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Unveiling a 72.5 GPa peak hardness in sustainable nanodiamond composite hard coatings via discharge energy control: A nanoindentation-Raman approach

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ABSTRACT

Sustainable nanodiamond composite (NDC) films hold promise for high-performance hard coatings thanks to coaxial arc plasma deposition (CAPD). This eco-friendly technique eliminates the need for external heating, chemical reactions, or Co substrate pre-treatment. CAPD boasts lower energy consumption and faster deposition rates, making it a sustainable solution for the growing demand for high-quality, environmentally friendly coatings. This study investigates the influence of discharge energy on the nanostructure and mechanical properties of these NDC films. Optimal discharge energy, ranging from 2.3 to 12 J/pulse, was meticulously explored. A combined nanoindentation-Raman approach reveals a significant correlation between discharge energy and film properties. Remarkably, at 7 J/pulse, a peak hardness of 72.5 GPa is achieved, surpassing other energy levels. Raman spectroscopy confirms maximum nanodiamond content at this energy level (evidenced by maximized A_{dia}/A_G ratio, indicating a higher diamond-to-graphite ratio), along with minimal graphitization. Additionally, the presence of *trans*-polyacetylene (t-PA) peaks (denoted as $A_{t\text{-}PA}$) revealed the existence of maximum grain boundaries ratio ($A_{t\text{-}PA}/A_G$), contributing to enhanced mechanical properties. Optimizing discharge energy tailors NDC film nanostructure, enhancing mechanical performance for advanced hard coatings.

1. Introduction

Nanocomposite superhard coatings (>40 GPa) are critical for high-performance cutting tools due to their unique nanocrystalline and amorphous nanostructure, offering a combination of strength, wear resistance, and low friction [1]. Among these, nanodiamond composite (NDC) films stand out. These films consist of a unique blend of nanocrystalline diamond and amorphous carbon phases [2], contributing to their exceptional hardness exceeding 50 GPa, making them highly desirable for cutting tools [3]. However, further advancements in hardness are crucial to improve wear resistance and tool longevity.

Coaxial arc plasma deposition (CAPD) is a promising technique for depositing various materials tailored for diverse applications [4,5]. CAPD generates highly energetic carbon ions, directly influencing film nanostructure and hardness. Increasing discharge energy from 1.8 to 144.0 J/pulse typically enhances plasma content ionization. Analysis of arc plasma emission reveals a notably high proportion of C^+ ions, which play a pivotal role in NDC growth and control nanodiamond crystallite size within the range of 2.4 to 15.0 nm [5]. However, surpassing a critical value of discharge energy can detrimentally affect film properties.

A crucial gap exists in understanding how discharge energy within CAPD influences the nanostructure and mechanical performance of NDC films. This knowledge gap hinders the optimization of NDC coatings for cutting tools, especially in achieving the desired balance between hardness (which leads to better wear resistance) and other critical properties.

To address this challenge, this research investigates the impact of varying discharge energy (from 2.3 to 12 J/pulse) on the properties of NDC films. Raman spectroscopy will be employed to analyze the

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nanostructure, while nanoindentation will measure their mechanical properties.

2. Experimental methods

NDC films were deposited onto unheated substrates in vacuum environment (≤10-ˆ4 Pa) from pure graphite target utilizing CAPD (ULVAC APG-1000). The substrate, a WC – 6 % Co (K-type, dimensions: φ10 × 5 mm), underwent only surface roughening to achieve an Ra of 0.25–0.3 μm without Co chemical pretreatment. Morphological characterization utilized SEM (JEOL, JSM6500F). Hardness and Young's modulus were measured using nanoindentation tests via nanoindentation (Picodentor HM500) from Fischer Instruments UK. Film homogeneity was ensured through 10 nanoindentation tests, and mean values for hardness and Young's modulus were determined. Structural analysis employed visible Raman spectroscopy (532 nm laser, Alpha 300R-confocal, Witec, Germany).

