

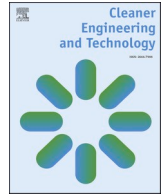
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Clean and durable thick nanodiamond composite hard coating deposited on cemented carbide towards sustainable machining: Eco-friendly fabrication, characterization, and 3-E analysis

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ABSTRACT

This research explores a sustainable approach for fabricating high-performance nanodiamond composite (NDC) hard coatings for dry machining. Aiming to address limitations in conventional coatings, such as environmental concerns, restricted film thickness, and compromised performance. The study utilizes Coaxial Arc Plasma Deposition (CAPD), a clean and efficient technique, to deposit thick (10 μm) NDC films directly on WC–Co substrates without chemical etching. Compared to traditional Chemical Vapor Deposition (CVD), CAPD offers significant advantages: lower temperature deposition, faster growth rate, and precise control over film thickness and morphology. The resulting NDC films boast exceptional durability due to their unique nanostructure, diamond nanocrystallites embedded in an amorphous carbon matrix. The addition of Al-interlayers (100–500 nm thickness) optimizes film properties. The optimal interlayer at 100 nm thickness not only mitigates the catalytic effects of Co but also enhances film hardness (50.4–58 GPa), Young's modulus (516–613.75 GPa), and adhesion (13–18.5 N) compared to films without an interlayer. Notably, the 100 nm Al-interlayer triples the deposition rate to 3.3 $\mu\text{m}/\text{h}$, achieving the desired thickness for effective hard coatings. The high density of grain boundaries within the films allows for exceptional stress release, enabling this increased thickness. Furthermore, these grain boundaries and the graphitic phase contribute to the film's superior tribological performance – a low coefficient of friction (0.1) and minimal wear rate ($1.5 \times 10^{-7} \text{ mm}^3/\text{N}\cdot\text{m}$) under dry machining conditions. These findings demonstrate the immense potential of CAPD-deposited NDC films as a sustainable alternative for advanced cutting tools, promoting environmental responsibility, economic viability, and energy efficiency.

1. Introduction

The manufacturing industry is undergoing a major transformation driven by environmental concerns, worker well-being, and economic efficiency (Jawahir et al., 2020; Yan et al., 2024). This shift towards sustainable machining practices prioritizes minimizing environmental impact without hindering technological progress (Shokrani et al., 2024). A key aspect of this shift is reducing resource consumption and minimizing environmental impact, especially within resource-intensive machining processes.

There are two main areas of focus for improving machining: increasing productivity and product quality through better tools and processes and adopting environmentally friendly approaches. Moving beyond basic “Reduce, Reuse, Recycle” principles, the industry is embracing a comprehensive “Reduce, Reuse, Recover, Redesign, Remanufacture, Recycle” framework (Jayal et al., 2010). This approach emphasizes technological advancements that decrease resource usage, worker health risks, and environmental footprint, while also promoting improved product development.

Evaluating the sustainability of machining practices involves a “3-E

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analysis" considering energy consumption, economics, and environmental impact. Numerous studies highlight the significant cost of cutting fluids, which can account for up to 15 % of a production workshop's total expenses (Astakhov, 2008). Reaching true sustainability in machining goes beyond just energy usage; it requires addressing waste generation and mitigating environmental pollution throughout the entire production process (Shokrani et al., 2024). This approach extends beyond machinery and processes to include the vital role played by cutting tools. Cemented carbide (WC–Co) tools excel in machining challenging materials, but for optimal performance, they often require wear-resistant coatings with specific properties. These properties include high hardness, a coefficient of friction less than 0.1, superior oxidation resistance, a wear rate lower than 10^{-6} mm³/N·m, and compatibility with self-lubrication or minimal quantity lubrication (MQL) (Yamamoto et al., 2018). As the industry seeks to improve cost-effectiveness and productivity, there's a growing need for longer-lasting cutting tools (Kumar et al., 2022). This necessitates advancements in hard coating technology, which often relies on physical and chemical vapor deposition (PVD, CVD) techniques for machining applications.

Diamond and related forms of hard carbon are highly desirable for protective hard coatings due to their exceptional thermal conductivity, extreme hardness, and excellent wear resistance. However, directly depositing diamond films onto WC–Co cutting tools often leads to weak adhesion between the coating and the tool. This is primarily caused by the Co atoms in the tool promoting the formation of graphite at the interface (Li and Hirose, 2007b). Additionally, the difference in thermal expansion coefficient mismatch between diamond film and the WC–Co tool can lead to cracks and the coating peeling off during the deposition process (Li et al., 2010).

To improve adhesion, usually addresses the catalytic effect of the Co atoms in WC–Co by pretreating the surface of the tool (Sahoo and Chattopadhyay, 2002). This pretreatment can involve chemical etching, adding an intermediate layer between the tool and the coating, or a combination of both (Endler et al., 1996; Li et al., 2008; Polini et al., 2006). However, chemical etching weakens the WC–Co tool itself, and overly aggressive etching can cause the tool to warp, which reduces its lifespan and weakens the adhesion of the coating (Sahoo and Chattopadhyay, 2002; Ye et al., 2016). Furthermore, the chemicals used for etching pose health risks to workers and environmental concerns.

An alternative approach to improve adhesion is to use an interlayer material that blocks the diffusion of Co from the tool into the coating and suppresses the catalytic effects at the interface. This interlayer helps the coating adhere to the tool while preserving the tool's mechanical properties (Endler et al., 1996; Raghuveer et al., 2002). Researchers have explored various materials for interlayers, including titanium, molybdenum, chromium, silicon, tantalum, and tungsten (Peng et al., 2020). The ideal interlayer material needs to suppress Co diffusion from substrate in to the film, and it should also have a thermal expansion coefficient that falls between those of diamond and WC–Co to minimize residual stress in the coating (Raghuveer et al., 2002). Among these options, aluminum (Al) stands out due to its affordability and widespread availability (Li and Hirose, 2007a, 2007b). Studies have shown that using Al interlayers significantly improves the adhesion of diamond coatings to WC–Co substrates (Li et al., 2009; Tang et al., 2010).

As an alternative coating, tetrahedral amorphous carbon (ta-C) materials boast comparable hardness, lower friction coefficients, and environmental compatibility, especially due to their suitability for PVD methods at low temperatures and in a vacuum. However, ta-C films are limited by their high internal stress (~9.2 GPa), which restricts film thickness to less than 1 µm and creates adhesion challenges (Murasawa et al., 2024b; Zhang et al., 2005).

To overcome these limitations and combine the benefits of diamond's high hardness and thick films with the cost-effectiveness and smooth surface of ta-C, nanodiamond composite (NDC) films emerge as a promising solution. NDC films are nanostructured carbon materials

composed of small (less than 10 nm) diamond crystals embedded within an amorphous carbon matrix (Ali et al., 2020a; Naragino et al., 2015). Deposited using the sustainable CAPD (coaxial arc plasma deposition) technique in a vacuum atmosphere on unheated WC–Co substrates, NDC films eliminate the need for chemical etching of the cobalt (Diab et al., 2024a; Egiza et al., 2024b). CAPD generates a highly energetic ionized carbon species, resulting in films with a high content of the desirable C sp³ bonding configuration and a low internal stress less than 4.5 GPa (Naragino et al., 2016b).

Researchers have explored various methods to improve the performance of NDC films, including doping with silicon (Diab et al., 2024b), boron (Egiza et al., 2023b), chromium (Egiza et al., 2016), incorporating carbon-based buffer layers (Ali et al., 2020b; Egiza et al., 2023a), and applying biasing voltage on the WC–Co substrate (Ali et al., 2019). However, undoped NDC films grown without chemical etching typically exhibit suboptimal adhesion (critical load of $L_{cr} = 13$ N), hardness of around 50 GPa, and a deposition rate of only 1 µm/h (Naragino et al., 2016a).

In this study, we aimed to address limitations in hard coatings for dry machining by depositing durable NDC films on WC–Co substrates using a clean CAPD process. This approach avoids external heating, chemical etching of the cobalt, and utilizes Al-interlayers of varying thicknesses (0, 100, 300, and 500 nm) to mitigate the catalytic effects of cobalt. Our research objectives were to evaluate the influence of the Al-interlayer thickness, identify the optimal thickness, characterize the mechanical and structural properties of the films, assess adhesion strength, analyze tribological performance for dry machining, and employ a 3-E analysis to confirm the potential of NDC coatings as a sustainable solution.

2. Experimental methods

This study systematically explores the eco-friendly deposition of NDC hard coatings on unheated K-type WC–Co substrates for sustainable machining. The primary focus is on understanding the impact of sputtering varied Al-interlayer thicknesses (0.0, 100, 300, and 500 nm) on NDC film properties. Prior to deposition, the WC–Co substrates (tablet-shaped, 10 mm diameter, 5.5 mm thickness) were meticulously prepared for subsequent mechanical and structural analyses (Fig. 1a and

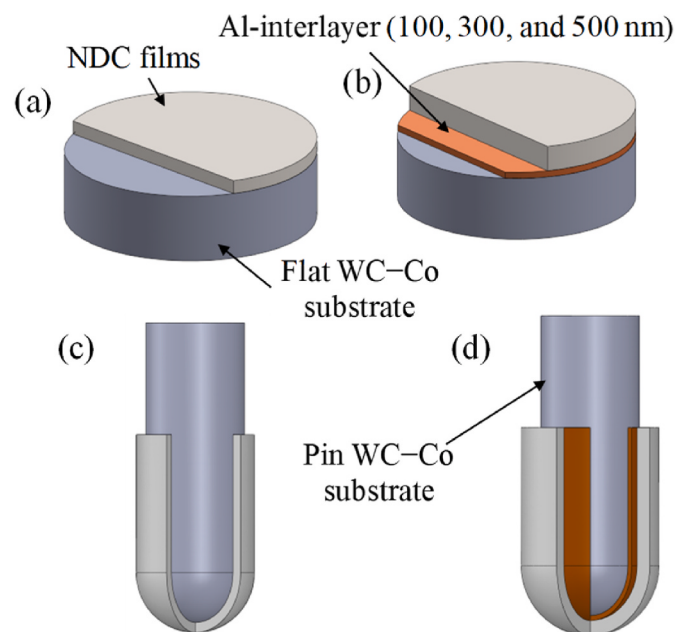


Fig. 1. Schematic representation of NDC films directly deposited on tablet and pin WC–Co substrate surfaces (a and c) and after inserting Al-interlayer (b and d) with thicknesses of 100, 300, and 500 nm.

b). Additionally, pin-shaped substrates (6 mm diameter) were designated for tribology tests (Fig. 1c and d). Two NDC film groups were fabricated, with Group 1 emphasizing growth rate and achieving maximum thickness in a single CAPD session, while Group 2 underwent controlled deposition for property analysis at approximately 10 μm thickness. Surface roughening and thorough cleaning were employed to enhance film adhesion. The NDC film deposition utilized CAPD with a graphite rod (99.99% purity, $\phi 10 \times 30$ mm) and a coaxial arc plasma gun (ULVAC, APG-1000, Japan) within a vacuum chamber. The arc plasma gun operated at a voltage of 100 V, repetition rate of 1 Hz, and with an arc discharge, maintaining the vacuum below 10^{-4} Pa.

