

# Effect of Deposition Time on the Morphological Features and Structure of DLC Coatings on Aluminum-T6 by PACVD

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**Received: 2 July 2022, Revised: 12 August 2022, Accepted: 18 August 2022**

**Abstract:** Diamond like Carbon (DLC) was deposited on aluminum substrate using Plasma Assisted Chemical Vapor Deposition (PACVD) route. Spattering, the surface was activated before deposition for increasing adhesion. Deposition time was varied from 60 minutes to 5 hours. Deposit was characterized using with grazing incidence X-ray diffraction and atomic force microscope. The mechanical property was measured using microhardness and roughness tester. The analysis showed that the deposit consisted of columnar growth of submicron and micron meter scale. Compared to substrate material, deposit showed higher hardness and roughness. These results show that growth of DLC layer includes three stages. The first stage is primary growth of nuclei, and then these nuclei join together in second stage. In third stage, secondary growth of these nuclei happens.

**Keywords:** Coating, DLC, Deposition Time, PACVD, Tribology

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Research paper

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## 1 INTRODUCTION

The PACVD technique is an appropriate method to deposit wear and corrosion resistant hard coatings which have excellent properties for several applications. In comparison to PVD methods, it offers the possibility of coating work pieces with complicated shapes homogeneously. Other advantage of PACVD method is the high adhesion. Tools deposited with hard coatings, like TiN, DLC, TiC, have already been used successfully for many industrial applications [1–3].

The PACVD process is influenced by several process parameters, like discharge voltage, current density, gas pressure and gas composition and flow rate [4–5].

Titanium nitrides have been successfully applied as coating materials due to their tribological properties, biocompatibility and affordable price. TiN is one of the most studied ceramic coatings [6–14], however other nitrides such as TiNbN and DLC may be interesting alternatives. In recent fifteen years, ternary TiBN and DLC coatings have been a subject of interest both for scientific research and for industrial application [6–20]. In comparison with the earlier developed TiN, TiB<sub>2</sub> and TiC binary coatings, the ternary coatings often combine the individual advantages of these binary coatings and have high hardness, wear resistance, low friction coefficient and good adhesion to substrate. The ternary coatings can be conveniently deposited on a substrate through a Plasma Assisted Chemical Vapor Deposition (PACVD) process. Combining some of the advantages of Chemical Vapor Deposition (CVD) and Physical Vapor Deposition (PVD), PACVD is operated at a temperature usually below the tempering temperature of most tool aluminums. Therefore, it is particularly suitable for large and complexly shaped extrusion dies and die-casting moulds [21].

The previous research [26] was on investigation of effect of gas flow ratio on characterizes DLC coating but in the present research, the influence of deposition time on properties of PACVD DLC coating on the 6061-T6 aluminum has been investigated.

## 2 EXPERIMENTAL DETAILS

DLC coatings with compositional gradients were deposited on a 6061-T6 aluminum substrate using a PACVD coating system equipped with a voltage-controlled pulse generator. The PACVD DLC deposition was conducted in the same industrial set plant. The cylindrical vacuum chamber, which is 500 mm in diameter and 700 mm in height, can be heated with an auxiliary heating system, the temperature of which is controlled by a thermocouple and kept constant at 270 °C. The substrate is put directly on the charging plate, which is also used as the cathode of the

system. The surrounding wall of the chamber is used as the anode of the system and the potential earth.

During coating, process parameters such as gas flow ratio, wall temperature, voltage duration of pulse-on and pulse-off time and total pressure were monitored. H<sub>2</sub>, Ar, N<sub>2</sub> and CH<sub>4</sub> gases were used as process gases for coating deposition. Total pressure was kept at 2 mbar and substrate temperature was controlled at 270 °C to avoid exceeding the tempering temperature of the 6061-T6 aluminum. Plasma Nitriding (PN) was used as pre-treatment to decrease hardness gradient between substrate and coating and spattering surface. The processing parameters for deposition are listed in “Table 1”.