3. Results and discussion

CAPD deposited sustainable NDC films on WC – Co substrates, eliminating external heating, harsh chemicals, and gaseous reactions compared to CVD methods. SEM analysis (Fig. 1a-b) showed a dense morphology with fine clusters and a thickness of 10 μm at 2 μm/hr deposition rate. Interestingly, the rate increased with discharge energy (1–4 μm/hr). Notably, CAPD achieved this thickness with low energy consumption (14 kWh/μm), comparable to other methods. This combination of dense structure, controllable thickness, and low energy consumption suggests excellent potential for NDC as sustainable hard coatings, particularly for cutting tools.

Fig. 1c-d depict the nanoindentation results, revealing a consistent trend: both hardness and Young's modulus display a direct correlation with variations in discharge energy. Films deposited at the lowest discharge energy (2.3 J/pulse) exhibited a hardness of 58 GPa and Young's modulus of 591 GPa. These values significantly increased to reach peak hardness (72.5 GPa) and Young's modulus (694 GPa) at the optimal discharge energy of 7 J/pulse (Fig. 1c). These improved mechanical properties are likely due to enhanced ionization of carbon species at higher discharge energies. However, it's important to note that higher discharge energies could also cause substrate heating and potential film graphitization.

The films deposited at the highest discharge energy (12 J/pulse) exhibited a decrease in both hardness (59 GPa) and Young's modulus (607 GPa). This deterioration, as will be further discussed in the context of Raman analysis, is likely due to excessive graphitization of the film's top layers. As the target-substrate distance is fixed through the study (20 mm), ions bombarding the film during deposition at excessively high energies (beyond the optimal level) may be responsible for this phenomenon.

Raman spectroscopy analysis revealed valuable insights into the nanostructure of the deposited NDC coatings (Fig. 2). Analyzing the spectra revealed seven distinct peaks. A prominent peak at 1337 cm^{-1}, close to the signature peak of single-crystal diamond (1332 cm^{-1}), confirmed the presence of embedded nanodiamond crystallites within the films. The slight shift (+5 cm^{-1}) suggests compressive internal stress within the NDC films, affirming the films dense structure.

This dense structure and the quality of the embedded nanodiamond crystals likely result from the C sp^3 bonds formed by highly energetic carbon ions (C^+) generated by the CAPD plasma process [5]. Additionally, peaks at 1170 cm^{-1} (t-PA_1) and 1496 cm^{-1} (t-PA_2) support the nanostructure of the films and the presence of embedded nanodiamond grains. These peaks correspond to vibrational modes of *trans*-polyacetylene (t-PA) C sp^2 chains at grain boundaries, indicating the presence of abundant grain boundaries within the film. These grain boundaries may act as barriers to dislocation movement, contributing to the enhanced mechanical properties of the NDC films.

Raman spectroscopy also identified a D-band at around 1345 cm^{-1}, similar to findings in nanocrystalline diamond deposited using CVD methods. This peak suggests the presence of disordered sp^2 carbon within the amorphous matrix of the NDC film. Additionally, the G-band at 1580 cm^{-1} indicates the presence of sp^2 bonded, graphite-like carbon.

Further analysis of the G-band revealed three sub-peaks: G_1 (1566 cm^{-1}), G_2 (1583 cm^{-1}), and G_3 (1620 cm^{-1}). These peaks correspond to different vibrational modes of carbon atoms in the amorphous graphitic phase. These findings suggest the presence of chain-dense tetrahedral amorphous carbon (G_1 peak) and amorphous diamond structures (G_2 & G_3 peaks) within the NDC films. These contribute to the dense structure and enhanced mechanical properties observed.

The intensity and sharpness (decreasing Full Width at Half Maximum, FWHM) of the G-peaks increased with increasing discharge energy from 2.3 to 7 J/pulse. This supports the role of tetrahedral amorphous carbon (ta-C) chains and amorphous diamond structures in the increasing hardness from 58 to 72.5 GPa. However, films deposited at the highest discharge energy (12 J/pulse) exhibited a significant increase in D- and G-peaks intensity and area, indicating excessive graphitization and adversely affecting film properties (resulting in a degraded hardness of 59 GPa).