Utilizing advanced characterization techniques, the study comprehensively analysed the composition, structure, and mechanical properties of NDC films. Energy-dispersive X-ray spectroscopy (EDX) coupled with scanning electron microscopy (SEM) unveiled the chemical composition and bonding, offering insights into bulk elemental composition through top-view, depth profiles, and cross-sectional mapping. Further chemical state examination near the film surface was achieved using X-ray photoemission spectroscopy (XPS) at BL12 of SAGA Light Source/Kyushu Synchrotron Light Source Center. Deconvolution of spectra at 350 eV incident photon energy precisely estimated the C sp^3 fraction.

The films' nanostructure was elucidated via visible Raman analysis using a Lambda Vision Raman spectroscopic system with a confocal microscope and a high-performance CCD detector, ensuring minimal thermal effects with laser power below 1.5 mW. Mechanical properties were evaluated through nanoindentation, blasting, and scratch tests. The hardness and Young's modulus of tablet samples were evaluated by nanoindentation with a Fisher Instruments HM500 nanoindenter at a load of 5 mN. Two methods assessed film adhesion: blasting with SiC particles 800# for fixed time (15 s) and scratch tests with a loaded diamond tip on 10 μm thick films.

Sustainable lubrication potential was explored through pin-on-disk tribometry under eco-friendly conditions (27 °C, 55% humidity). An Al_2O_3 counterpart material simulated difficult-to-cut materials, operating at a normal load of 2.94 N and a speed of 20 cm/s on a 120 m length wear track. Wear depth and volume were measured with an Olympus LEXT OLS 5000 3D measuring laser microscope, and optical images of wear tracks were observed to comprehend wear mechanisms under simulated machining conditions. 3-E analysis was conducted, encompassing energy consumption, cost-effectiveness, and environmental impact, providing a comprehensive assessment of NDC coatings in comparison with comparable hard coatings. This comprehensive assessment aimed to provide a detailed understanding of NDC film properties, contributing to advancements in sustainable coating technology.

3. Results and discussion

3.1. Morphological and topographical characteristics

This study successfully deposited nanodiamond composite (NDC) films on WC-Co substrates using an eco-friendly CAPD method in a vacuum atmosphere, eliminating the need for chemical etching and hazardous gases. The incorporation of a sputtered Al-interlayer (0, 100, 300, or 500 nm) replaced the traditional and harmful chemical etching with $\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2$, promoting worker safety and environmental sustainability. This approach also avoids detrimental effects on WC particle sub-surfaces, which can lead to associated coating failures such as films buckling (Inspektor et al., 1997; Xu et al., 2007).

SEM coupled with EDS analysis of films cross-sections (Fig. 2) revealed successful deposition of a uniform and dense “cauliflower-like” structure. This morphology consists of fine clusters of NDC film with a controlled thickness of 10 μm and no defects like droplets or pores.

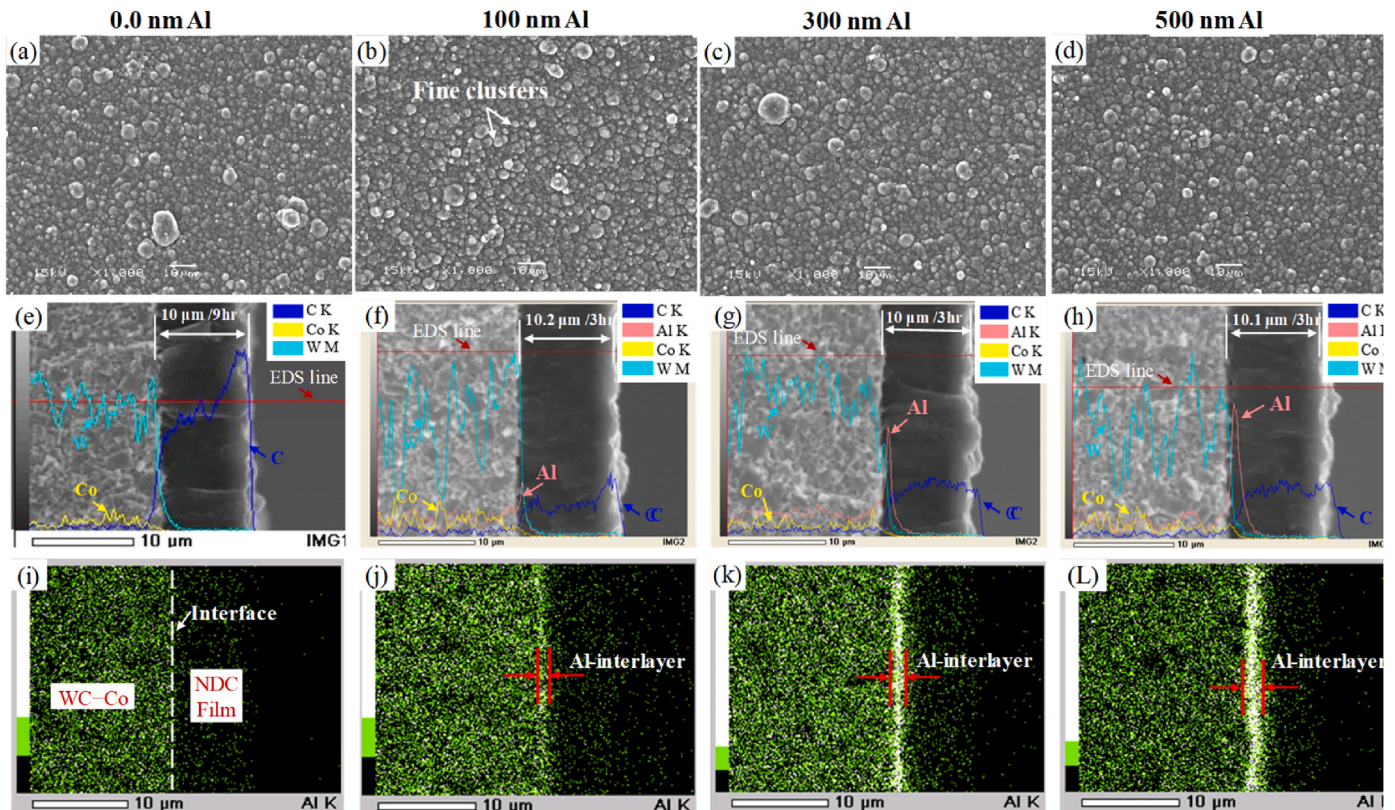


Fig. 2. (a–d) Top-view SEM images of NDC films, and (e–h) EDS depth profiles and (i–L) mapping illustrate the diffusion of the Al-interlayer sputtered with different thicknesses (0.0, 100, 300, and 500 nm) at the WC–Co substrate–NDC film interface.

Importantly, EDS flattened Co spectra confirmed that the Al-interlayer effectively blocked cobalt diffusion from the substrate into the film. This successful inhibition was further corroborated by EDS mapping, demonstrating the interlayer's ability to suppress the catalytic effects of cobalt, ultimately influencing the film's properties.

An interesting observation was the discrepancy between the thickness of sputtered Al-interlayer and its apparent thickness in the EDS monochrome mapping, where the Al element is highlighted in white and other elements appear in green (Fig. 2i–l). This difference is attributed to the rapid quenching caused by the CAPD process, which promotes the diffusion of Al atoms into the NDC film, forming an Al-carbide interfacial layer. While this phenomenon causes a thickness discrepancy, it offers a significant advantage: the Al-carbide layer enhances film adhesion to the WC–Co surface, crucial for long-term durability in machining applications.

Beyond improved adhesion, the Al-interlayer also tripled the deposition rate to 3.3 $\mu\text{m/h}$ compared to films deposited without an interlayer (1 $\mu\text{m/h}$). This substantial increase translates to significant cost benefits for large-scale industrial applications. The high surface energy and reactivity of the Al-interlayer likely contribute to this improvement. This altered surface chemistry may influence the adsorption of atoms and surface activity, potentially focusing the plasma plume and attracting more carbon ions, ultimately leading to the formation of a denser film rich in the desirable C sp^3 bonding configuration.

EDS confirmed the dominance of carbon in all NDC films, evident from the strong carbon peaks in the spectra (Fig. 3). This indicates a successful deposition process. The consistent weak cobalt signal across all films suggests minimal cobalt diffusion from the substrate and consistent elemental composition throughout the film thickness. Interestingly, only films with the Al-interlayer showed weak Al peaks, further supporting the effectiveness of the interlayer in blocking cobalt diffusion.

XPS surveys corroborated the robustness of the coatings. No peaks corresponding to substrate elements were detected, indicating a well-defined film without surface contamination. The strong presence of

carbon peaks (C 1s) and weak oxygen peaks (O 1s) are likely due to adsorbed oxygen on the film surface during or/and after deposition (Egiza et al., 2018). These analyses of morphology and composition reinforce the effectiveness of the CAPD method in producing high-quality NDC coatings.

The Al interlayer effectively hinders the formation of graphitic carbon at the interface, which arises from the catalytic effects of Co. This is achieved by shielding highly energetic carbon species from direct contact with Co atoms in the substrate. Prior research suggests that the Al interlayer readily undergoes oxidation during deposition, forming a dense aluminum oxide layer that acts as a robust diffusion barrier for Co (Li et al., 2014a, 2014b; Ye et al., 2016). This mechanism is supported by the presence of molten sputtered Al with enhanced mobility compared to its solid state. The molten Al reacts with oxygen to form a dense oxide layer, as observed in Fig. 4. EDS mapping confirms this by revealing high-intensity peaks for both oxygen and aluminum, indicative of an aluminum oxide layer responsible for Co suppression.

Furthermore, Al atoms may diffuse into the WC–Co substrate, leading to the formation of an Al–Co alloy at the interface (Park et al., 2014). This alloy helps to suppress the presence of free cobalt atoms, thereby limiting its catalytic effect on carbon. The establishment of an Al–Co metallic bond at the interface likely strengthens the interlocking adhesion between the Al-interlayer and the WC–Co substrate.

The surface topography of the NDC films is a combination of the WC–Co substrate's inherent features and the characteristic “cauliflower” growth pattern of the embedded diamond clusters. 3D laser confocal microscopy revealed that the WC–Co substrate consistently maintained a desired roughness of $R_a = 0.15\text{--}0.2\ \mu\text{m}$ (Fig. 5). Interestingly, the presence and thickness of the Al-interlayer significantly impacted the final surface roughness of the NDC films.

