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RESIDUAL STRESS ANALYSIS BY DIFFERENT TENSIONS OF DLC FILMS ON TIAL$_6$V$_4$ AND 3016 STEEL ALLOYS[1]

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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 Titanium alloy ($TiAl_6V_4$) substrate. The comparative method used at three different bias tensions of -550 V, -650 V and -750 V showed that residual stress increases with increasing bias voltage but with a non-linear behaviour.

Key words: Diamond-like carbon; Residual stress; 3016 steel alloy, $TiAl_6V_4$ alloy.

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1 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 form gases 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 than 900 GPa and it is 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 DLC an important material for high performance and high technology products. It is used in high technology applications on a 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. This stress is due to the difference of thermal expansion after the material cooling process, which causes an internal stress defined as residual stress. It may causes defects on material or reduction in mechanical resistance. Hence, to improve better quality on diamond-like materials it is necessary to study these residual stresses and find ways to decrease it during the film growing process. To study this internal stress, it is possible to use experimental or theoretical model. With a good residual stress characterization method, it is possible to evaluate how it affects the materials and, consequently, its properties. On other hand, it is also possible to use mathematical models with theoretical content to calculate, for example, the modulus of stress. While an experimental method permits to see the behavior of a material based on his properties, mathematical model is important to compare and to understand which variables are affecting these results. Then, to reach better results, it is important to study residual stress by experimental and theoretical models. Since residual stress is energy stuck in a molecular structure, it is important to use methods for measuring inter-molecular behavior as molecular vibrations. Raman spectroscopy is an inelastic scattering method, which assesses the interaction of an incident light and phonons emitted by a new molecular vibration mode due to an energy exchange between the incident light and the phonons.(4) There are many advantages in analyzing molecular structure using Raman spectroscopy, such as non-destructive characterization method and high sensitive to strain, Then, this characterization method is a good analysis tool of the energy emitted by these vibrations, showed on a raman analysis by its new wave number spectrum. For residual stress analysis, the Raman spectrum must be considered such as frequency shift, peak type and line width.(5) In a Raman spectrum, the molecular vibrations are measured by the wave number α which in the absence of strain is defined as ω_{j0}. In the presence of residual stress, the Raman spectrum peaks

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will shift on a new wave number ω_j which is used to calculate the stress inside the material by $\Delta\omega_j$. Thus, the residual stress is shown in a Raman spectrum as a variation of wave number by the Equation 1.

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

This shift on a Raman spectrum occurs when a film/substrate material are under internal stress, dislocating the peak on the spectrum. To calculate the residual stress, many authors use a deduced equation from crystalline silicon [100] under biaxial stress:(6)

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

Where

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

Then, using Equation 2 and the condition of no polarization settings for incident scattered light, an average value can be obtained.(6)
The equation may be used to any kind of film/substrate relation. Although the authors use the equation for crystalline silicon under stress, the stress factor k changes for each crystalline material and orientation,(5) which results in a new general Equation 4.

$$\sigma \text{ (MPa)} = k\Delta\omega\text{(cm}^{-1}\text{)} \quad (4)$$

Thus, the aim of this paper is to analyze the behavior of residual stress on DLC film deposited over two different substrates, such as titanium alloy ($TiAl_6V_4$) and a 3016 steel alloy by applying different bias voltage and comparing the residual stress behavior using Raman spectroscopy and a theoretical model.

2 METHOD

The method used on this study is a comparative analysis of residual stress in a DLC film deposited over a 3016 steel alloy and a $TiAl_6V_4$ with different tensions. This method is divided in three steps:

- DLC film growth process – a DLC film was grown by a PECVD reactor over the substrate by three different tension conditions such as -550 v, -650 v and -750 v. Each deposition process has been working for 90 min keeping pressure at 1.5 x 10^{-1} Torr and constant 3 sccm gas flow during growth process. Silicon plasma to guarantee the adherence of the film was applied during 20 minutes with a pressure of 1.5 x 10^{-1} Torr;
- raman characterization – by Raman spectrum analysis it is possible to identify a wave number shift thus the residual stress in the film. The spectrum has been produced by a micro-Raman system, model RENISHAW 2000 with wavelength visible excitation of 514,5 nm using argon laser. To calibrate, it is used a crystalline diamond based on the unique peak on 1.332 cm^{-1};
- residual stress analysis – the residual stresses are calculated and analyzed as a dependent variable of tension generated during growth process. Comparing the difference force to delaminate the film from substrate and the wave number shift, it is possible to have a quantitative and qualitative analysis of residual stress behavior.