To quantify the nanostructure of NDC films, crucial ratios derived from Raman analysis are utilized, namely the intensity ratio and the integrated area ratio such as I_D/I_G and A_D/A_G, recpectively (Fig. 3). The

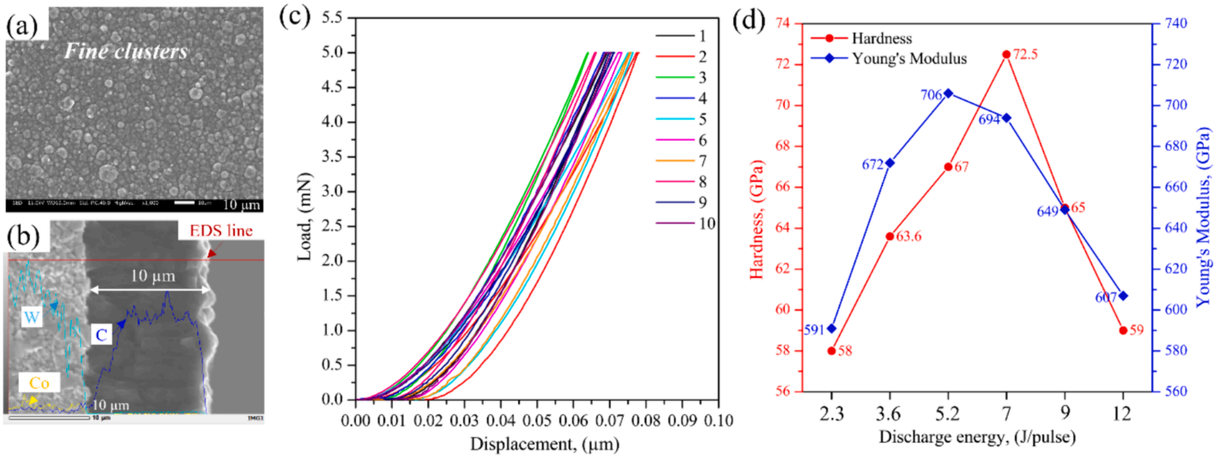

Fig. 1. SEM images of the NDC film: (a) top view and (b) cross-section, along with nanoindentation results for (c) the film deposited at 7 J/Pulse, and (d) all samples plotted as a function of discharge energy.

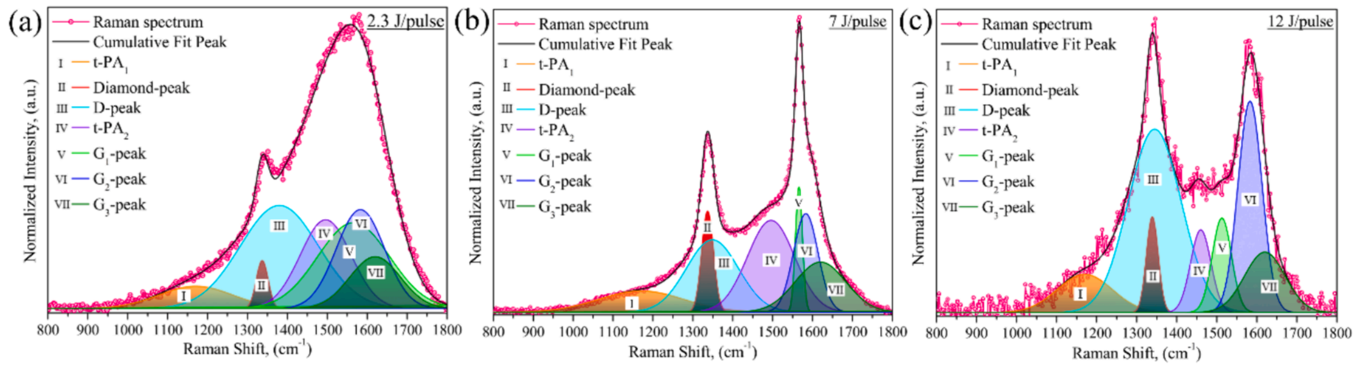

Fig. 2. Deconvoluted Raman spectrum of NDC coatings deposited at different discharge energy levels (see supplementary data for all measured Raman spectra).