While the roughness remained relatively constant with increasing interlayer thickness (100–500 nm), it was consistently lower compared to the uncoated substrate. Notably, films deposited directly without an interlayer exhibited the highest roughness after deposition with an increase in R_a and R_z values of approximately $0.05\text{--}0.06\ \mu\text{m}$ compared to

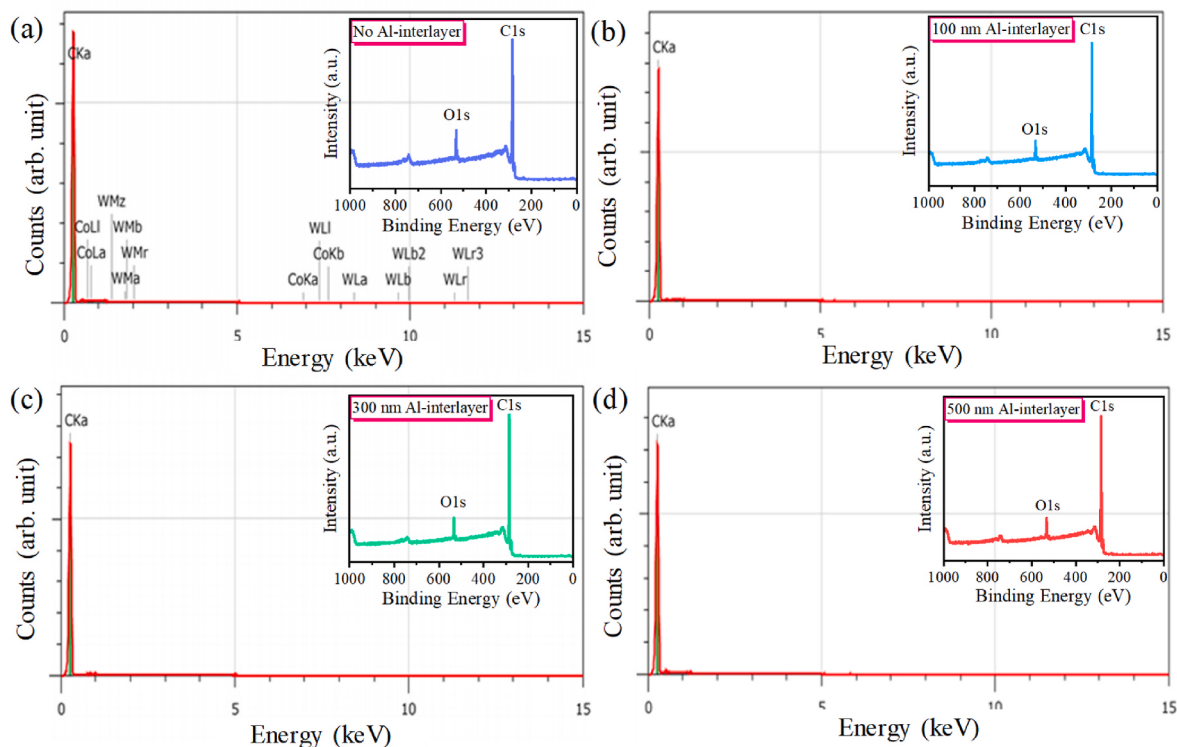


Fig. 3. Bulk and surface elemental composition investigated using top-view EDS and XPS-survey (onset) techniques on NDC films deposited with Al-interlayer at different thicknesses: (a) 0.0, (b) 100, (c) 300, and (d) 500 nm.

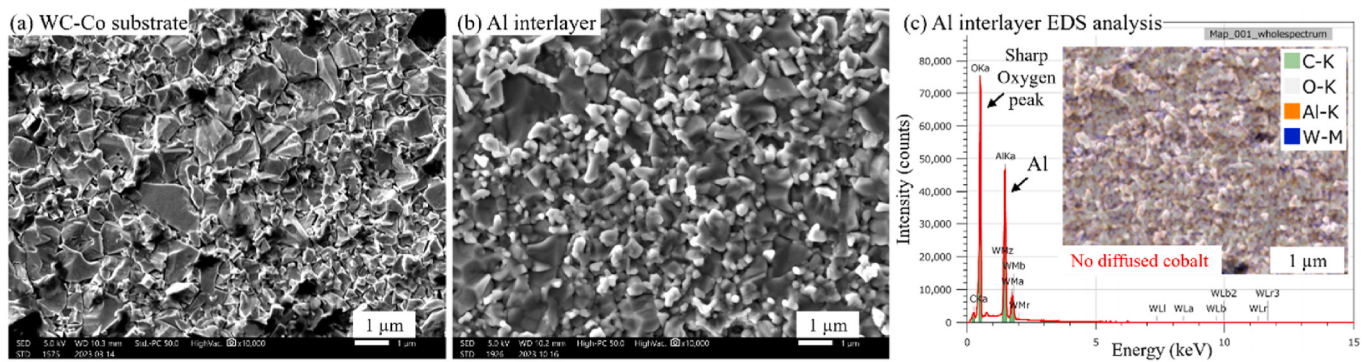


Fig. 4. Top-view SEM images on WC–Co substrate: (a) before deposition, (b) with Al-interlayer, and (c) Al/O EDS mapping showing Al and O peaks with no Co diffusion.

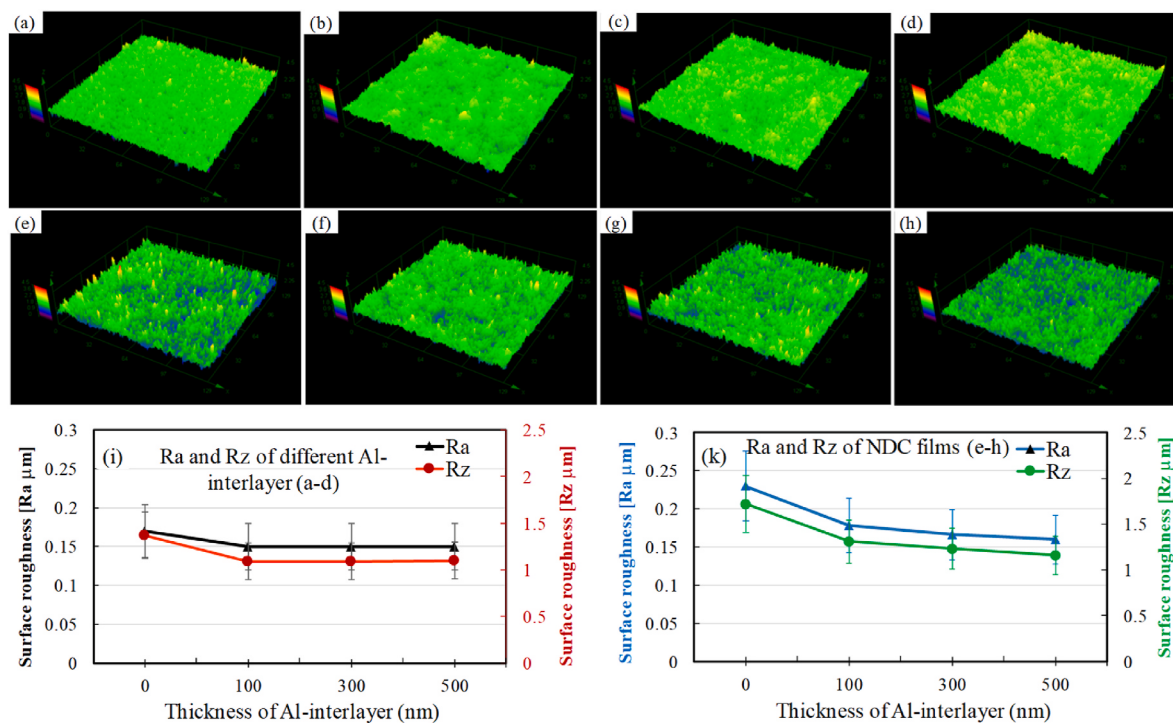


Fig. 5. 3D images of Al-interlayer surfaces at varying thicknesses (a) 0.0, (b) 100, (c) 300, and (d) 500 nm, along with their corresponding NDC films (e–h), and summarized surface roughness measurements (Ra and Rz) of (i) the various Al-interlayers, and (k) NDC films.

the substrate. Conversely, films with increasing interlayer thicknesses displayed a slightly higher roughness of Ra and Rz values at only 0.03–0.04 μm compared to their corresponding substrates, but ultimately resulted in a smoother surface compared to the films without the interlayer. This suggests that the Al-interlayer plays a crucial role in reducing the overall surface roughness, potentially due to the formation of the Al-carbide interfacial layer. It's important to note that despite the slight increase in roughness with interlayers, both NDC film groups (with and without) can be categorized as having a smooth surface, inheriting the initial substrate roughness and achieving a significant thickness (10 μm) compared to traditional diamond and hard DLC films, which are typically much thinner (Murasawa et al., 2024a; Salvadori et al., 2006).

3.2. Mechanical properties

The mechanical properties of the NDC films varied significantly based on the thickness of the incorporated Al-interlayer (Fig. 6). Load-

displacement curves (Fig. 6a) revealed a considerably larger area for the film with a 100 nm Al-interlayer, indicating a higher resistance to plastic deformation compared to films with other interlayer thicknesses. This suggests that the 100 nm Al-interlayer enhances the film's plasticity.

Furthermore, hardness (H) and Young's modulus (E) exhibited the same trend (Fig. 6b). Films with the 100 nm Al interlayer demonstrated the highest values, with a hardness of 58 GPa and a Young's modulus of 613 GPa. In comparison, films without an interlayer showed a hardness of 50.4 GPa and a Young's modulus of 516 GPa, while the WC–Co substrate itself had a hardness of 22 GPa and a Young's modulus of 527 GPa. This enhancement is attributed to the 100 nm Al interlayer's ability to suppress the negative catalytic effects of cobalt at the interface. Cobalt can promote the transformation of sp^3 bonds (diamond-like) in the carbon film (NDC) to sp^2 bonds (graphite-like), resulting in a softer material. The Al interlayer hinders this graphitization process by inhibiting direct contact between the NDC and the WC–Co substrate, thereby promoting the formation of a harder, more diamond-like film.

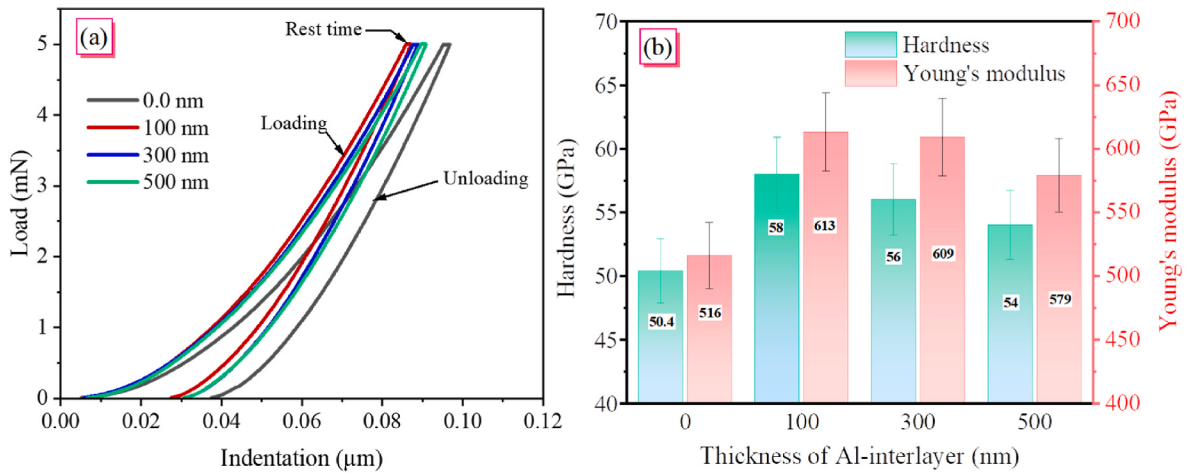


Fig. 6. (a) Nanoindentation average curves of NDC films with different Al-interlayer thicknesses (0.0, 100, 300, and 500 nm), and (b) corresponding hardness and Young's modulus.

This is further supported by the strong diamond peak observed in Raman spectroscopy (refer to sec. 3.3 for details).

However, increasing the thickness of Al-interlayer beyond 100 nm proved counterproductive. Thicker interlayers (300 nm and 500 nm) resulted in a decrease in both hardness and Young's modulus (down to 54 GPa and 52 GPa, respectively). This is likely due to excessive Al diffusion into the film, forming a thicker, softer interfacial layer rich in aluminium with increasing interlayer thickness.

