EGIZA, M., DIAB, M.R., ALI, A.M., MURASAWA, K. and YOSHITAKE, T. 2024. Sustainable super-hard and thick nanodiamond composite film deposited on cemented carbide substrates with an interfacial Al-interlayer. *Materials letters* [online], 364, article number 136369. Available from: https://doi.org/10.1016/j.matlet.2024.136369

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2024

Materials Letters 364 (2024) 136369

Contents lists available at ScienceDirect

Materials Letters

journal homepage: www.elsevier.com/locate/matlet

Sustainable super-hard and thick nanodiamond composite film deposited on cemented carbide substrates with an interfacial Al-interlayer

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ARTICLE INFO

Keywords:
Nanocomposites
Arc plasma
Mechanical properties
Al-interlayer
Catalytic effects
Surface interface

ABSTRACT

Super-hard nanodiamond composite (NDC) films, synthesized via cathodic arc plasma deposition on unheated WC − Co substrates, offer an eco-friendly solution for cutting tools. A 100 nm-thick Al-interlayer mitigates Co catalytic effects, improving adhesion and yielding smooth and dense 10 μm-thick films at a deposition rate of 3.3 μm/hr. These grain-boundary-rich nanostructured films, with an impressive 58 GPa hardness attributed to a substantial 70 % C sp^3 fraction, prove optimal for hard coatings. The Al-interlayer effectively suppresses Co catalytic effects, forming a dense Al-oxide layer, enhancing film hardness and adhesion (Lcr = 18.6 N). NDC films present a promising eco-friendly option for high-performance hard coatings.

1. Introduction

Cutting tools play a vital role in manufacturing efficiency and costs. However, frequent tool replacement due to limited lifespans escalates machining costs. Cemented carbides (WC − Co) are commonly used for machining difficult-to-cut materials but face wear resistance limitations [1]. To address this challenge, WC − Co tools have been coated with hard or super-hard films aims to mitigate wear and extend tool lifetimes. Diamond coatings offer superior properties, yet adhesion challenges persist [2]. Surface pretreatment involving chemical etching is essential but introduces chemical hazards affecting health and the environment. Additionally, a low deposition rate and substrate heating up to 800 °C increase the product total cost and alter substrate properties. Tetrahedral amorphous carbon (ta-C) emerges as an alternative with comparable hardness to diamond, lower friction coefficients, and environmental compatibility [3]. However, high internal stress within ta-C films hinders adhesion and limiting film thickness to less than 1 μm [4].

Nanodiamond composite (NDC) films deposited by coaxial arc plasma deposition (CAPD), comprising nanodiamond crystallites within an amorphous carbon (a-C) matrix, present a promising solution. Deposition through CAPD on WC − Co substrates, conducted in vacuum without Co chemical etching or substrate heating, aligns with sustainability principles [5]. CAPD generates highly energetic ionized carbon species, resulting in NDC films with high sp^3 content and low internal stress (≤4.5 GPa) [6,7]. However, film's adhesion is limited to a critical load of 13 N. To overcome this limitation, incorporating cost-effective and widely available intermediate-layer, such as aluminium (Al), may contribute to mitigating cobalt diffusion and ensure adhesion while preserving the substrate's mechanical characteristics.

The research aims to deposit sustainable NDC film with enhanced hardness, thickness, and adhesion in vacuum without external substrate heating and chemical Co etching, incorporating Al-interlayer at the interface towards cutting tool advancement.

2. Experimental methods

A 10 μm single-layer NDC film, incorporating a sputtered 100 nm Al-interlayer, was deposited on unheated WC − 6 % Co substrates (Ra 0.15 ~ 0.20 μm, Fig. 1e (onset)) using CAPD (in-depth deposition, refer to [7]). Morphological characterization utilized SEM/EDS (JEOL, JSM-6500F), and surface roughness parameters (Ra and Rz) were determined with a 3D confocal laser microscope (LEXT OLS5000, Olympus, UK). Mechanical properties were assessed through nanoindentation tests

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https://doi.org/10.1016/j.matlet.2024.136369
Received 15 February 2024; Received in revised form 22 March 2024; Accepted 25 March 2024

(Picodentor HM500, Fischer Inst. UK), while adhesion was evaluated via scratch tests (Anton Paar RST^3). Structural analyses involved visible Raman spectroscopy (Alpha 300R-confocal, Witec, Germany) and X-ray photoemission spectroscopy (XPS) at the SAGA Light Source Proposal Nos. 1704022S.

