MODIFICATION OF CVD DIAMOND COATING PROPERTIES THROUGH STRUCTURAL GRADIENT ENGINEERING

Alexander Gaydaychuk, Sergei Zenkin, Alexander Mitulinsky, Stepan Linnik
National Research Tomsk Polytechnic University, 30 Lenina Ave., 634050 Tomsk, Russia,
Gaydaychuk@tpu.ru, zen@tpu.ru, mitulinsky@tpu.ru, linniksa@tpu.ru

This study investigates gradient diamond coatings synthesized via hot-filament chemical vapor deposition (HFCVD) on Si and SiC substrates. The coatings exhibit a continuous structural transition from microcrystalline diamond (MCD) near the substrate to nanocrystalline or amorphous carbon phases at the surface. Dry sliding tribological tests against an aluminum alloy revealed that the gradient architecture strongly influences wear resistance, friction behavior, and aluminum adhesion. Raman spectroscopy confirmed the retention of structural gradients throughout the film thickness and demonstrated a clear correlation with tribological performance.

Keywords: gradient coatings; diamond; hot filament; friction; wear; structure; Raman spectroscopy.

Introduction

Diamond-based coatings are among the most effective solutions for machining non-ferrous metals, offering high hardness, low chemical reactivity, and excellent thermal conductivity. However, conventional homogeneous coatings-either monolithic microcrystalline (MCD) or nanocrystalline (NCD) diamond are often limited by residual stress, poor interfacial toughness, and abrupt structural transitions that promote crack formation under cyclic loading conditions.

To address these limitations, multilayered and gradient diamond architectures have been developed. Multilayer coatings incorporate alternating MCD/NCD or NCD/DLC layers to improve stress relaxation and arrest crack propagation. These coatings have demonstrated improved flank wear resistance and moderate resistance to aluminum adhesion.

Gradient diamond coatings represent a more recent and promising approach. These films feature a continuous transition in grain size, phase composition, and sp^3/sp^2 bonding from the substrate interface to the surface, eliminating internal interfaces and enabling smoother stress distribution. Experimental evidence suggests that such gradient structures enhance resistance to thermal fatigue, minimize interfacial delamination, and reduce friction in aluminum contact conditions, especially under elevated temperature and stop-start loading [1].

This study aims to evaluate the functional performance of three gradient diamond coatings with varying microcrystalline zone thicknesses under dry sliding contact with aluminum alloy.

Results and discussions

Gradient diamond coatings were synthesized in a custom-designed hot-filament chemical vapor deposition (HFCVD) reactor.

The deposition process employed a CH_4–H_2 gas mixture with a fixed hydrogen flow of 200 mL/min and a constant pressure of 20 Torr, regulated by throttle-controlled pumping. Tungsten filaments operated at 2200 °C and were positioned 10 mm above the substrates. The total deposition time was 8 hours, divided into 48 intervals of 10 minutes. During each interval, the methane flow rate was increased linearly by 0.6 mL/min, resulting in a total increment of 28.8 mL/min over the entire process. Initial methane flow rates were adjusted per sample to control the microcrystalline base layer thickness:

G4: 4.0 → 32.8 mL/min (≈5 µm MCD base)

G8: 8.0 → 36.8 mL/min (≈1 µm MCD base)

G12: 12.0 → 40.8 mL/min (≈0.5 µm MCD base)

The choice of flow rate ramp and 10-minute time intervals was guided by the reactor's gas exchange dynamics. The gas refresh time in the chamber was estimated at ~38 minutes, meaning the system exhibits a relatively slow filtration response. Based on this, the maximum safe rate of methane change without creating abrupt composition jumps was calculated to be approximately 0.74 mL/min^2. The implemented linear ramp corresponds to an average rate of only ~0.058 mL/min^2—more than an order of magnitude below this limit. This ensured that the evolving gas composition remained well mixed and allowed the formation of a continuous structural gradient throughout the film.

As a result, the coatings exhibited a smooth transition from microcrystalline diamond (MCD) at the substrate interface to nanocrystalline diamond (NCD), ultrananocrystalline diamond (UNCD), or diamond-like carbon (DLC)-like top layers. The total film thickness was ~7 µm in all samples. Coating structure and phase composition were confirmed via SEM cross-sectional imaging (Fig.1) and Raman spectroscopy.