To gain a deeper understanding of the mechanical behaviour, the

H^3/E^2 ratio was analysed. This ratio reflects the film's resistance to plastic deformation. The film with the 100 nm Al-interlayer displayed an 8.3% increase in the H^3/E^2 ratio (0.52 GPa) compared to the film without an interlayer (0.48 GPa). This signifies a significant improvement in resisting plastic deformation under external forces. Additionally, the plasticity index (H/E) and the brittle fracture resistance (H^3/E^2) exhibited an upward trend. This is potentially due to the confinement of the plasma plume during deposition caused by the presence of the Al-interlayer. A higher plasticity index suggests both elastic and plastic

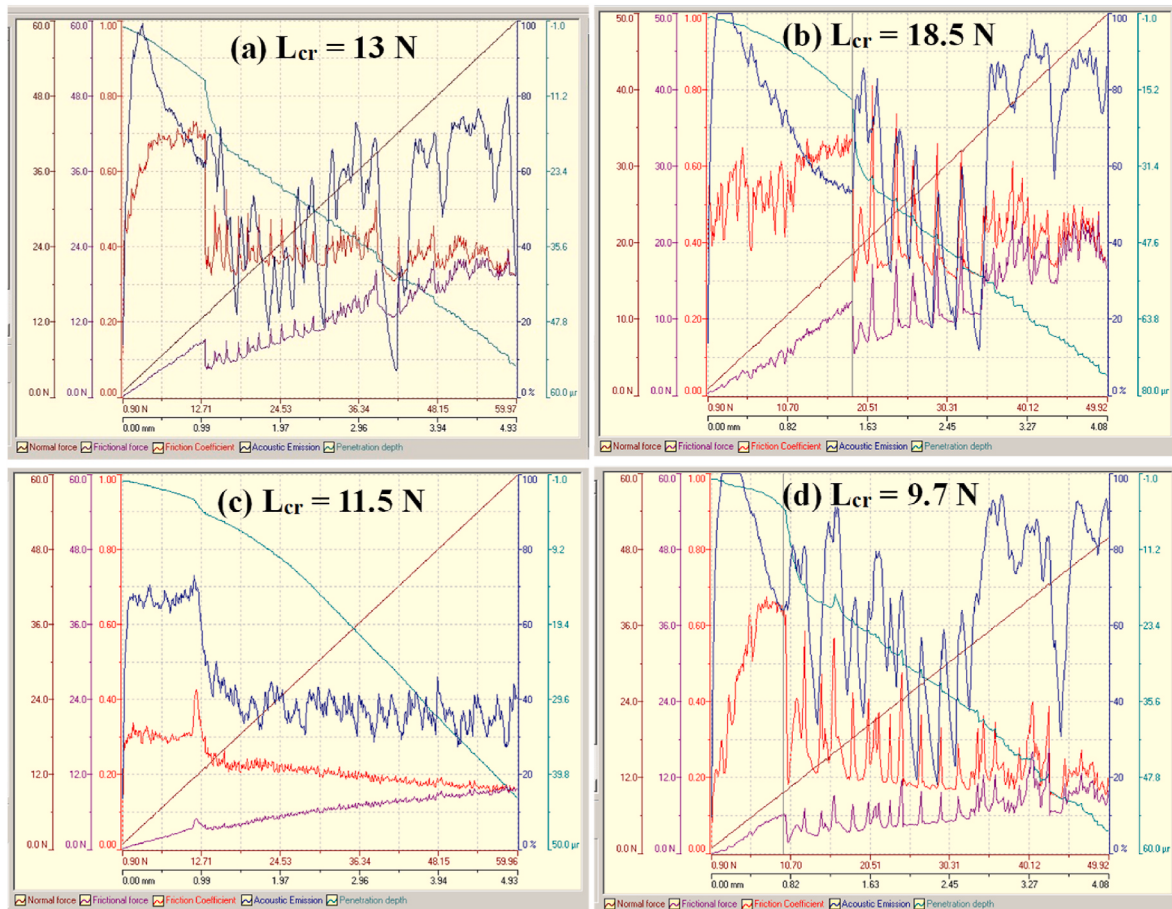


Fig. 7. Scratch test results of NDC films deposited with different Al-interlayer thicknesses: (a) 0.0, (b) 100, (c) 300, and (d) 500 nm.

characteristics, potentially contributing to wear resistance. Notably, the observed H/E ratio of the NDC film (0.095) was close to that of diamond ($H/E \approx 0.1$), indicating promising wear resistance characteristics.

The 100 nm thick Al-interlayer significantly improves the mechanical performance of NDC films by enhancing plasticity, hardness, and resistance to plastic deformation. The following section will delve into the film structure and wear resistance to provide a comprehensive understanding of their overall mechanical behaviour.

To comprehensively assess the mechanical durability of the NDC films, we employed scratch tests and abrasion blasting tests. The scratch tests were conducted on the NDC films deposited with varying Al-interlayer thicknesses (Fig. 7). The critical load, which indicates the force required to initiate film delamination, served as the key parameter.

Films deposited without an Al-interlayer exhibited a critical load of only 13 N. This value significantly increased to 18.5 N for films deposited on a 100 nm-thick Al-interlayer. This remarkable improvement highlights the effectiveness of the optimized 100 nm Al-interlayer in enhancing adhesion strength. Consequently, compared to films deposited with different interlayer thicknesses, the NDC films with the 100 nm interlayer demonstrate superior adhesion to the WC-Co substrate.

Understanding the mechanism behind the adhesion strength of NDC films is vital for their successful application. Examining the fracture spots with optical microscopy (Fig. 8) revealed the presence of Al remnants on the substrate surface after film delamination. This observation is further supported by EDS and SEM analysis of the interface.

The EDS spectra showed a more intense Al peak for the film deposited on a 500 nm Al-interlayer compared to the one deposited on a 100 nm interlayer. Similarly, SEM images confirmed the presence of more Al remnants on the substrate for the thicker interlayer. These findings suggest that with increasing Al-interlayer thickness, not all the Al reacts to form a beneficial Al-carbide interfacial layer.

This incomplete reaction likely leads to a layer of pure Al near the substrate, resulting in the weakest bonding (9.7 N) observed for films with 300 nm and 500 nm interlayers. Conversely, the weaker Al peak and fewer remnants observed for the 100 nm interlayer indicate a more complete reaction, leading to a stronger Al-carbide interfacial layer and superior adhesion strength (18.5 N).

Incorporating an Al-interlayer demonstrably improves adhesion by suppressing the negative catalytic effects of cobalt at the interface and

promoting the formation of a strong Al-carbide interfacial layer. This layer provides superior chemical bonding compared to conventional mechanical interlocking, leading to a significant increase in adhesion strength for films with the optimal 100 nm Al-interlayer thickness.

Abrasion blasting tests were conducted to further validate the effectiveness of the Al-interlayer in enhancing adhesion strength (Fig. 9). All samples were exposed to 800# SiC particles for a fixed duration of 15 s. The resulting wear spots and the critical blast time (time to film delamination) were analysed. A smaller wear spot and a longer critical blast time indicate stronger adhesion.

The film deposited with a 100 nm Al-interlayer displayed the most desirable outcome - the smallest wear area and a significant 13.8% increase in critical blast time (3.3 s) compared to the film without an interlayer. This improvement was even more pronounced (73.68%) compared to the film with a 500 nm Al-interlayer.

Two factors contribute to the superior performance of the 100 nm Al-interlayer film. First, the increased hardness observed for this interlayer thickness enhances erosion resistance, allowing the film to withstand particle bombardment for a longer duration. Second, as discussed previously (refer to Fig. 8), the 100 nm interlayer promotes the formation of a more complete Al-carbide interfacial layer, resulting in a stronger bond that resists delamination during the blasting test.

However, increasing the Al-interlayer thickness beyond 100 nm appears detrimental to erosion resistance. The weakened chemical bonding observed at the interface for thicker interlayers likely contributes to this effect. In these cases, delamination during the blast test may not be solely due to interfacial bond failure, but may also involve other factors related to the weakened interface.

3.3. Structural properties

Unveiling the nanostructure of the NDC films is critical to explain their improved characteristics. A combination of Raman spectroscopy and synchrotron-based XPS provides valuable data on composition and bonding, offering a comprehensive picture of the films' structure.

Raman spectra (Fig. 10) of NDC films with and without an Al-interlayer, compared to a CVD nanodiamond coating, all exhibit a distinct peak around 1332 cm^{-1} , confirming the presence of a diamond phase. Notably, the NDC film with a 100 nm Al-interlayer shows a more

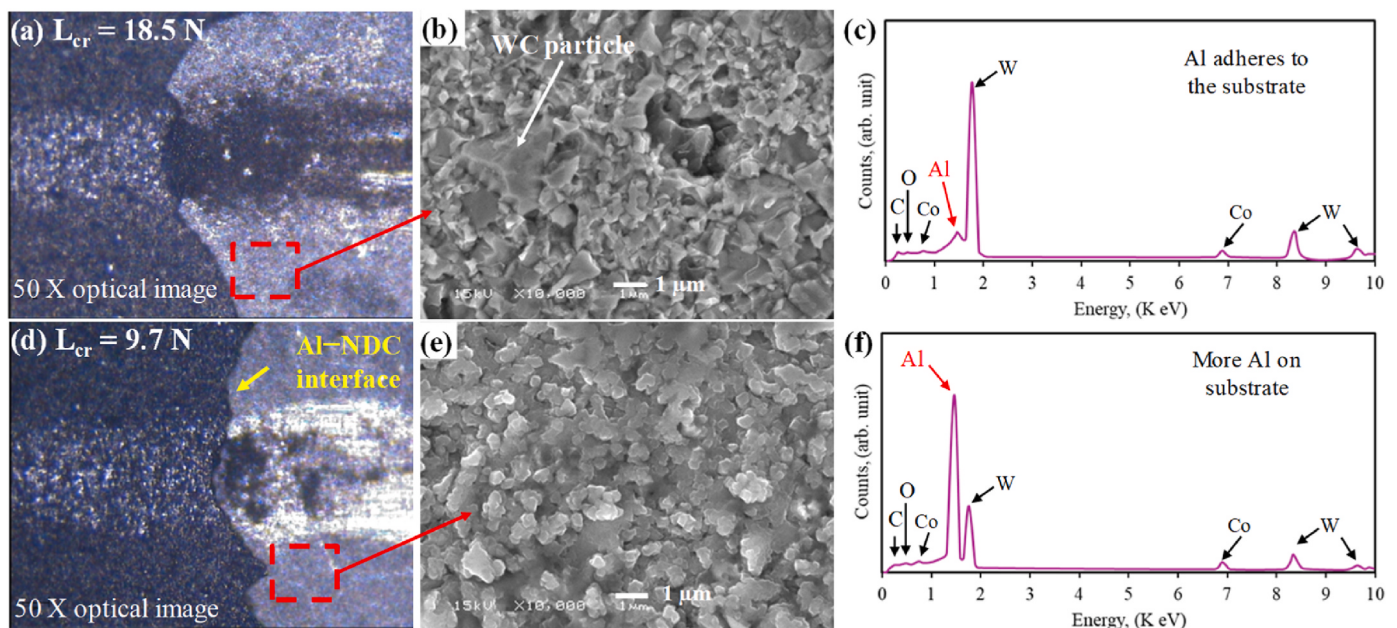


Fig. 8. Fracture optical images (a and d), SEM images (b and e), and top-view EDS spectra (c and f) of NDC films deposited with Al-interlayer thicknesses: (a, b, and c) 100 nm and (d, e, and f) 500 nm.