3. Results and discussion

NDC films revealed a homogenous morphology with a surface roughness of Ra = 0.16 μm and Rz = 1.3 μm (Fig. 1a and b). This surface roughness remained consistent after sputtering a 100 nm-thick Al-interlayer (Fig. 1a). Cross-sectional SEM/EDS analysis reveals a 10 μm-thick film deposited at a rate of 3.3 μm/hr, compared to the NDC film without the Al-interlayer, which has a deposition rate of only 1 μm/hr [7]. This dense structure, free of droplets and pores, signifies successful cathodic arc deposition. Both the NDC films and Al-interlayer were deposited without external heating, preserving substrate properties, including cobalt stability. At high temperatures (~800 °C), cobalt forms spherical shapes facilitating its diffusion onto the coatings. This approach aligns with sustainability goals by avoiding the need for external substrate heating during the deposition process.

The Co phase, seen as light-grey areas in Fig. 1c and e, bonds the WC particles (dark-grey) in the WC – Co substrate, enhancing its mechanical toughness [8]. However, catalytic effects from non-etched Co reportedly induce graphitization, diminishing film hardness [9]. EDS depth profiles (Fig. 1c) exhibit a flattened Co spectrum for the NDC film, confirming restricted Co diffusion due to the Al-interlayer. EDS mapping indicates the Al-interlayer's thickness exceeding 100 nm, forming an Al-carbide phase. The Al-interlayer shields C species from direct Co contact, inhibiting graphitic carbon formation. It oxidizes, forming a dense aluminium oxide layer (Fig. 1e and f), suppressing Co diffusion. EDS mapping verifies high-intensity peaks for oxygen and aluminium, indicating an oxidized Al layer. Al atoms may diffuse into the substrate, forming an Al-Co alloy that hinders free cobalt atoms, promoting interlocking adhesion at the interface. The observed effectiveness of the Al-interlayer in restraining Co diffusion and suppressing graphitization at the NDC-substrate interface underscores its pivotal role in enhancing film properties.

Compared to the uncoated WC – Co substrate (22 GPa hardness), the NDC film showcased superior mechanical properties with a hardness of 58 GPa and a Young's modulus of 613.75 GPa. Employing the scratch test, crucial for assessing coating-substrate adhesion, the study revealed detailed tangential force, coefficient of friction, and acoustic emission (Fig. 2a), aiding in determining the critical load for coating delamination. The NDC coating, with an Al-interlayer, exhibited enhanced adhesion, evident from the higher critical load of 18.6 N, while the NDC film without an interlayer displayed a lower critical load of 13 N [6]. Additionally, Fig. 2a and b highlighted that the NDC coating fractured at a higher penetration resistance, attributed to the Al-interlayer and the formation of the Al-carbide phase.

The optical examination of the fracture spot in Fig. 2c verified residual Al remnants attached to the substrate surface. This observation was substantiated through EDS and SEM analysis at the detachment interface, as illustrated in Fig. 2d. The EDS results revealed prominent W peaks, weak Al peaks, and Co peaks, while the SEM images displayed particles of WC along with remnants of Al adhered to the substrate. These collective findings underscore the improved adhesion properties resulting from the deliberate inclusion of an Al-interlayer in the NDC coating. This strategic enhancement holds promise for elevating the overall performance and durability of the coating in practical applications.