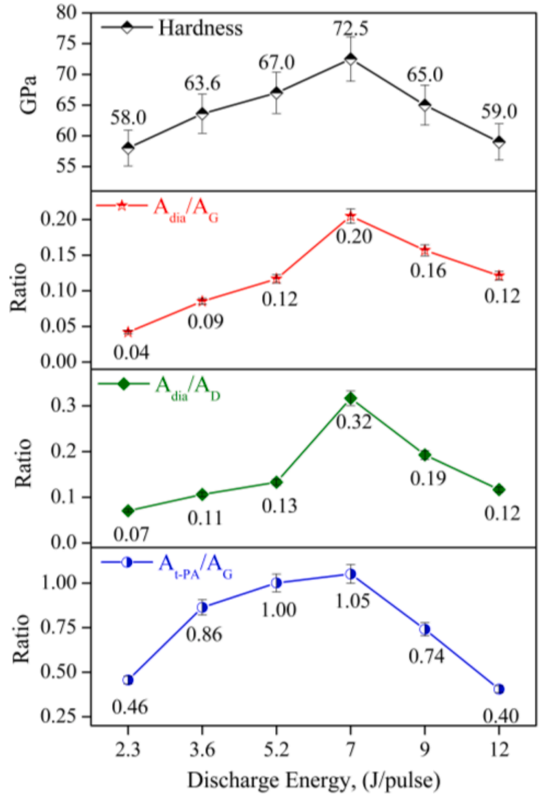

Fig. 3. Correlation between NDC film hardness and various area ratios (diamond peak to G peak (A_{dia}/A_G), diamond peak to D peak (A_{dia}/A_D), and *trans*-polyacetylene peak to G peak ($A_{t\text{-}PA}/A_G$)) as a function of discharge energy.

I_D/I_G or A_D/A_G ratio reflects the relative abundance of disordered carbon, while the $A_{t\text{-}PA}/A_G$ and A_{dia}/A_G ratio provides insights into diamond content and crystallinity quality [6]. With increasing discharge energy, these ratios exhibit trends correlating with observed hardness changes, with A_{dia}/A_G reaching maximum of 0.2 at 7 J/pulse, suggesting optimal diamond content for this energy level.

The improved hardness observed at 7 J/pulse is attributed to the presence of nanodiamond grains and inherent features within the amorphous carbon matrix, leading to a high proportion of C sp^3 bonding and a dense structure. Additionally, grain boundaries effectively suppress internal stress, facilitating the attainment of significant film thickness (10 μm) during growth. This comprehensive Raman analysis elucidates the structure–property relationship in NDC films, thereby facilitating the optimization of their performance in cutting tools applications.

4. Conclusion

This study investigated the impact of varying discharge energy (2.3–12 J/pulse) on the mechanical and structural properties of sustainable NDC films deposited on WC–Co substrates using CAPD. The CAPD process eliminated the need for external heating, harsh chemicals, or gaseous reactions, promoting safety and cost-effectiveness. Results demonstrated the deposition of thick (10 μm) films with a dense, rich-grain-boundary nanostructure confirmed by t-PA peaks in Raman spectroscopy. A linear correlation between film hardness and the area under the diamond peak at 1337 cm^{-1} was found in the Raman spectra of the film. A peak hardness of 72.5 GPa and Young's modulus of 694 GPa was achieved at the optimal discharge energy (7 J/pulse), coinciding with minimal graphitization and the highest diamond content (evidenced by a maximum A_{dia}/A_G ratio of 0.2). However, at higher discharge energy (9–12 J/pulse), film graphitization increased, while the A_{dia}/A_G ratio indicative of diamond content deteriorated to 0.12. A nanoindentation-Raman approach provided valuable insights into this correlation, highlighting the critical role of discharge energy in tailoring the nanostructure (diamond formation vs. graphitization) and, consequently, the mechanical properties of NDC films. This facilitates developing high-performance and sustainable NDC coatings for demanding cutting tools applications.

CRediT authorship contribution statement

Mohamed Egiza: Writing – review & editing, Writing – original draft, Project administration, Methodology, Formal analysis, Data curation, Conceptualization. **Mohamed Ragab Diab:** Writing – original draft, Visualization, Methodology. **Hoda Atta:** Validation, Methodology. **Mahmoud M. Abdelfatah:** Validation, Methodology, Investigation. **Abdelhamid El-Shaer:** Supervision, Methodology, Investigation. **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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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.matlet.2024.136684.