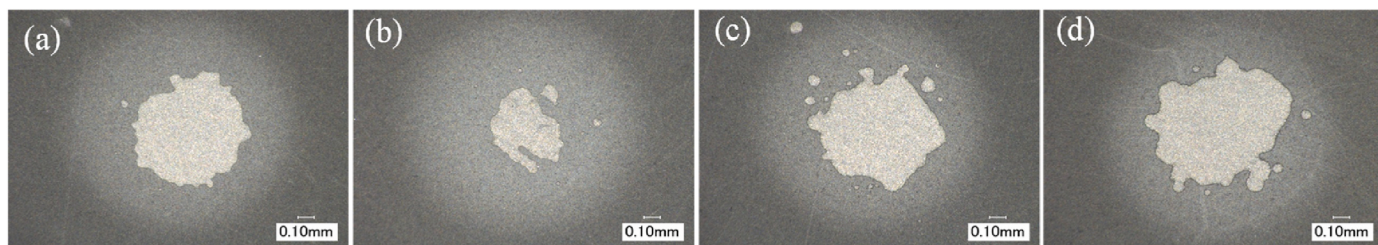


Fig. 9. Microscopic images of blasting spot measurements using SiC particles after 15 s exposure time on NDC films with various Al-interlayer thicknesses: (a) 0.0, (b) 100, (c) 300, and (d) 500 nm.

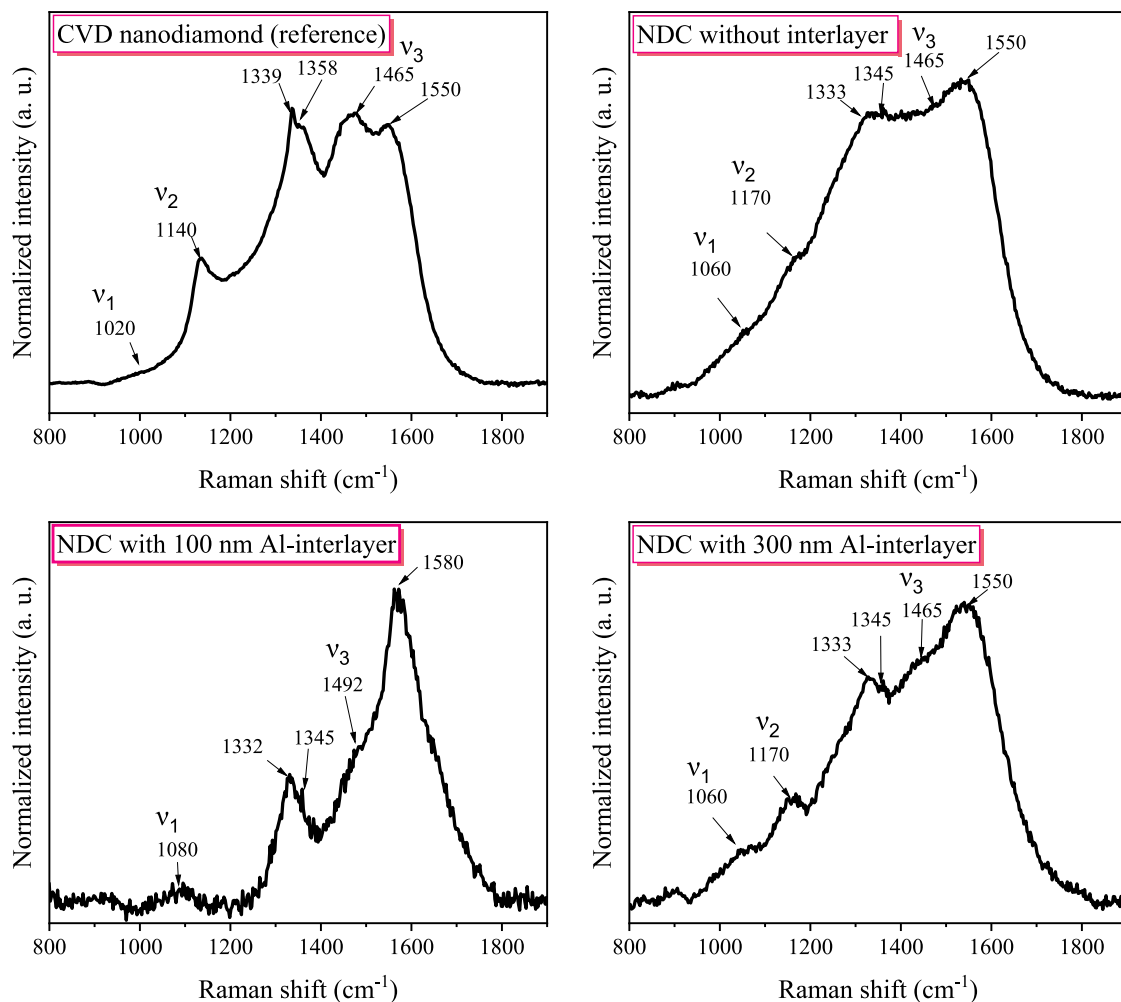


Fig. 10. Visible Raman analysis compares NDC films deposited with and without Al-interlayer to a reference single crystalline diamond.

intense diamond peak, which correlates well with its measured hardness. This suggests that the Al-interlayer effectively suppresses the negative catalytic effects of cobalt and improves the quality of NDC growth. Interestingly, the peak position for NDC films (1332 cm⁻¹) is slightly shifted lower compared to CVD diamond (1339 cm⁻¹), indicating a more relaxed state in the NDC films. This could potentially be attributed to the stress-relieving effect of the 100 nm Al-interlayer.

The overlap between the diamond peak and the D-peak (1345 cm⁻¹) suggests a nanostructure similar to CVD nanodiamond films, consisting of diamond nanocrystals embedded within an amorphous or graphitic carbon matrix. Additionally, the G-peak around 1580 cm⁻¹ signifies a dense tetrahedral amorphous carbon structure, which likely contributes

to the films' enhanced mechanical and tribological properties.

The Raman spectrum reveals three additional peaks (ν_1 , ν_2 , and ν_3) that are characteristic of the trans-polyacetylene (t-PA) phase. These peaks primarily correspond to the symmetrical stretching vibration of C=C bonds and potentially also involve C-H stretching vibrations. The presence of these t-PA peaks indicates the existence of numerous grain boundaries (GBs) within the films. This observation aligns with previous studies reported in (Pfeiffer et al., 2003; Shen et al., 2019). These GBs act as interfaces between the diamond nanocrystals and the amorphous carbon matrix, as well as within the diamond grains themselves. They play a crucial role in promoting diamond phase formation, act as stress relaxation sites, and potentially improve sliding properties and

self-lubrication, which aligns well with the goal of sustainable dry machining practices.

XPS analysis using synchrotron radiation was employed to elucidate the chemical bonding environment and quantitatively determine the C sp^3 content within the NDC films deposited with varying Al-interlayer thicknesses (0–500 nm).

Fig. 11 presents the high-resolution C 1s spectra deconvoluted into four distinct peaks, each corresponding to different chemical environments of carbon and oxygen atoms within the film. The peak at 284.5 eV signifies sp^2 -bonded carbon (C=C), indicative of graphitic or amorphous carbon structures. The second peak at 285.07 eV represents sp^3 -bonded carbon (C–C), a characteristic feature of the diamond phase (Egiza et al., 2019).

Two additional peaks were observed at higher binding energies. The peak at 286.57 eV is attributed to carbon-oxygen single bonds (C–O/C–O–C), potentially due to surface contamination. Similarly, the peak at 288.32 eV corresponds to carbon-oxygen double bonds (C=O/COOH), possibly arising from surface oxides. These shoulder peaks suggest potential oxygen adsorption on the film surface during or after deposition (Egiza et al., 2018).

Importantly, the estimated C sp^3 fraction ($C\ sp^3/(C\ sp^3 + C\ sp^2)$) exhibited a strong correlation with film hardness. The NDC film deposited with a 100 nm Al-interlayer displayed the highest C sp^3

fraction (72 %) and the highest hardness (58 GPa). This film also showed the most intense diamond peak in Raman analysis (refer to Fig. 10), demonstrating consistent results across various characterization techniques. This analysis underlines the crucial role of C sp^3 bonding in influencing film hardness.

3.4. Tribological properties

Traditional machining practices heavily rely on cutting fluids, raising environmental and health concerns (Goindi and Sarkar, 2017; Niketh and Samuel, 2017). These fluids often contain hazardous chemicals that can lead to dermatitis, skin infections, respiratory diseases, and even cancer with prolonged exposure. Sustainable manufacturing practices are crucial, and dry machining, eliminating the need for cutting fluids altogether, is a compelling solution.

The dry machining offers a sustainable alternative to traditional cutting fluids, but it presents challenges. Tools experience increased wear due to the absence of lubrication, requiring superior wear resistance to maintain performance. Additionally, minimizing friction between the tool and workpiece is crucial for efficient machining and energy consumption. Therefore, successful dry machining necessitates materials with both exceptional wear resistance and low friction coefficients (Westkämper and Alting, 2000).