To investigate the mechanisms behind the substantial film hardness (58 GPa) and significant thickness (10 μm) influenced by the inserted Al-interlayer, spectroscopic and synchrotron-based analyses were conducted. Raman spectra (Fig. 3a) of the NDC coating on the Al-interlayer closely resembled CVD nanodiamond bands, with six discernible peaks, including t-PA$_1$ (1085 cm^{-1}), diamond (1332 cm^{-1}), D-peak (1345 cm^{-1}), t-PA$_2$ (1492 cm^{-1}), and G-peak (1580 cm^{-1}, composed of G$_1$ and G$_2$ peaks). The prominent peak at 1332 cm^{-1} in the NDC coating spectrum, akin to single-crystalline diamond, serves as unequivocal evidence of the first-order diamond phase, enhancing mechanical properties. Peaks on t-PA$_1$ and t-PA$_2$ shoulders confirm numerous grain boundaries, formed by the nanodiamond phase, acting as strength-enhancing obstacles and enabling the substantial film thickness (10 μm) at a notable deposition rate of 3.3 μm/hr. The partial overlap of the D-peak (1345 cm^{-1}) with the diamond peak indicates the presence of amorphous or graphitic carbons at grain boundaries, potentially influencing overall mechanical response. The G-peak, divided into G$_1$ and G$_2$ peaks at 1580 cm^{-1}, signifies the in-plane stretching mode (E2g) of the C = C sp^2 bonds in the amorphous graphitic phase, further confirming the effectiveness of the 100 nm Al-interlayer in enhancing both the mechanical and structural properties of the film.

To quantitatively assess the C sp^3 fraction, crucial for determining film hardness, the films underwent XPS analysis (Fig. 3b). The resulting C 1 s spectra, deconvoluted [6], revealed peaks assigned to sp^2-bonded carbon (C = C), sp^3-bonded carbon (C – C), carbon–oxygen single bonds (C–O/C–O–C), and carbon–oxygen double bonds (C = O/COOH) at binding energies of 284.5, 285.07, 286.63, and 288.23 eV, respectively. Noteworthy shoulder peaks suggested oxygen adsorption during and after film deposition. The sp^3 fraction, calculated as sp^3/(sp^3 + sp^2), was

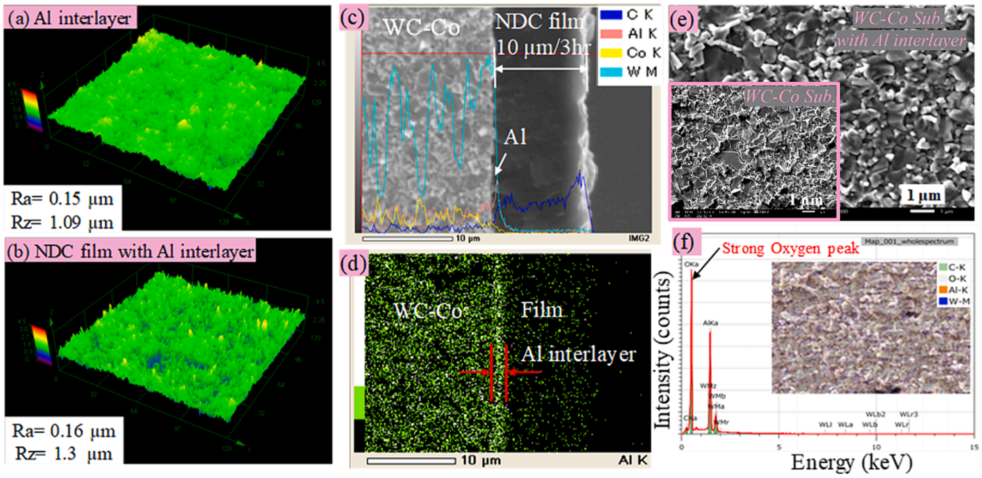

Fig. 1. 3D topography of (a) Al-surface-interlayer and (b) NDC films with Al-interlayer, (c) cross-sectional SEM image featuring EDX depth profiles and (d) corresponding mapping, and top-view (e) SEM and (f) EDS mapping.