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Supplementary data

Unveiling a 72.5 GPa Peak Hardness in Sustainable Nanodiamond Composite Hard Coatings via Discharge Energy Control: A Nanoindentation-Raman Approach

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Raman analysis:

Fig.1 presents the deconvoluted Raman spectra of the nanodiamond composite (NDC) films deposited on WC−Co substrates using the coaxial arc plasma deposition (CAPD) process. The discharge energy varied from 2.3 to 12 J/pulse during deposition.

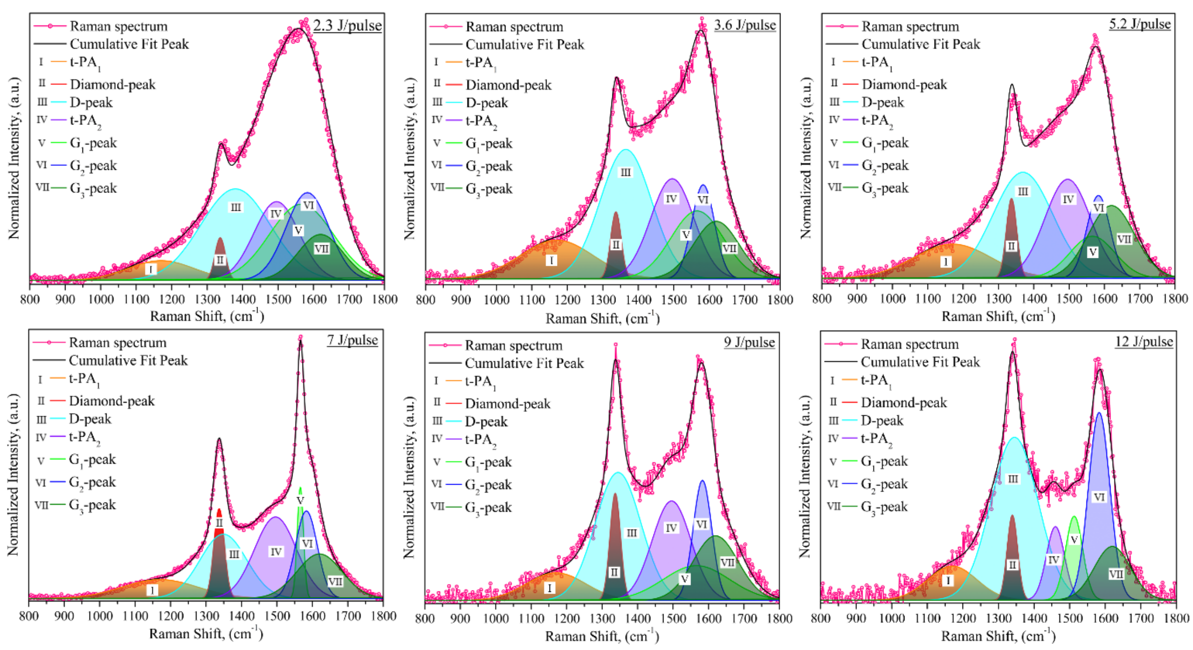

Fig. 1 (Colour online) Deconvoluted Raman spectrum of NDC coatings deposited at various discharge energy levels.

Supplementary data

Influence of discharge energy on deposition rate:

The discharge energy parameter exerts a significant influence on the growth rate of NDC coatings. As evident in Fig. 2, increasing the discharge energy from 2.3 J/pulse to 12 J/pulse leads to a corresponding enhancement in the deposition rate from 1.0 µm/hr to 4.0 µm/hr.