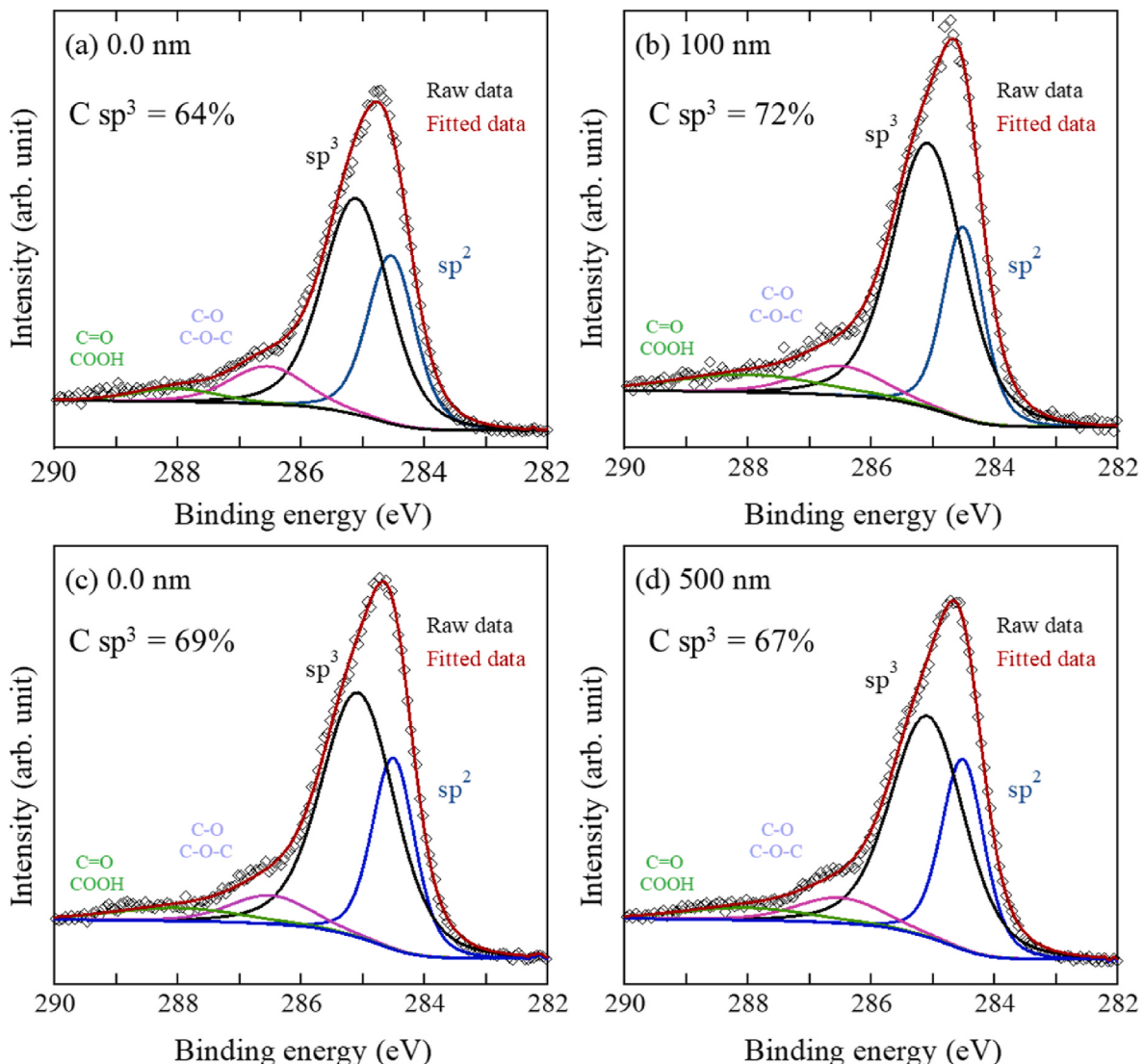


Fig. 11. C1s X-ray photoemission spectra of NDC films deposited on WC–Co substrates with different thicknesses of Al-interlayer.

NDC films, with their unique nanostructure and properties, are promising candidates for dry machining applications. These films combine nanodiamond grains embedded within an amorphous carbon matrix, offering a synergistic effect of enhanced hardness and toughness. The presence of nanodiamond grains contributes significantly to enhance the film's hardness (58 GPa) with a high C sp^3 fraction (72 %), crucial for resisting wear during machining. Furthermore, the numerous grain boundaries and amorphous carbon matrix enhance toughness through mechanisms like interface-induced microcracks and dislocation obstruction, preventing crack propagation and improving overall wear resistance.

Beyond hardness and toughness, NDC films exhibit exceptional tribological properties, making them well-suited for dry machining environments (Fig. 12). They achieve a remarkably low and stable friction coefficient of 0.1, comparable to other nanocrystalline diamond coatings with similar hardness (58 GPa) (Chen et al., 2017). The average coefficient of friction (COF) under dry sliding conditions was 0.1 for the NDC coating, compared to 0.31 for the uncoated substrate, demonstrating a significant friction reduction of 68 %. This outstanding performance can be attributed to several key mechanisms. (i) Smoothing of the contact interface: during the initial running-in stage, asperities on the contacting surfaces are worn down, leading to a smoother interface with reduced friction. (ii) tribo-layer formation: as machining progresses, a protective tribo-layer forms on the contact interface. This layer is formed through

surface passivation and the rehybridization of sp^3 -bonded carbon atoms in the film to sp^2 -bonded configurations. This sp^2 phase acts as a solid lubricant, further minimizing friction. (iii) solid lubrication: the rehybridized sp^2 phase within the tribo-layer acts as a solid lubricant, significantly reducing friction and facilitating smoother machining operations.

Wear resistance of the cutting tool material is a critical factor for successful dry machining. This section evaluates wear using a 3D laser confocal microscope, and the results in Figs. 13 and 14 clearly demonstrate the superior performance of the NDC film with a 100 nm Al-interlayer.

This film exhibited the lowest wear volume ($54,000 \mu m^3$, wear rate $= 1.5 \times 10^{-7} mm^3/(N.m)$), a smaller wear area, and a shallower wear depth ($2 \mu m$) compared to the film without an interlayer ($2.4 \mu m$). Additionally, analysis of the wear track on the alumina (Al_2O_3) counterpart material revealed minimal transferred film material and a narrower track width for the film with the 100 nm Al-interlayer. This suggests significantly reduced material transfer during the wear test.

These results align perfectly with the dry machining criteria of a coefficient of friction (COF) ≤ 0.1 and a wear rate $\leq 10^{-6} mm^3/(N.m)$ (Westkämper and Alting, 2000). Minimizing friction not only reduces heat generation but also helps prevent tool wear and thermal softening of the workpiece. This translates to better dimensional accuracy, improved surface integrity of machined parts, and cost-effectiveness

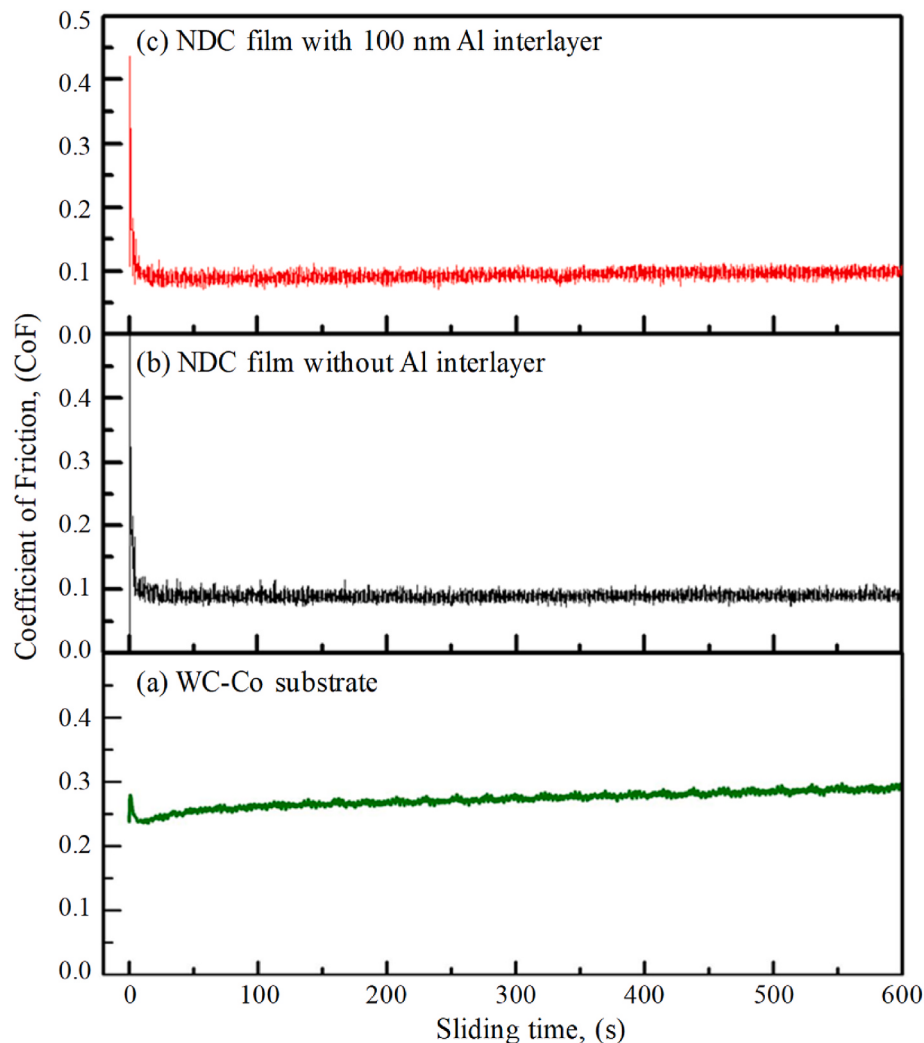


Fig. 12. Friction curves of (a) WC-Co, (b) NDC films without Al-interlayer, and (c) NDC films with 100 nm Al-interlayer, against Al_2O_3 counterpart without lubrication at room temperature.

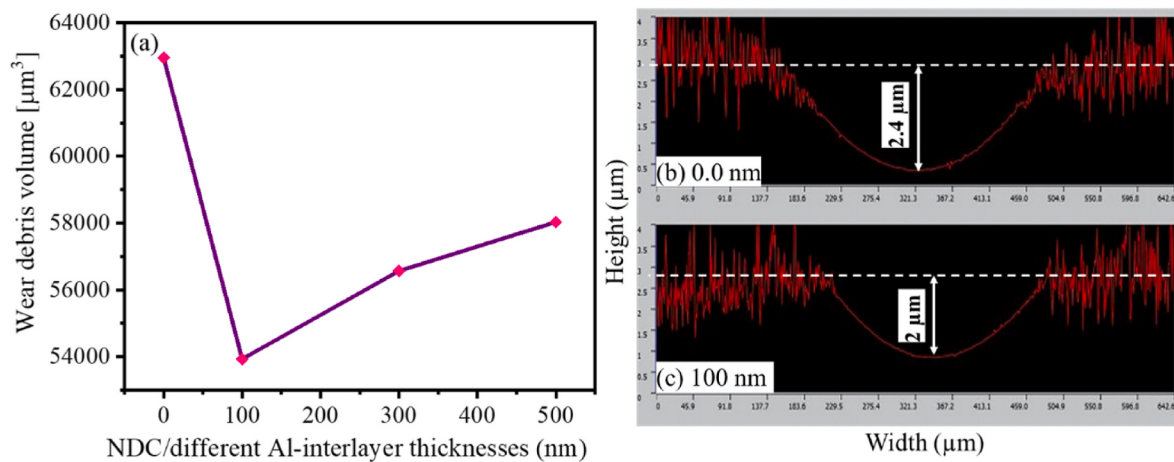


Fig. 13. (a) Wear debris volume of NDC films and corresponding resulting wear depth of films deposited (b) without and (c) with a 100 nm Al-interlayer.