**Table 1** PACVD and PN variables

Variable	PACVD	PN
CH <sub>4</sub> / (CH <sub>4</sub> +N <sub>2</sub> )	0.3	-
N <sub>2</sub>	0.25 mL/min	0.25 mL/min
CH <sub>4</sub>	mL/min 0.1	-
H <sub>2</sub>	1.6 mL/min	1.6mL/min
Ar	0.6 mL/min	0.6mL/min
%33	%33	Duty cycle
8 KHz	8 KHz	Frequency
650 V	650 V	Voltage
2 mA	2 mA	Current
2 mbar	2 mbar	Pressure
270 °C	270 °C	Temperature
120 min	60 to 300 min	Time

The crystalline structure of the coatings was determined by grazing incidence X-ray diffraction (GIXRD) in the continuous scanning mode using CuK $\alpha$  radiation ( $\lambda = 0.154056$  nm). The full-width at half-maximum (FWHM) of the Bragg peaks is used to approximate grain size based on the Scherrer formula [22]:

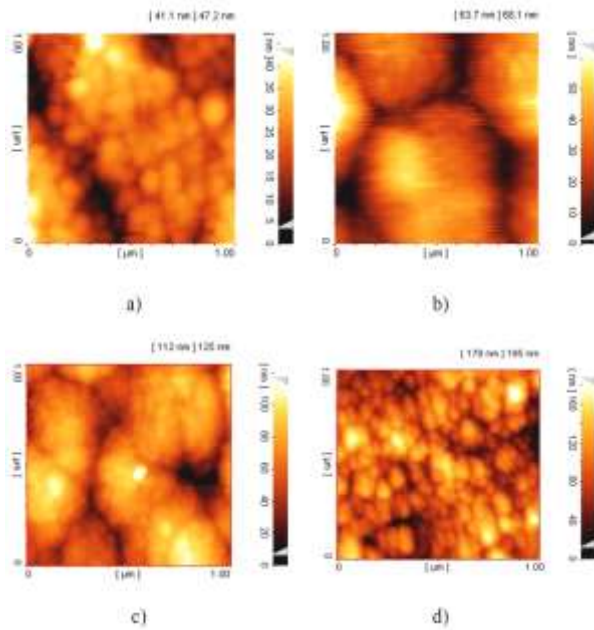
$$D = \frac{(0.9\lambda)}{(\beta \cdot \cos \theta)} \quad (1)$$

Where, D is grain size,  $\beta$  is the FWHM of the Bragg peak, and  $\theta$  is the Bragg reflection angle. The film morphology is studied by atomic force microscopy (AFM).

## 3 RESULTS AND DISCUSSION

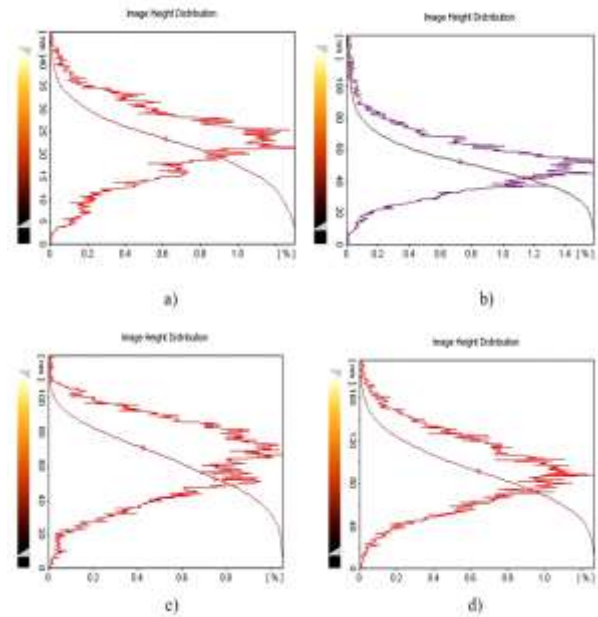
Figures 1(a) to 1(d) show morphology of DLC deposits deposited for time intervals of 60, 120, 150 minutes and 5 hours, respectively. DLC deposit deposited for 60 min (“Fig. 1(a)”) is incomplete. The nuclei of DLC deposited over substrate materials are clearly visible.

