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Deposition and Analysis of DLC Thin Films Obtained on 7075 Aluminum Alloy

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Abstract. In this study a-C:H (hydrogenated amorphous carbon) thin films were deposited on the 7075 Al alloy without and with admixture gas (N_2) using a DC CVD (direct current chemical vapor deposition) method. The structural and mechanical properties were analyzed using Raman spectroscopy, SEM and nanoindentation. We obtained hardness of a-C:H thin film without and with N_2 equal to 27.3 GPa and 21.4 GPa, respectively. Values of the Young's modulus were equal to 135.5 GPa and 205.2 GPa, respectively.
Keywords: a-C:H film, CN film, hardness, Young's modulus, 7075 Al alloy

1. INTRODUCTION

Due to the high strength-to-weight ratio, aluminum alloys are commonly used materials in aircraft and automotive industry. However, the low hardness and wear resistance and high friction coefficient limit its applications. DLC (diamond-like carbon) coatings are excellent candidates for coating of standard Al alloys (2024, 6061, and 7075) due to their high hardness, excellent wear resistance, low coefficient of friction and chemical inertness.

This coating is usually alloyed with chemical elements in order to influence the coating properties. Deposition of the a-C thin film on a surface of Al alloy may lead to extension of lifetime [1-4]. Amorphous carbon layers may contain hydrogen (a-C:H) and nitrogen (a-C:N). Several authors investigated mechanical and tribological properties of carbon based coatings deposited also using different precursors under constant substrate bias [3, 5]. They used some materials as Ti alloy and aluminum substrates [1-4], also steel substrates [6-9].
In this study a-C:H thin films were deposited on the 7075 Al alloy without and with admixture gas (N_2) using a DC CVD method. The aim of the presented paper has been the comparison of mechanical properties and microstructure of the listed thin films in respect of admixture of gas N_2.

2. EXPERIMENT

Cylindrical 7075 aluminum alloy with diameter 20 mm and height 5 mm and mirror polished Si substrates were used for deposition of the coatings. The roughness was R_a = 0.1 μm. DLC thin films were deposited by DC PE-CVD process in a vacuum installation type UVNIPA-1-001 described previously [5] using a DC power supply. Prior to deposition, substrates were cleaned for 10 min with Ar ions within the deposition cycle. Background pressure was 10^{-1} Pa and working pressure was maintained around 20 Pa according to gas flow. Argon and nitrogen (Ar/N_2) gas flow ratio was set up to 120/0 cm^3/min for sample 1 and 100/20 cm^3/min for sample 2. The deposition voltage was 1 kV and the temperature was kept bellow 250ºC. The structural properties of DLC films were evaluated by SEM (JEOL 7500F) and Raman spectroscopy with 632.8 nm radiation from a He–Ne laser. The acquired Raman spectra were fitted with a Gaussian line to illustrate the D and G peak positions, G peak full width at half maximum (FWHM) and I_D/I_G and A_D/A_G ratio. The measurements of mechanical properties were carried out using nanoindentor (NHT CSM Instruments) with Berkovich tip in 20 Hz sinus mode by maximum force of 300 mN.

3. RESULTS AND DISCUSSION

3.1. Raman spectroscopy

The Raman spectra of DLC films deposited with different gas flow are shown in Fig. 1. Spectra of the films contain the typical diamond-like carbon D band attributed to the disorder-allowed optical zone mode (Alg) of microcrystalline graphite sheets and G band associated with optically allowed zone (E2g mode) of the aromatic ring in graphite [10].

The D peak arises owing to the limitation in the graphite domain size induced by grain boundaries or imperfections, such as substitutional N atoms and sp^3 coordinated carbon and nitrogen atoms.

A small change in I_D/I_G, A_D/A_G ratio, G and D peak position and FWHM (Tab. 1) with varying nitrogen amount in the gas mixture can be observed. We can see the I_D/I_G and A_D/A_G ratio tendency to grow with the N_2 contents in the gas mixture, but the difference is very low. The I_D/I_G rises as the number of rings per cluster increases and the fraction of chain groups (disorder) falls. The I_D/I_G is also in direct proportion to the in-plane correlation length L_a or domain size [11].

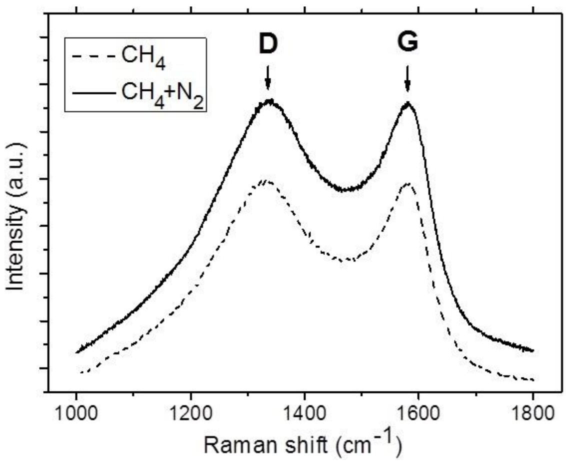


Fig. 1. Raman spectra of the DLC layers

The G peak position increases from 1576 cm^{-1} to 1578 cm^{-1} with nitrogen volume increase. It is generally accepted that increase in the I_D/I_G ratio and shifting of the G-peak toward higher wavenumber are caused by the increase of in the graphite-like component in the CN films and the sp^2-bonded carbon clusters size [12]. This indicates that, the much nitrogen in the gas mixture, the more sp^2 bonds in the film.