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3 RESULTS AND DISCUSSION

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

Table 1. Raman analysis of DLC deposited over a 3016 steel alloy

Bias (V)	D band (cm^{-1})	G band (cm^{-1})	I_D / I_G
-550	1353.93	1546.72	0.384
-650	1307.67	1536.69	0.237
-750	1303.03	1541.02	0.388

The low I_D / I_G ratio indicates high sp^3 bounds on the diamond-like structure. The intensity has been measured by two Gaussians curves fitted and a linear background (Figures 1, 2 and 3). By increasing bias voltages, the D and G band ratio vary by a non-linear behavior where at -650 v the DLC has more sp^3 bounds than -750 volts, which have a higher intensity ratio.

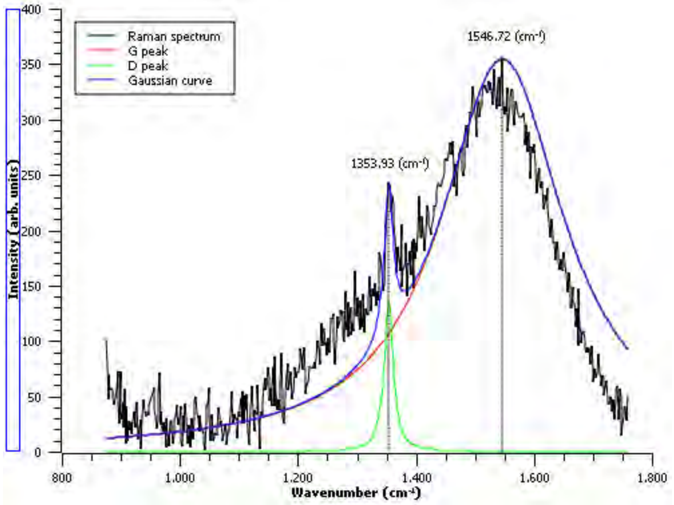

Figure 1. D and G curves of a DLC film deposited over a 3016 steel alloy under -550 v deposition tension.

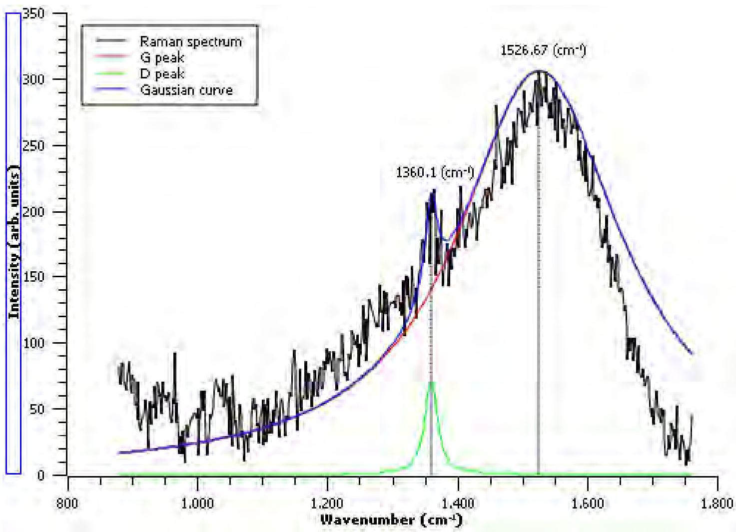

Figure 2. D and G curves of a DLC film deposited over a 3016 steel alloy under -650 v deposition tension.