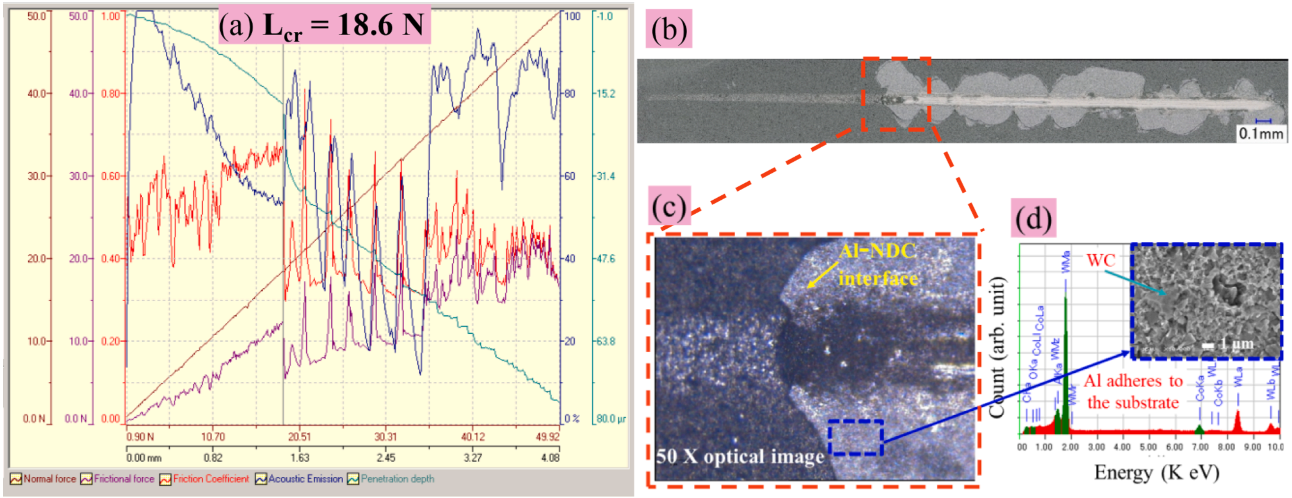

Fig. 2. Adhesion scratch test of NCD films (a) synchronized results of scratch test, (b) optical image of scratch track, (c) optical image of fracture spot, and (d) EDS top-view examination after detachment of the film (SEM-onset).

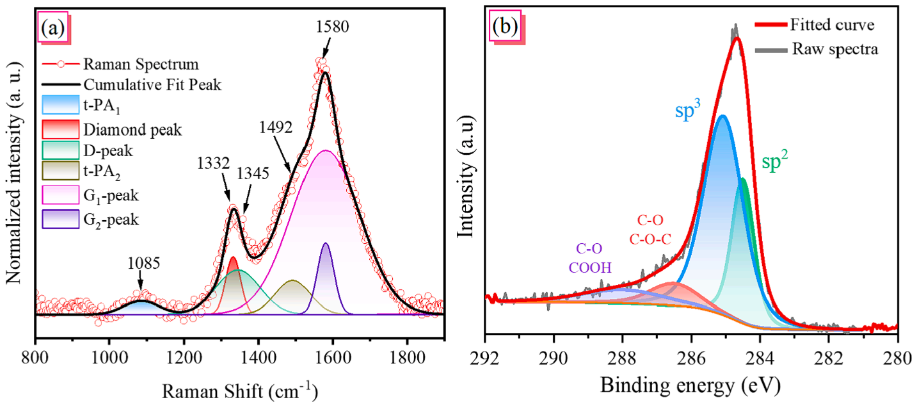

Fig. 3. (a) Visible Raman analysis and (b) decomposed C1s XPS spectra of NDC film deposited with Al-interlayer acquired using synchrotron radiation.

notable at 70 % for NDC films with an Al-interlayer, aligning with concurrently measured hardness and Young's modulus values. This observation highlights the effective mitigation of Co catalytic effects by the Al-interlayer, promoting the formation of C sp^3 bonds and ultimately elevating the NDC film's hardness to an impressive 58 GPa.

4. Conclusion

The sustainable deposition of super-hard and thick NDC films on WC – Co substrates, achieved through CAPD at a notable rate of 3.3 µm/hr without external heating or Co chemical etching, ensures safety and cost-effectiveness. Incorporating an optimized 100 nm Al-interlayer significantly enhances film adhesion, evidenced by a critical load of 18.6 N. Effectively countering Co catalytic effects, the interlayer forms a dense Al-oxidized layer and Al-carbide phase at the interface. The films exhibit a rich-grain-boundaries nanostructure with uniform morphology and an impressive thickness of 10 µm. XPS analyses confirm a high fraction of C sp^3 bonds (70 %), resulting in an impressive film hardness of 58 GPa. This study provides valuable insights for optimizing NDC film properties, promising high-performance thick films for cutting tool applications.