Compared to that, deposit deposited for 120 minutes and above covers the substrate almost completely. Black part in “Fig. 1(a)” was interpreted as a porosity of DLC film. The existence of the porosity means the DLC deposit is incomplete, i.e., it does not cover the surface completely. On the other hands, “Fig. 1(b)” almost does not have black part. This means that DLC deposit in “Fig. 1(b)” covers the substrate almost completely. The surface topography of DLC deposit showed the columnar structure very fine. Island growth of DLC coating is formed in columnar structure.



**Fig. 1** Microstructures of DLC deposits deposited for times: (a): 60, (b): 120, (c): 150, and (d): 300 minutes, respectively.

Figure 2 shows nucleation size distribution measured over a large number of nuclei. We see that in all cases the nucleation size is relatively small and all deposits show a clear peak in the distribution curve. Only in 150 minutes, nucleation size distribution show two peaks. Then in 300 minutes, that shows a clear peak. These results show that growth of DLC layer includes three stages. The first stage is primary growth of nuclei, and then these nuclei join together in second stage. In third stage, secondary growth of these nuclei happens.



**Fig. 2** Nucleation size distribution in samples deposited for various times: (a): 60 minutes, (b): 120 minutes, (c): 150 minutes, and (d): 300 minutes.

DLC deposition is a nucleation and growth phenomena which are time dependent. Nucleation is an important step in forming an adherent DLC coating. Nucleation activity itself is a probabilistic phenomenon. Hence, DLC island density and island size distribution are time dependent functions during the existence period in the CVD reactor [23]. DLC deposit deposited for 60 min shows the form of islands. This is because the nucleation events occurring on a catalyzed surface are a probabilistic process. Once nucleation events take place, the DLC grains grow into columnar structure. The number of nucleating sites increases with time, creating more columnar structure. In the next stage, the nuclei acted as the deposition sites for the deposition reaction and the coating was extended into 2D direction, centering on the columnar structure and covering full surface.

The deposits deposited for longer times (120 min and greater) also show the additional nuclei present above the base layer. This is because the substrates like aluminum become catalytic when surface of substrate spatters. The catalytic sites on the initial deposits act as nucleating sites for additional nuclei.

The as-formed coating has the catalytic activity required for the autocatalytic reaction, and this promoted the nucleation and growth of the coating in the third direction. The formation of a new layer on the previously deposited layer could be seen in the coatings deposited for longer existence time and such morphologies are also reported [24]. It may be noted

that the mean roughness is much larger by increasing time (“Fig. 3”).

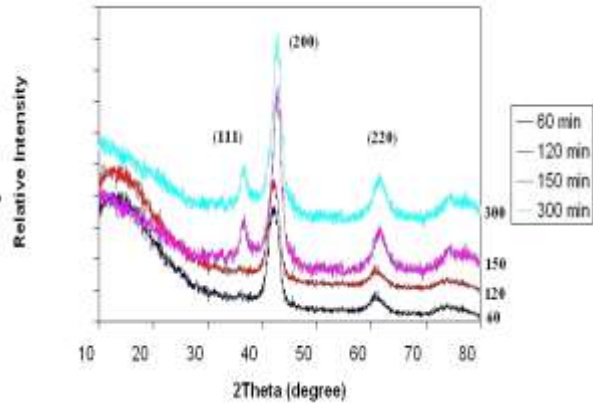


Fig. 3 Change of roughness with deposition time.

Figure 4 shows XRD plots for DLC deposits deposited for various time durations. Peaks are wide which suggest that coating is semicrystalline a mixture of amorphous and microcrystalline. He et al. [25] have reported a semicrystalline DLC coating on aluminum.