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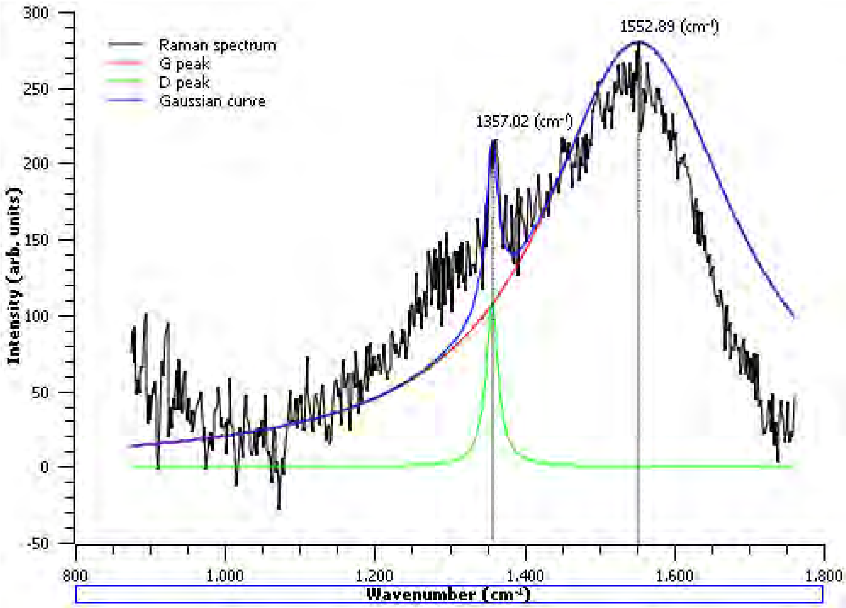

Figure 3. D and G curves of a DLC film deposited over a 3016 steel alloy under -750 v deposition tension.

Using the same method to assess the amorphous level of the film deposited on a $TiAl_6V_4$ alloy, the intensity ratio is shown below:

Table 2. Raman analysis of DLC deposited over a $TiAl_6V_4$ titanium alloy

Bias (V)	D band (cm^{-1})	G band (cm^{-1})	I_D / I_G
-550	1352.39	1525.13	0.265
-650	1352.39	1522.04	0.283
-750	1352.39	1559.06	0.3583

Different from 3016 steel alloy, the growth process of $TiAl_6V_4$ indicates that increasing the bias voltage the DLC become more amorphous since higher intensity ratio, more sp^2 bounds on the DLC crystalline structure.

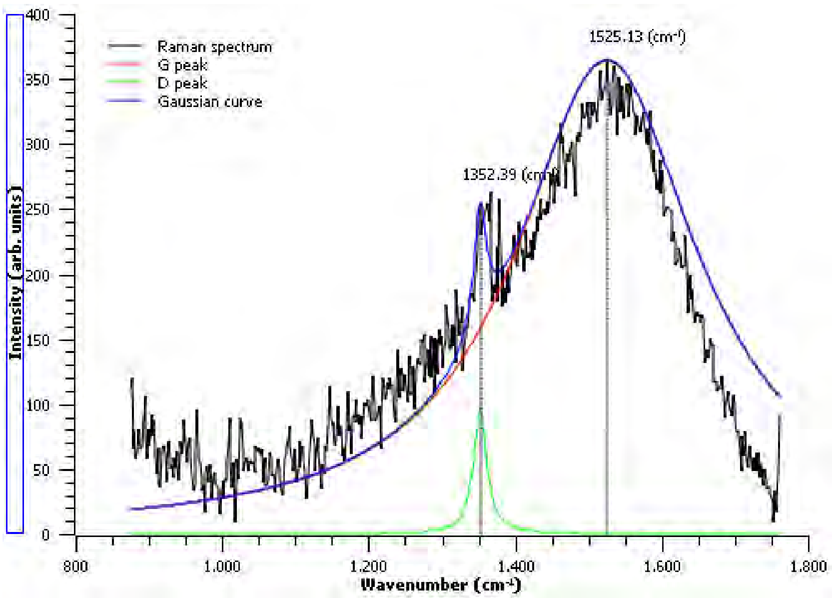

Figure 4. D and G curves of a DLC film deposited over a $TiAl_6V_4$ titanium alloy under -550 v deposition tension.