CRediT authorship contribution statement

Mohamed Egiza: Writing – original draft, Project administration, Methodology, Formal analysis, Conceptualization. **Mohamed Ragab Diab:** Writing – original draft, Project administration, Methodology, Formal analysis, Conceptualization. **Ali M. Ali:** Writing – review & editing, Methodology. **Koki Murasawa:** Visualization, 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.

Acknowledgments

This work was supported by Advanced Machining Technology and Development Association, JST A-STEP Stage II (AS2915051S).

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.matlet.2024.136369.

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Supplementary materials

Sustainable super-hard and thick nanodiamond composite film deposited on cemented carbide substrates with an interfacial Al interlayer

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Analysis of nanoindentation measurements:

The load-displacement curves derived from the analysis of fifteen randomly selected points on a polished specimen (with a surface roughness, Ra, of less than 20 nm) are illustrated in **Fig. 1**. In comparison to the uncoated WC−Co substrate, which exhibited a hardness of approximately 22 GPa, the NDC film displayed significantly enhanced mechanical properties with a hardness of 58 GPa and a Young's modulus of 613.75 GPa.

The average load-displacement curve was further utilized to estimate the elastic and plastic properties of these films. The Young's modulus (E), determined by the harmonic interatomic potential slope, plays a pivotal role in their performance. These films exhibit heightened hardness influenced by factors such as ion energy, bonding characteristics, and microstructure. Energetic ion bombardment effects are reflected in a plasticity index (H/E = 0.0945) and improved brittle fracture resistance (H^3/E^2 = 0.518 GPa). Beyond elastic-plastic properties, the plastic resistance index (H/E) underscores wear resistance, with the observed ratio of 0.0945 in the NDC film indicating minimal plastic deformation and elevated wear resistance, suggestive of a more diamond-like nature. Notably, nanoindentation measurements reveal a high elastic recovery value (R = 0.785) for the NDC coating, aligning with that in CVD diamond [1, 2]. Consequently, NDC films demonstrate suitability for coating applications requiring robust wear resistance, as well as for applications demanding durable and protective coatings in harsh environments.

Supplementary materials

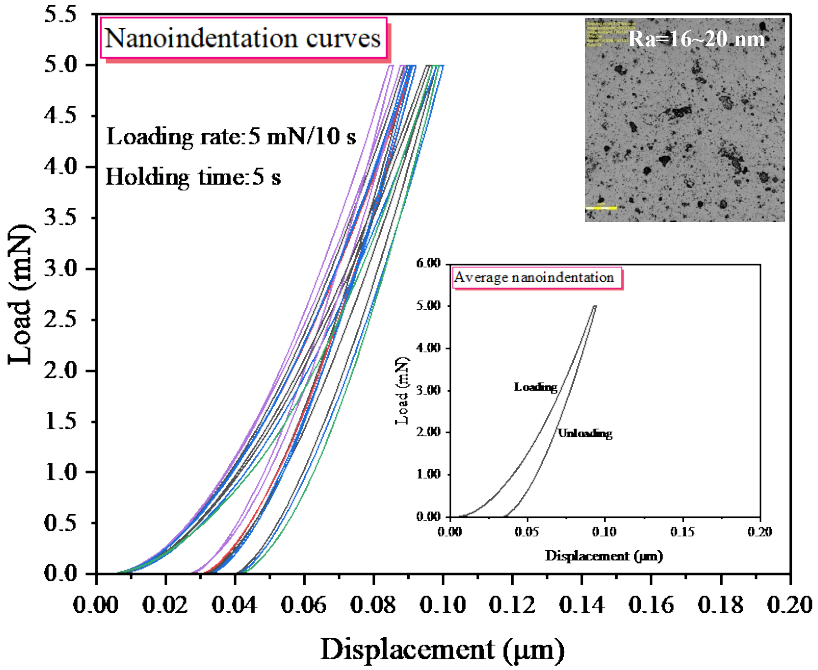

Fig. 1 Nanoindentation load-displacement curves acquired at distinct points on polished NDC films (onset), along with their corresponding average curve.

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