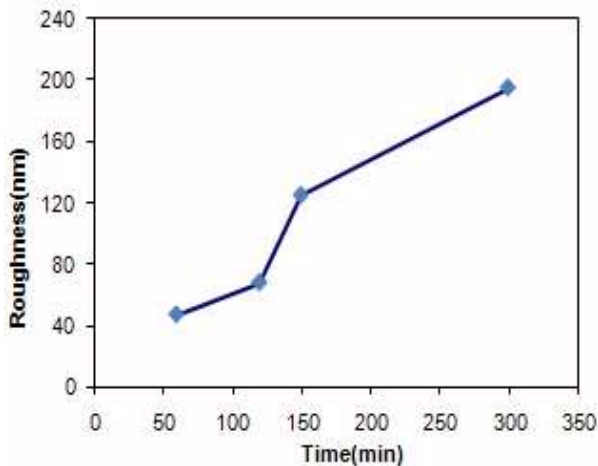


Fig. 4 2XRD plots for DLC deposits deposited for various times.

A single broad peak indicates that the deposit is microcrystalline with preferred orientation (200). This orientation is dense, so DLC layer shows high hardness. By increasing deposition time, structure was denser and also hardness increased (“Fig. 5”)

SEM images show the thickness of layer plus the rate of growth, both of them increased by increasing time. (“Fig. 5”)

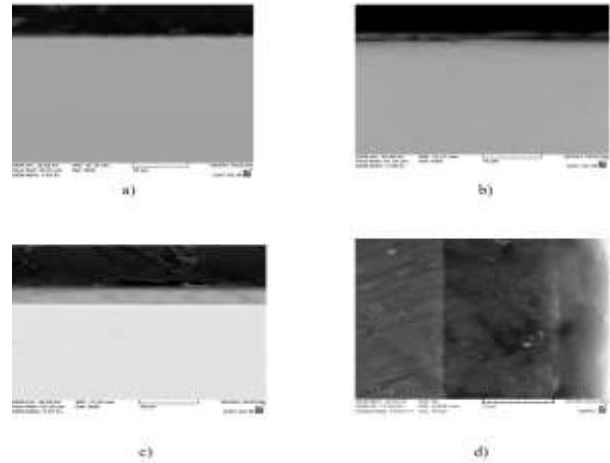


Fig. 5 SEM images of deposited DLC thin films for various time: (a): 60, (b): 120, (c): 150, and (d): 300 minutes.

To assess the mechanical properties of the DLC coating, microhardness measurements were done with a load of 50 g, and “Fig. 6” presents statistics of 4 measurements. The micro hardness of the substrate before and after nitriding is 440 HV0.05 and 960 HV0.05. It must be mentioned that the load is high enough to have both coating and substrate materials as interacting materials during indentation. Increase in deposition time produces a thicker coating. For a fixed indentation load, as the deposition time increases, contribution from coating towards measured hardness increases. This in turn leads to an increase in the hardness value. This clearly shows that coating is much harder than the substrate material.

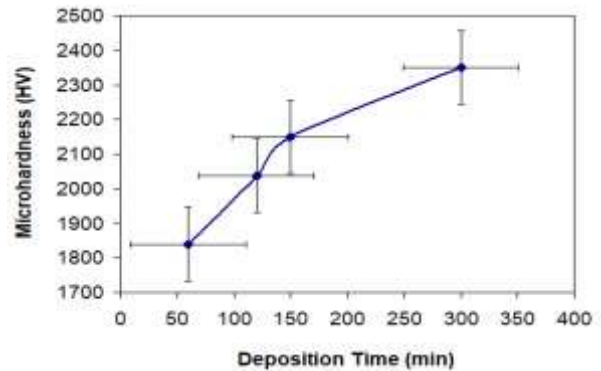


Fig. 6 Measured hardness values of the coating deposited for different durations.

#### 4 CONCLUSIONS

- DLC deposits were deposited on aluminum for different time durations. Very fine nuclei in the deposit were observed the form of islands.

- These results show that growth of DLC layer includes three stages. The first stage is primary growth of nuclei, and then these nuclei join together in second stage. In third stage, secondary growth of these nuclei happens.

- Compared to substrate material, deposit showed higher hardness and roughness.

- XRD plots show a single broad peak which indicates that the deposit is microcrystalline with preferred orientation (200). This orientation is dense, so DLC layer shows higher hardness than plasma nitriding and substrate. By increasing deposition time, structure was denser and also hardness increased.

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