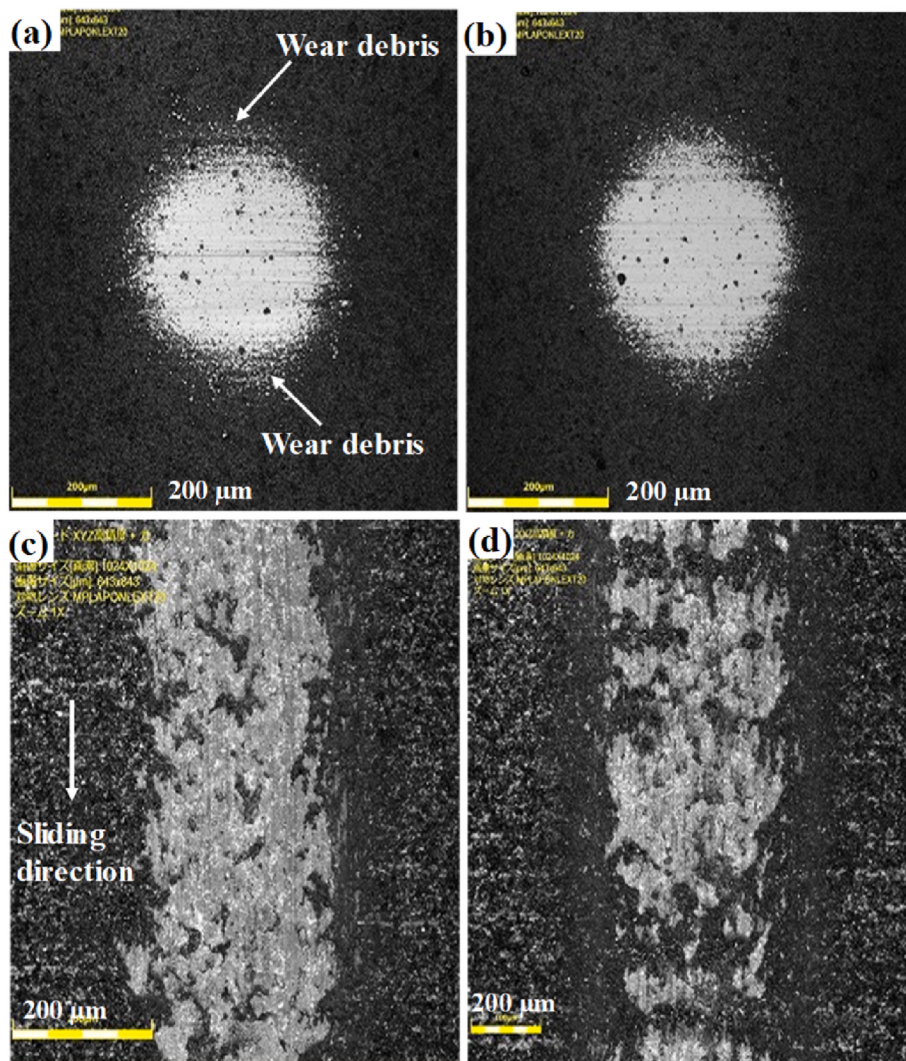


Fig. 14. (a and b) Worn areas and (c and d) wear tracks of the NDC films deposited (a and c) without and (b and d) with a 100 nm Al-interlayer.

through extended tool life and precision machining.

The calculated debris volume also aligns with the wear depth, area, and track width measurements, further reinforcing the superior wear resistance of the NDC film with the 100 nm Al-interlayer. The

combination of the Al-interlayer and the resulting enhanced film hardness synergistically minimize wear and material transfer during dry machining.

This comprehensive low COF and wear resistance assessment

consistently highlight the NDC film with a 100 nm Al-interlayer as a highly promising candidate for sustainable and efficient dry machining processes. These films offer the potential for enhanced tool durability, reduced environmental impact, and cost savings in manufacturing.

4. 3-E analyses of sustainable NDC coatings

4.1. Energy consumption

This section explores the energy consumption and sustainability

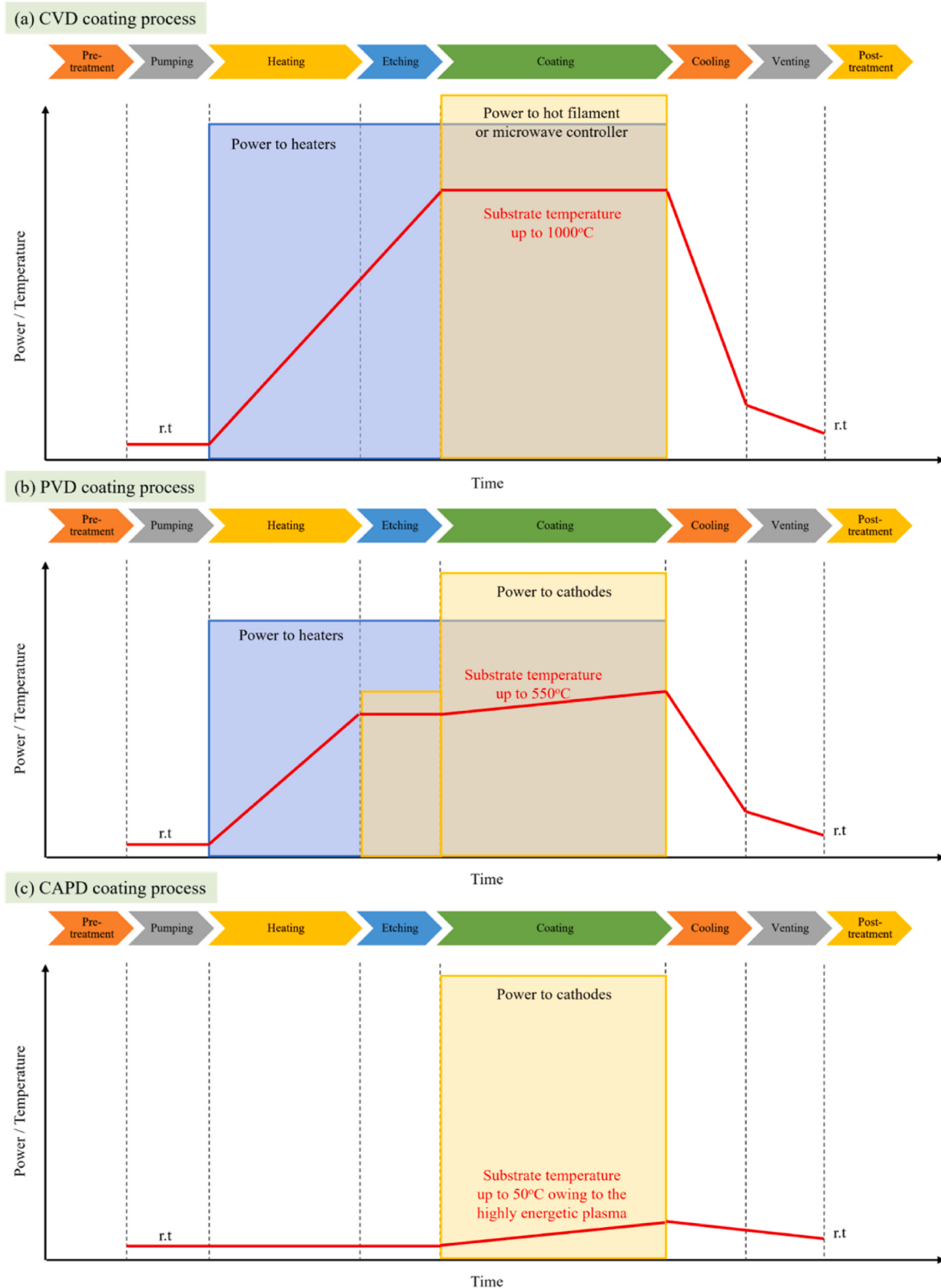


Fig. 15. Schematic illustration of the energy consumption during typical CVD (a), PVD (b), and CAPD (c) coating process.

benefits associated with the CAPD technique for producing NDC coatings. Fig. 15 provides a schematic comparison of the CAPD process with other deposition techniques like Chemical Vapor Deposition (CVD), Magnetron Sputtering Deposition (MSD), and Cathodic Arc Evaporation (CAE) (Greczynski et al., 2023; Greene, 2017). It highlights the key features of CAPD that contribute to lower energy consumption.

Firstly, CAPD ensures a clean deposition environment by achieving a high base vacuum pressure ($<10^{-4}$ Pa) through efficient pumping. This minimizes contaminants such as water vapor from humid environment in the deposited coatings, leading to sub-atomic percent levels. This clean environment translates to lower energy requirements during the deposition process.

Secondly, the CAPD technique fabricates NDC coatings at room temperature, eliminating the need for external heating typically required in other methods (Egiza et al., 2024a). This allows highly energetic ions to bombard the substrate surface, promoting dense and adherent film growth, particularly beneficial for cutting tool applications.

Thirdly, CAPD utilizes a high voltage on the arc plasma gun to generate highly energetic carbon species like C^+ , C^{++} , C_2 dimers, and C atoms. This facilitates an ultra-fast quenching process under supersaturated conditions, promoting efficient film growth (Naragino et al., 2015). The CAPD approach offers versatility in terms of substrate compatibility, allowing deposition on various materials like polymers, tempered steel, or lightweight Al-Mg alloys with optimized deposition parameters.

Furthermore, CAPD offers a sustainable advantage by eliminating the need for chemical etching of cobalt, which is a crucial step for adhesion in traditional methods. Over-etching with H_2SO_4/H_2O_2 solutions can weaken the WC-Co substrate bond, leading to premature coating failure (Inspektor et al., 1997). These chemicals also pose health and environmental risks and contribute to higher production costs (Sivarajan and Padmanabhan, 2014). The CAPD process deposits NDC coatings directly onto WC-Co substrates, avoiding cobalt chemical pretreatments or in-situ etching steps altogether.

Finally, CAPD boasts a high deposition rate (3.3 $\mu\text{m}/\text{h}$), significantly reducing fabrication time and costs. Combined with a substantial achievable thickness (10 μm) and superior tribo-mechanical characteristics compared to CVD diamond and ta-C films (Madhavi et al., 2022; Schalk et al., 2022), NDC coatings produced by CAPD represent a promising advancement in sustainable coating technology.

Table 1 provides a compelling energy consumption analysis comparing the CAPD technique with established methods like CVD, MSD, and CAE for fabricating thin films (Gassner et al., 2016). The table breaks down the energy contributions of individual process components like pumps, heaters, cathodes, and ventilation systems.

The CAPD process excels in energy efficiency. The cathodic arc gun

consumes the most energy within CAPD (77 %), translating to approximately 50.48 kWh. Other components like pumps (10.6 kWh), heating (0 kWh), etching (0 kWh), and cooling (1 kWh) contribute minimally.

In contrast, the CAE process consumes a total of 101 kWh, with roughly half (52 kWh) dedicated to the coating step. Heating and etching both contribute significantly (22 kWh and 20 kWh, respectively) in CAE, and their main energy consumption comes from heaters, with cooling requiring a minor 7 kWh.

The trend continues with MSD, consuming a total of 112 kWh with over three-quarters (87 kWh) used in the coating step. Within the coating step, cathodes are the primary energy consumer at 60 kWh, exceeding half the total deposition energy. Similar to CAPD, minor contributions come from heating (18 kWh), etching (6 kWh), and cooling (1 kWh).

The CVD process exhibits the highest overall energy consumption at a staggering 974 kWh. Nearly half (437 kWh) is used for heating, while one-third (326 kWh) goes towards the coating step. Furnaces and auxiliary heaters dominate energy consumption during both heating and coating, accounting for 394 kWh and 193 kWh, respectively. Ventilation, pumping, and auxiliary heaters used in the cooling step contribute the remaining 22% of the total energy for CVD.

Compared to CAPD, CVD, MSD, and CAE techniques consume 1830 %, 122%, and 100 % more energy, respectively. These traditional methods also exhibit significantly longer process cycle times (increased by 510 %, 63.89 %, and 15%, respectively). It's important to note that despite these differences in energy consumption and processing times, all four techniques achieve a similar coating thickness of 10 μm (except for MSD at 2.9 μm and CAE at 2.5 μm).

This clearly demonstrates the significant energy efficiency advantages offered by the CAPD technique for producing thin films. CAPD achieves comparable coating thickness with substantially lower energy consumption and faster processing times compared to traditional methods.

4.2. Economic analysis

Economic considerations, including equipment costs, operating expenses, and overall cost-benefit analysis, are crucial when evaluating advanced surface engineering processes.

Plasma CVD, for instance, incurs a marginally higher water and electricity consumption (estimated at 20%) compared to traditional CVD methods. However, this increase represents less than 3% of the overall process turnover, making it a negligible factor. Similarly, all four deposition techniques (CAPD, CVD, MSD, and CAE) require comparable space and labour resources.