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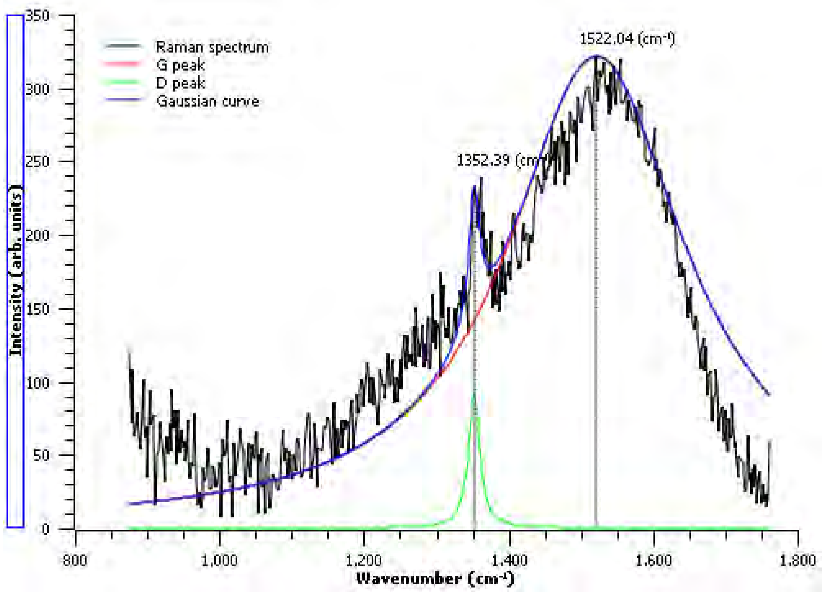

Figure 5. D and G curves of a DLC film deposited over a $TiAl_6V_4$ titanium alloy under -650 v deposition tension.

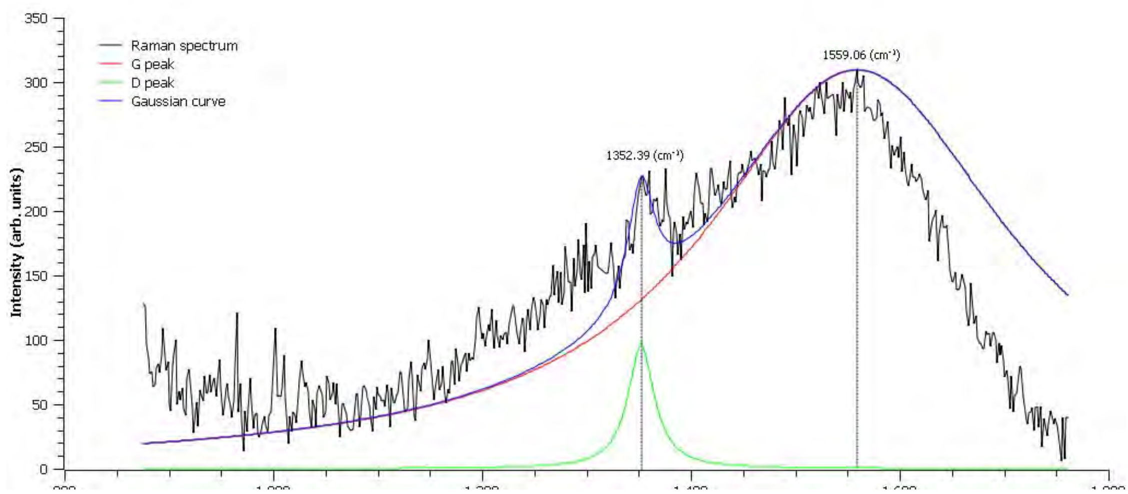

Figure 6. D and G curves of a DLC film deposited over a $TiAl_6V_4$ titanium alloy under -550 v deposition tension.