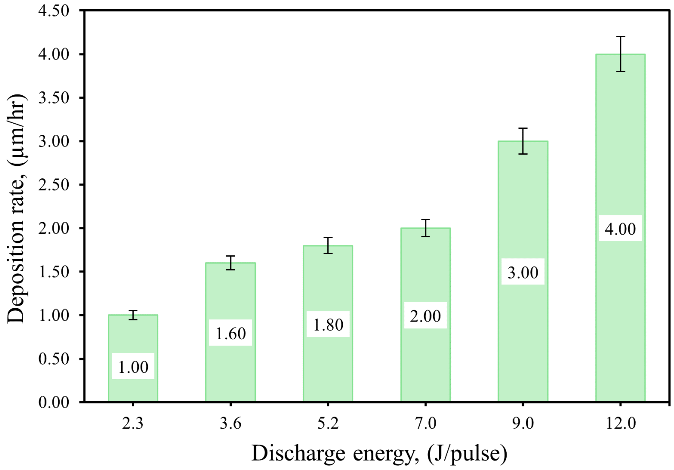

Fig. 2 (Colour online) Correlation between deposition rate and discharge energy variations.

Energy consumption analysis of NDC film deposited via CAPD:

The deposition of high-performance coatings plays a crucial role in various industrial applications. However, conventional coating techniques can be energy-intensive [1]. Among these methods, CAPD technique offers a promising solution due to its superior energy efficiency.

Within the CAPD framework, the cathodic arc gun is the principal energy consumer, accounting for roughly 88% of the total energy used. This translates to an estimated consumption of 126 kWh per deposition process, assuming an optimized discharge energy of 7 J/pulse. In contrast, auxiliary components such as pumps, heating, etching, and cooling contribute minimally to the overall energy usage, typically consuming around 11.6 kWh combined.

It's important to note that the total energy consumption in NDC coating production can be estimated using equation (1):

$$\text{Total energy consumption} = (E_{\text{discharge}} \times t_{\text{deposition}}) + E_{\text{others}} \qquad (1)$$

Where, $E_{\text{discharge}}$ is the coating energy consumption (KW), $t_{\text{deposition}}$ is deposition time (h), and E_{others} is other components like pumps, heating, etching, and cooling (kWh).

Supplementary data

Energy efficiency comparison with other deposition techniques

CAPD demonstrates significant advantages in energy efficiency compared to other common coating methods. It was reported that total energy consumption values of 974 kWh, 112 kWh, and 101 kWh for Chemical Vapor Deposition (CVD), Magnetron Sputtering Deposition (MSD), and Cathodic Arc Evaporation (CAE), respectively [2]. Notably, CAPD exhibits a comparable consumption of 138 kWh with an optimized discharge energy of 7.0 J/pulse.

Furthermore, CAPD boasts considerably shorter process cycle times. While CVD, MSD, and CAE require cycle times of 18.5 hours, 4.92 hours, and 3.45 hours, respectively, CAPD can achieve similar results within a 5-hour cycle under comparable discharge energy conditions.

The efficiency of CAPD is further accentuated by the thickness of coatings produced by each technique. Fig. 3 highlights that CVD, MSD, CAE, and CAPD yield coatings with thicknesses of 10 µm, 2.9 µm, 2.5 µm, and 10 µm, respectively. These results demonstrate that CAPD achieves comparable coating thickness while consuming considerably less energy and time.

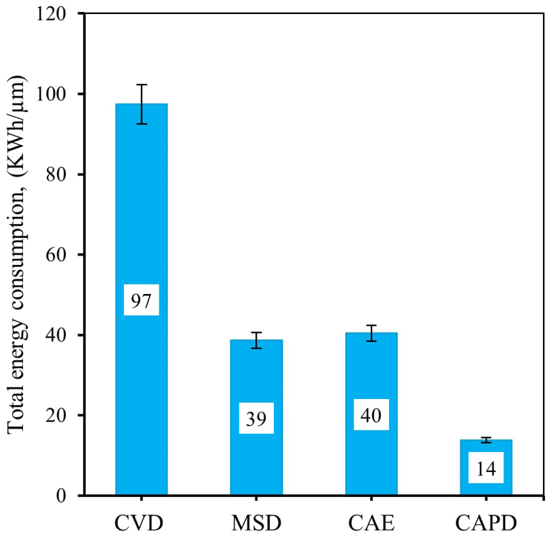

Fig. 3 (Colour online) Comparison of energy consumption rates (kWh/µm) among CVD, MSD, CAE, and CAPD techniques

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