Equipment cost and batch size become more significant factors when comparing PVD and CVD techniques. The relative simplicity of the

Table 1

Energy analysis for CAPD technique in comparison with CVD, MSD, and CAE technique (Gassner et al., 2016).

Case study	CVD	MSD	CAE	CAPD (our work)
Process cycle time	18 h 30 min	4 h 55 min	3 h 27 min	3 h
Coating material	TiCN/Al ₂ O ₃	TiN	TiCN	NDC
Substrate material	Cemented carbide	Cemented carbide	Cemented carbide	Cemented carbide
Material fluxes	N ₂ , CH ₄ , CO ₂ , H ₂ , and Al (in situ chlorinated)	Ar, N ₂ , and four rectangular Ti targets	Ar, C ₂ H ₂ , and N ₂	Pure graphite target
Deposition temperature	750–1150 °C	350–600 °C	200–600 °C	Room temperature
Layer thickness	2.5 μm + 7.5 μm	2.9 μm	2.5 μm	10 μm
Total energy consumption	974 kWh	112 kWh	101 kWh	50.48 kWh
Coating energy consumption	326 kWh	87 kWh	52 kWh	49.48 kWh (Arc 38.88 kWh and Pumping 10.6 kWh)
Heating energy consumption	437 kWh	18 kWh	22 kWh	–
Etching energy consumption	–	6 kWh	20 kWh	–
Cooling energy consumption	211 kWh	1 kWh	7 kWh	1 kWh
Total energy consumption rise, %	1830 %	122 %	100 %	–

plasma CVD hot-wall reactor compared to more sophisticated PVD equipment translates to a lower cost. Currently, a plasma CVD plant is estimated to be 60–80% less expensive than its PVD counterpart. While batch size is important, a direct comparison awaits further advancements in upscaling plasma CVD technology.

The CAPD technique offers distinct economic advantages. Firstly, its straightforward design (as shown in Fig. 16) translates to a significantly lower capital cost compared to other methods. The CAPD apparatus consists of just three main components: a pumping system with a cooling chiller (similar to MSD), a novel plasma arc gun, and a cylindrical chamber (common in both MSD and CAE).

Secondly, CAPD boasts exceptionally low running and maintenance costs, as detailed in Table 1. The elimination of external heaters, entry gases, and the affordability of the pure graphite target rod with 10 mm diameter compared to MSD targets all contribute to the cost-effectiveness of the CAPD technique. Additionally, CAPD emerges as an environmentally friendly alternative due to its reduced energy consumption.

4.3. Environmental impact

Sustainability is a growing concern due to climate change and resource limitations. Initiatives like the European Green Deal and Horizon Europe program highlight the importance of research and innovation in achieving the UN's Sustainable Development Goals (Griggs et al., 2013).

In manufacturing, environmental considerations often focus on lubricants and tool durability, impacting health, equipment wear, waste management, and worker safety (Bendig et al., 2023; Kumar et al., 2022). Replacing harmful lubricants in metal cutting not only minimizes environmental hazards and improves working conditions but also

streamlines cleaning processes in micro-manufacturing.

Traditional techniques like CVD have a significant environmental footprint compared to CAPD. CVD processes consume large quantities of chemical gases and utilize hazardous chemicals like sodium hydroxide solution and water, leading to high material waste (Greczynski et al., 2023; Greene, 2017). In contrast, CAPD offers a cleaner alternative. It eliminates the need for heating, hazardous chemicals, and cutting fluids throughout the entire process, from deposition to machining.

While PVD techniques have adopted target recycling practices, detaching hard coatings for reuse remains a challenge. Recycling coated carbide scraps often incurs additional costs and generates waste chemicals. Future strategies for recycling coated tools within a circular economy should prioritize alloy design and material architecture that facilitate easy detachability and recyclability. This approach, coupled with deposit return systems for used resources, is crucial for responsible development, production, and use of coated tools.

The CAPD technique stands out as a clean and dry method, free from hazardous materials and waste chemicals. This environmentally friendly approach, as illustrated in Figs. 15 and 16, and Table 1, positions CAPD as a preferred technique for meeting the technological requirements of a green transition in the manufacturing industry.

5. Conclusion

This study successfully deposited NDC films on unheated WC–Co substrates using the CAPD technique. CAPD offers a clean and sustainable fabrication approach by eliminating external heating, chemical etching, and hazardous gas introduction during film growth. To address potential Co catalytic effects at the interface, the study investigates Al-interlayers of varying thicknesses (0, 100, 300, and 500 nm) sputtered onto substrates before NDC deposition. A comprehensive analysis of the

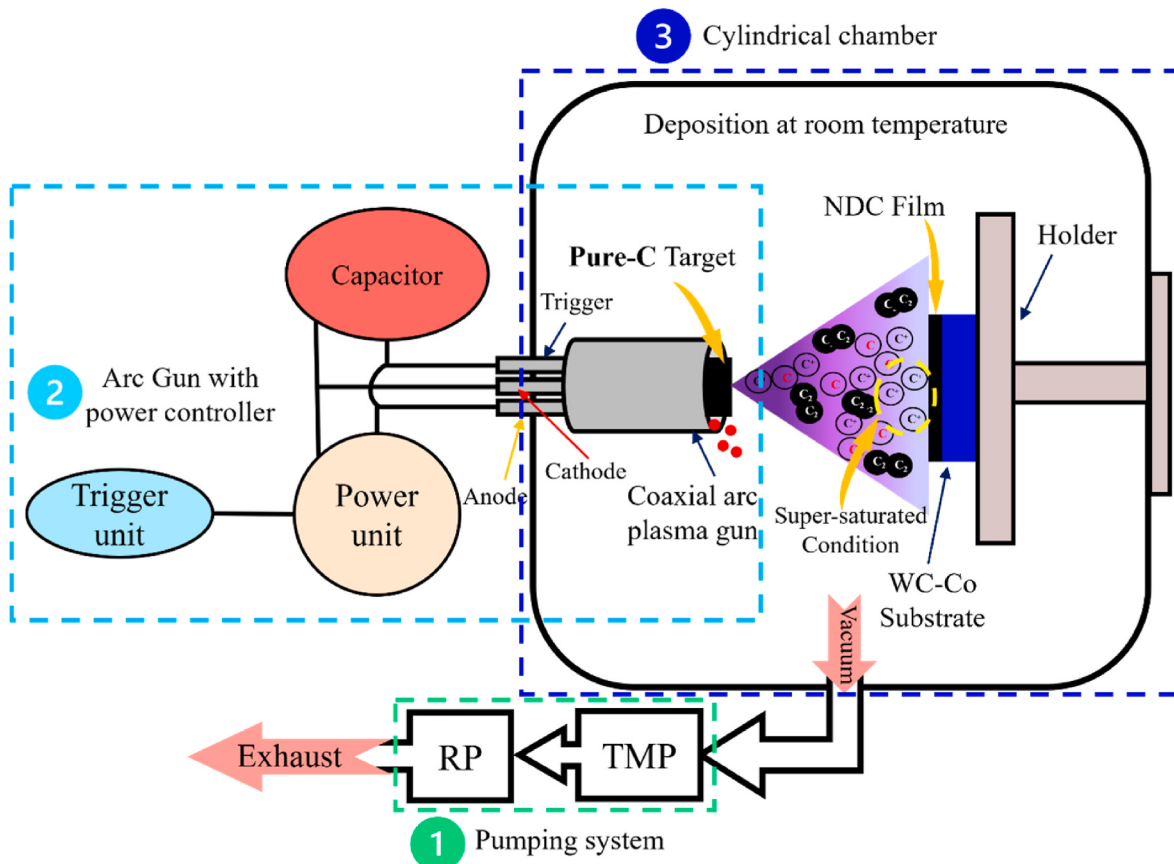


Fig. 16. Design and components of CAPD technique.

mechanical, structural, and tribological properties of the resulting NDC films was conducted. Additionally, a 3-E analysis encompassing energy consumption, economic considerations, and environmental impact confirmed the potential of NDC films as a sustainable hard coating solution for machining applications.

The results demonstrate a significant influence of the Al-interlayer on NDC film growth. Compared to films deposited directly on WC–Co substrates, incorporating a 100 nm Al-interlayer achieved a remarkable 10 μm thickness with a tripled deposition rate of 3.3 $\mu\text{m}/\text{h}$. Furthermore, films deposited on the 100 nm Al-interlayer exhibited superior performance compared to thicker 300 nm and 500 nm alternatives. These films displayed improved hardness (increased from 50.4 GPa to 58 GPa compared with 22 GPa of the WC–Co substrate) and Young's modulus (increased from 516 GPa to 613 GPa compared with 527 GPa of the WC–Co substrate). The Al-interlayer effectively suppressed Co catalytic effects, contributing to the enhanced hardness. Raman spectroscopy confirmed the presence of an intense diamond peak at 1332 cm^{-1} and a maximum C sp^3 fraction of 72 %, supporting the observed increase in hardness.

Significantly improved adhesion was also observed for NDC films deposited on the 100 nm Al-interlayer. Scratch tests revealed an increase in adhesion from 13 N to 18.5 N compared to films deposited directly on WC–Co substrates. Blasting tests further corroborated this improvement. Cross-sectional EDS depth profiling and mapping confirmed the formation of an Al-carbide interfacial layer, which is attributed to the enhanced adhesion.

The NDC films exhibited a consistently low COF of 0.1 and demonstrated high wear resistance (wear rate of $1.5 \times 10^{-7} \text{ mm}^3/\text{N.m}$), satisfying the criteria for dry machining (COF ≤ 0.1 and wear rate $\leq 10^{-6} \text{ mm}^3/\text{N.m}$). Additionally, the NDC films displayed a smoother surface compared to films deposited without an interlayer ($R_a = 0.18 \mu\text{m}$ and $R_z = 1.3 \mu\text{m}$ vs. $R_a = 0.23 \mu\text{m}$ and $R_z = 1.7 \mu\text{m}$). This smoother surface, in combination with the high film hardness and unique nanostructure, is believed to play a key role in reducing COF and enhancing wear resistance. The presence of grain boundaries and a graphitic phase facilitated self-lubrication through C sp^2 tribo-layer transfer, further contributing to improved lubricity, wear resistance, and overall longevity, particularly during dry machining of challenging materials like Al_2O_3 .

The CAPD technique itself aligns well with sustainability principles. With its energy-efficient, clean, and room-temperature process, the CAPD method utilizes a cathodic arc gun that consumes only 77 % of the total energy. This translates to lower energy consumption compared to traditional CVD, MSD, and CAE techniques. Furthermore, CAPD boasts economic viability due to its simple design and the absence of external heaters and entry gases, leading to lower capital and running costs. Eliminating the need for hazardous chemicals, heating, and cutting fluids solidifies CAPD's position as a clean and environmentally friendly alternative for sustainable manufacturing.

Future research will focus on optimizing deposition parameters to further enhance film hardness and adhesion strength. These advancements will provide valuable insights to bolster the performance and sustainability of NDC coatings within the framework of sustainable manufacturing practices.

CRedit authorship contribution statement

Mohamed Egiza: Writing – review & editing, Writing – original draft, Project administration, Methodology, Formal analysis, Conceptualization. **Mohamed Ragab Diab:** Visualization, Validation, Methodology, Investigation. **Ali M. Ali:** Methodology, Investigation. **Koki Murasawa:** Validation, Methodology. **Tsuyoshi Yoshitake:** Writing – review & editing, Supervision, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial

interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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