By analyzing the Raman spectrum peaks shown on Figures 1, 2 3 is possible to calculate the residual stress between the film and 3016 steel allow. Varying bias voltage it is possible to analyze the influence of tension applied over residual stresses.

Table 3. The measuring data of diamond-like carbon of Raman shift over a 3016 steel substrate by different bias (v)

	Characteristic peak of diamond-like carbon					
	D peak			G peak		
	1st peak	2nd peak	$\Delta\omega$	1st peak	2nd peak	$\Delta\omega$
-550v and -650v	1353.93	1360.1	6.17	1546.72	1526.67	20.05
-650v and -750v	1360.1	1357.02	-3.08	1526.67	1552.89	26.22

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

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Table 4. Residual stress analysis of DLC coating over a 3016 alloy

ΔV (v)	$\Delta\omega$ (cm^{-1})	Residual Stress (GPa)
-550 and -650	20.05	-5012.5
-650 and -750	26.22	-6555

According to Raman spectrum analysis, the residual stress increases with bias voltage increasing. This linear relation is useful to identify the parameters that influence the residual stress on the film and substrate surface. However, the D peak which characterizes the disorder level of a DLC film has an unusual behaviour when it is measured by shift on Raman spectrum. By analyzing the variation of wave number, the D peak decreases, resulting in a negative value as shown in table 2 on -650 and -750 of D band. This shift may be explained as the good crystalline structure ordering with almost sp^2 bounds which decreases the D band that represents the disorder of the crystalline structure in a sp^2 and sp^3 mix as amorphous carbon a-C and Ta-C. By the ternary phases diagram, an amorphous carbon film has more sp^2 bounds than sp^3 whereas diamond-like carbon with these bounds and ordered are close to graphite than tetrahedral amorphous carbon. For good film properties, especially for tribological uses, residual stress decreases film quality. On other hand, analyzing the titanium alloy (Table 5).

Table 5. The measuring data of diamond-like carbon of Raman shift over a $TiAl_6V_4$ substrate by different bias (v)

	Characteristic peak of diamond-like carbon					
	D peak			G peak		
	1st peak	2nd peak	$\Delta\omega$	1st peak	2nd peak	$\Delta\omega$
-550v and -650v	1352.39	1352.39	0	1525.13	1522.04	-3.08
-650v and -750v	1352.39	1352.39	0	1522.04	1559.06	37.02

Different from 3016 steel alloy, the results indicated on Table 4 shows a non-variation of the D peak, which consists of no changes on disorder structure. However, by increasing bias voltage the residual stress achieve a higher value, different from the first bias voltage comparison (-550 v and 650 v) which has a negative variation as the 3016 alloy. Using Equation 4 and k factor as -250 of a silicon surface between diamond-like carbon and the substrate it is possible to calculate the residual stress of each diamond-like film.

Table 6. Residual stress analysis of DLC coating over $TiAl_6V_4$ alloy

ΔV (v)	$\Delta\omega$ (cm^{-1})	Residual Stress (GPa)
-550 and -650	-3.08	-770
-650 and -750	37.02	-9255

The raman spectrum and the mathematical model indicates a non-linear behavior of the residual stress over both alloys analyzed. Even the behavior of the 3016 steel alloy shows a high residual stress by increasing the bias voltage, the titanium alloy studied on this paper indicates that the residual stress may modify considerably by increasing bias voltage.

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4 CONCLUSION

This study assesses the residual stress by controlling the bias voltage applied by plasma-enhanced chemical vapor deposition method (PECVD). The Raman spectrum has shown a high residual stress on high voltages applied. Even the film has the same crystalline structure, evaluated by the D and G band ratio, the residual stress increased as the bias voltage increases. Comparing the 3016 steel and TiAl6V4 titanium alloys, this research indicates the non-linear behavior of the residual stress inside the substrates. Hence, by comparing difference bias voltage applied over the substrates, it is possible to improve better DLC materials controlling the variables of PECVD process like pressure, temperature, gas flow and time.

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