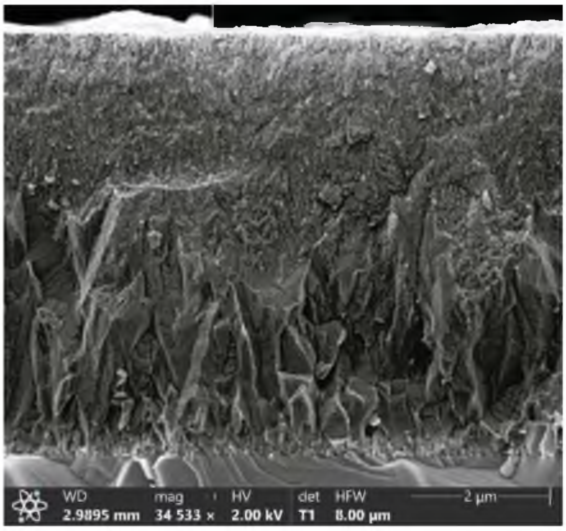

Fig. 1. SEM image of the cross section of sample G4

The Raman analysis of samples G4, G8, and G12 demonstrates a clear structural evolution from more ordered, diamond-rich coatings to increasingly disordered, sp^2-dominated films. Sample G4 exhibits the highest sp^3 content (36.9%) and lowest grain boundary polymer signal (*ItPA/IG* = 0.53), consistent with nanocrystalline diamond. In contrast, G12 shows significant degradation of diamond quality, with reduced sp^3 fraction (23.5%) and enhanced disorder (*ID/IG* = 0.68) and polymeric boundary content (*ItPA/IG* = 1.11). These trends confirm that increasing methane concentration during growth promotes sp^2 phase formation and grain boundary proliferation, shifting the material from NCD to ultrananocrystalline/amorphous-like regimes.

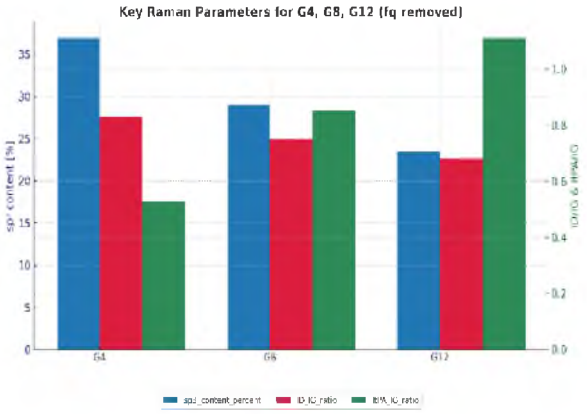

Fig. 2. Comparative data of Raman spectra of samples

Tribology testing protocols were tailored to the architecture of each gradient coating by applying multiple loads and sliding speeds per sample, enabling targeted activation of different sublayers (surface, transition, MCD zone).

Each load condition was tested in 5 repeated 30-second friction cycles with 30-second pauses between them, emulating the stop–start loading typical in interrupted machining.

Before the main tribological test cycles, all coated specimens were subjected to a low-load run-in procedure at 2 N and 0.2 m/s sliding speed. The process continued until the coefficient of friction stabilized within ±5% for at least 30 seconds, or until a total sliding distance of 50 m was reached. This step was implemented to eliminate transient effects related to surface adjustment and ensure that measurements reflect steady-state behavior.

Tribological performance correlated strongly with these structural characteristics. The G4 coating demonstrated superior wear resistance and stable friction properties, making it suitable for high-load applications. However, its harder surface showed moderate aluminum adhesion. The G12 coating, while less wear-resistant, provided the lowest aluminum adhesion due to its graphitic top layer, which acted as a solid lubricant. The G8 coating displayed intermediate properties, with variable friction behavior that depended on the specific loading conditions.

These findings align with existing literature on gradient diamond coatings. The superior performance of G4 confirms previous observations that higher sp^3 content improves wear resistance [2]. The reduced aluminum adhesion in G12 supports recent findings about the lubricating effects of graphitic surface layers [3]. The intermediate behavior of G8 suggests that optimal coating performance may require careful balancing of structural gradient parameters.

Conclusion

This study demonstrates that structural gradients in CVD diamond coatings strongly influence their functional behavior, as confirmed by Raman spectroscopy and theoretical tribological performance predictions. A higher sp^3-phase content and lower trans-polyacetylene signal were associated with improved mechanical stability, lower friction, and reduced wear under elevated loads. Among the tested samples, G4 showed the most favorable combination of structural and tribological properties, while G12, with higher sp^2 content and grain boundary density, was predicted to exhibit reduced wear resistance but potentially lower aluminum adhesion. These results highlight the importance of controlled methane modulation during deposition for tailoring coating performance to specific applications.

References

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