Table 1. Raman spectra Gaussian fitting results

Sample	D position	G position	FWHM	I_D/I_G	A_D/A_G
1 – CH_4	1337.8	1576.2	110.8	1.11	2.78
2 – CH_4+N_2	1345	1578.3	112.7	1.15	2.86

3.2. SEM analysis

The SEM images of the deposited DLC layers are in Fig. 2. The pictures a) and b) (samples 1 and 2) show the cross section of the Si substrates scanned under angle of 45º. We can see that, the thickness of the layers 1 and 2 is around 14 μm and 11 μm, respectively.

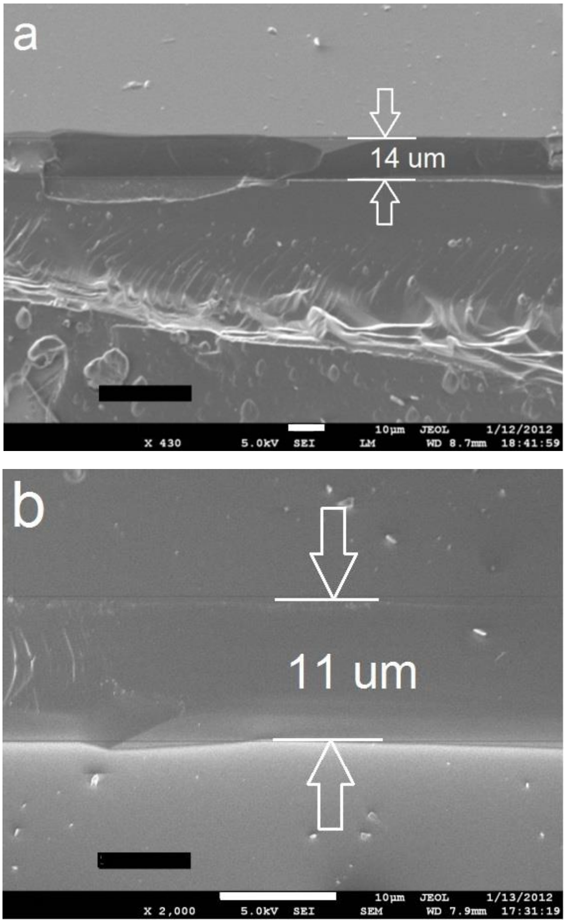
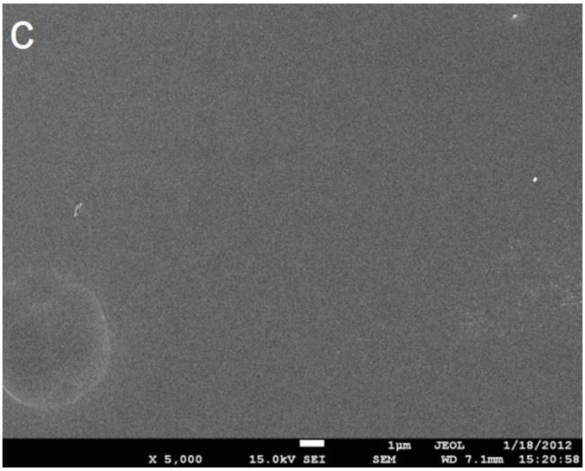


Fig. 2a and 2b. SEM images of DLC layers

The pictures c) and d) show the surface of the investigated samples. We can see a homogenous surface with very low surface roughness.



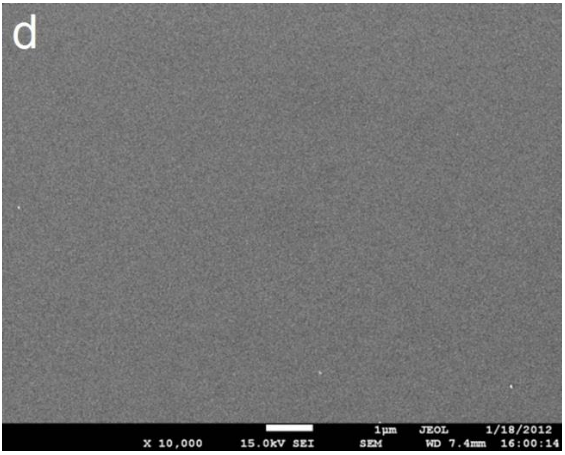


Fig. 2c and 2d. SEM images of DLC layers.
The thickness of layers 1 (a) and 2 (b) as well as the thin surface morphology of samples 1 (c) and 2 (d)

3.3. Hardness and Young's modulus

Measured hardness achieved the value 27.3 GPa for thin film 1 (Fig. 3) and 21.4 GPa for thin film 2 (Fig. 4) deposited with N_2 admixture. Young's modulus value achieved 135.5 GPa for thin film 1 (Fig. 3) and 205.2 GPa for thin film 2 (Fig. 4), deposited with N_2 admixture.

