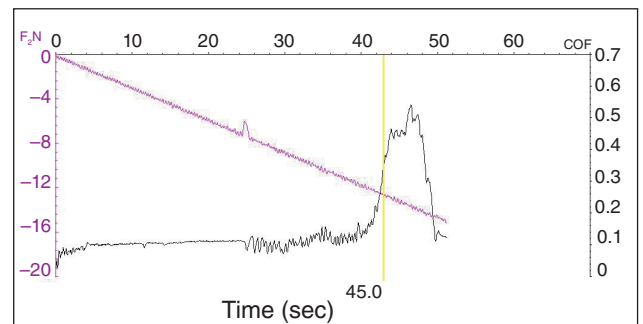


Figure 5: Tension point of film delamination for deposition at -650 V bias voltage.

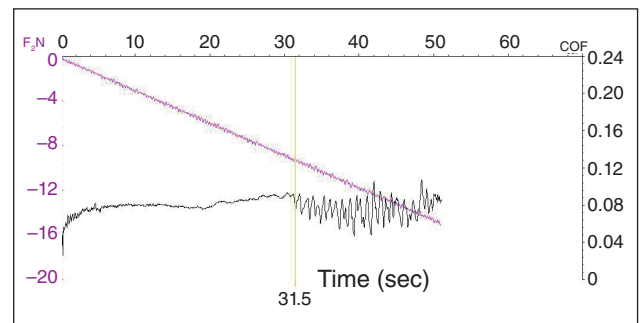


Figure 6: Tension point of film delamination for deposition at -750 V bias voltage.



Figure 7: Optical microscopy image of 5 N load scratch on DLC film deposited at -750 V bias. No delamination occurs.

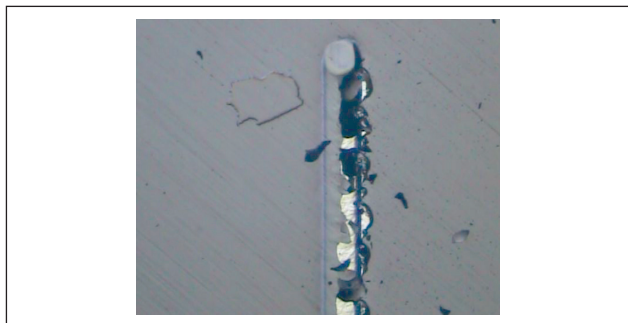


Figure 8: Optical microscopy image of 10 N load scratch on DLC film deposited at -750 V bias. DLC film has delaminated from substrate.

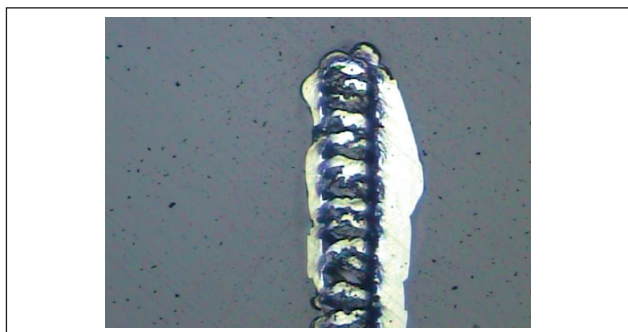


Figure 9: Optical microscopy image of 15 N load scratch on DLC film deposited at -750 V bias. DLC film is removed from substrate.

CONCLUSION

Residual stress occurs on every thin film deposited on substrates above ambient temperatures. Due to different thermal expansion coefficient of materials, these stresses arises during the cooling process from deposition temperature. Controlling the variables of deposition process it is possible to control this energy confined in film and the DLC film adhesion to the substrate. The AISI 4050 molybdenum alloy steel was an adequate choice as substrate, due to the good adherence and friction resistance of the deposited

DLC. This study evaluates the behavior of residual stress by controlling the bias voltage applied in the plasma-enhanced chemical vapor deposition method (PECVD). The Raman spectrum has shown higher residual stresses for films with higher bias voltages applied. At the different bias voltages applied the DLC films has kept the same crystalline structure, evaluated by the D and G band ratio, meaning that the film adherence to the substrate changed due to residual stresses in the film. Residual stress in the DLC films can be adjusted by controlling PECVD process variables, as bias voltage applied, to improve film adherence to substrate, without changing crystalline structure of the film.

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