Hardness of thin film 1, deposited without admixture gas is near upon the values presented in works [13-15], where listed thin films were deposited with negative bias – 600 V. On the other hand, measured values of Young's modulus are higher in 50% in comparison to [13] and in 25% lower in comparison to [5]. Arose differences could be caused by different pressure in a vacuum chamber as well as by different flow of the used precursor. Presence of graphite-like component in the CN films causes the hardness decrease and Young's modulus increase in CN films. On the other hand, graphite-like component is a very good lubricant. As a consequence, we can expect the coefficient of friction decrease what is a reason of N_2 admixture during the DLC deposition. However, COF was not evaluated.

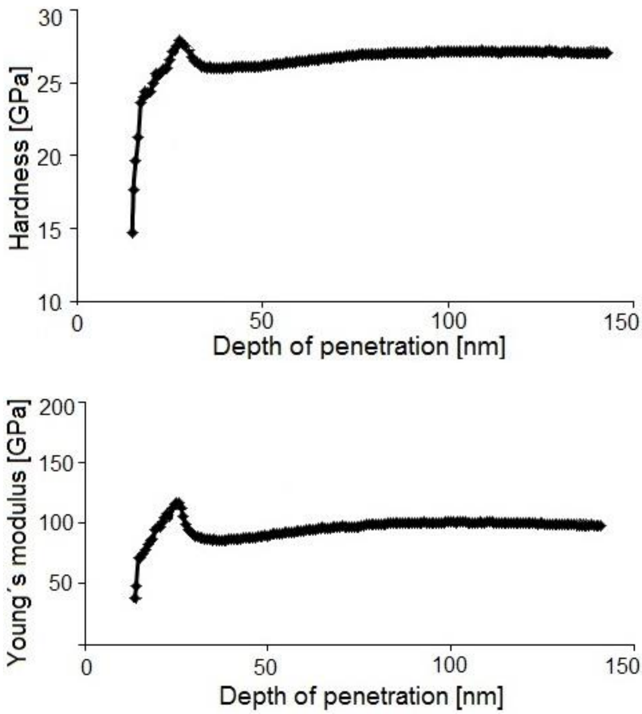
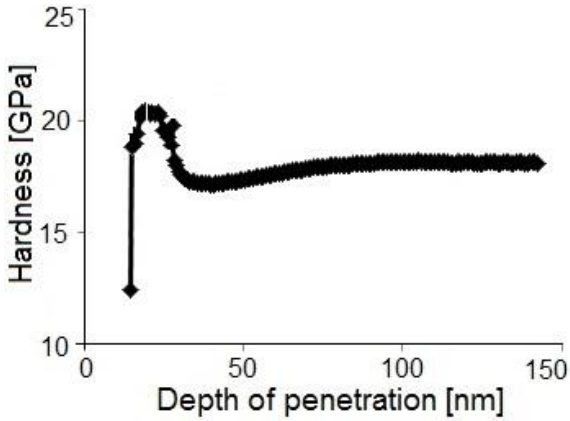


Fig. 3. Hardness and Young's modulus of layer 1 – CH_4



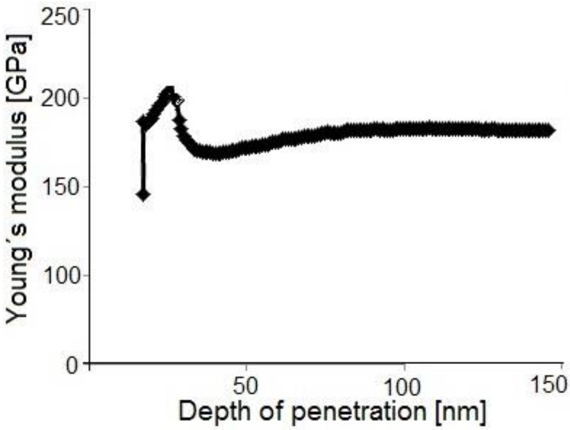


Fig. 4. Hardness and Young's modulus of layer 2 – CH_4 + N_2

4. CONCLUSIONS

The paper presents the evaluation of two DLC thin films deposited upon the identical conditions. Thin film 2 was deposited with N_2 admixture. Upon the analysis, evaluation and comparison, it can be stated that:

- Hardness and Young's modulus are comparable to the published values.
- N_2 as an admixture significantly decreases hardness up to 25% and increases Young's modulus up to 30%, respectively.
- Thin film width deposited with N_2 admixture decreases up to 20%.
- Higher nitrogen volume in the gas mixture caused the more sp^2 bonds in the CN film and thereby higher amount of graphite-like component in CN film. Presence of graphite-like component causes the hardness decrease

and Young’s modulus increase as well as the film growth rate decrease. Consequently, DLC thickness decreases with N_2 admixture.

- Influence of nitrogen volume on the mechanical and tribological properties of CN thin film with current bias change will be the task for further research.

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