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High dynamic stiffness mechanical structures with nanostructured composite coatings deposited by high power impulse magnetron sputtering

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Abstract 

Nanostructured Cu:CuCN\textsubscript{x} composite coatings with high static and dynamic stiffness were synthesized by means of plasma-enhanced chemical vapor deposition (PECVD) combined with high power impulse magnetron sputtering (HiPIMS). Scanning electron microscope (SEM) images and energy-dispersive X-ray spectroscopy (EDS) mapping from cross-sectioned samples reveals a multi-layered nanostructure enriched in Cu, C, N, and O in different ratios. Mechanical properties of the coatings were investigated by Vickers micro-indentation and model tests. It was observed that copper inclusions as well as copper interlayers in the CN\textsubscript{x} matrix can increase mechanical damping by up to 160\%. Mechanical properties such as hardness, elastic modulus and loss factor were significantly improved by increasing the discharge

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power of the sputtering process. Moreover the coatings loss modulus was evaluated on the basis of indentation creep measurements under room temperature. The coating with optimum properties exhibited loss modulus of 2.6 GPa. The composite with the highest damping loss modulus were applied on the clamping region of a milling machining tool to verify their effect in suppressing regenerative tool chatter. The high dynamic stiffness coatings were found to effectively improve the critical stability limit of a milling tool by at least 300%, suggesting a significant increase of the dynamic stiffness.

1. Introduction

High precision engineering demands mechanical systems to be robust and predictable in their performance, requiring the mechanical structures to be rigid under both static and dynamic loading conditions. Mechanical structures designed for high static stiffness often exhibit low dynamic stiffness (product of static stiffness and loss factor) due to the diminished friction damping in its joint interfaces under high compression pre-load, since joint interface friction damping contributes 90% to the damping of a mechanical structure [1]. On the other hand, structures designed for high dynamic stiffness with incorporated joint interface friction damping might deteriorate robustness due to the macro slippage at the joint interface area. Therefore, materials of high loss modulus (product of elastic modulus and loss factor) are highly demanded to construct high static and dynamic stiffness structures for high precision engineering purposes.

Vibration damping is a critical property for mechanical structures that are subjected to severe vibrations that inherently lead to mechanical failure in components, such as turbine blades [2], machining tools [3], and bearings [4]. A better damping property effectively reduces dynamic response, attenuates acoustic emissions at resonance, while it enhances the robustness and lifetime of components. Engineering materials for mechanical construction either possess high elastic modulus and low damping (such as metals and ceramics) or high damping but low elastic modulus (such as rubbers and polymers) as seen in the loss-stiffness map [5]. Accordingly, it is of an utmost objective to artificially synthesize high loss modulus materials for high dynamic stiffness structures [6].
The underlying mechanism of materials ‘intrinsic damping’ at grain boundaries (similar for interfaces) is explained as viscous slip of disordered atoms and vacancy/atom diffusion between the grains [7]. Particularly in the disordered atom group model, grain boundaries are assumed to be heterogeneous consisting of ordered and disordered regions. The disordered atoms can pass over one another by squeezing the atoms around them. Damping is activated while the weak elastic link between disordered atoms is broken by incoming vibrational waves that consume mechanical energy. ‘Internal friction’ originating from grain boundaries (between grains of similar composition) and interfaces (between grains of different composition) causes damping in materials. Nanostructured materials such as carbon nanotubes [8] with maximized internal surface area (grain boundaries and interfaces) to volume ratio normally exhibit high damping properties. Although these materials are unstable due to the high energy stored at the grain boundaries [6], in composites, the structure can be stabilized by e.g. a metal matrix structure that confines the high free surface energy.

Early studies on cast iron had clearly demonstrated the effect of different types of graphite inclusions on the damping property of the carbon-metal composites [9, 10]. Gray cast iron with graphite flake inclusions was shown to possess the highest damping property compared to malleable and high strength cast iron. Interference patterns on optical coatings revealed that grey cast has a larger local strain concentration and local strain variation than other types of cast iron [9, 10]. It was pointed out that ‘non affine deformation’ due to inhomogeneous strain distribution is an essential phenomenon for achieving high loss modulus composites [11]. The phenomenon was later referred to as ‘non-affined local strain distribution’.

Nanostructured materials with ultra-fine grain size (<10 nm) possess large grain boundary surfaces and low impedance to dislocation mobility due to grain boundary sliding [12]. This can be either accommodated by diffusion flow while grains slide over each other or by dislocation flow, which dominates at low temperatures due to the lower stress requirements. Nanostructured crystalline materials have a high fraction of grain boundary volume. For grain sizes of 10 nm, 14-27% of all atoms reside in a region within 0.5-1 nm of a grain boundary [13]. Further reducing the grain size to 5 nm will increase the percentage of atoms in grain boundary region to 27-49% [14].
In this scenario, several scholars reported their work by impregnating multi-walled carbon nanotubes [8, 15-18], carbon nanocomposites [8, 17, 19], nanographite platelets [20], carbon filaments [21] and carbon nanotube coatings [22] into epoxy and other polymers.

Flexible graphite, made of exfoliated graphite flakes (grain size of ~180 nm) without binder, exhibits loss factor of about 0.15-0.18 and storage modulus of about 1-1.4 GPa tested by three point bending method [23]. When pyrolyzed pitch is added to graphite coke particles, the synthetic graphite showed higher elastic modulus (~10 GPa) and lower damping (~0.007) [24]. Moreover, extruded synthetic graphite with coarse grains seems to have higher damping factor (0.7±0.1%) and higher elastic modulus (11.6 GPa) than that made by isotropic compression with fine grains (ζ=0.33±0.06%, E=9.71 GPa) [24].

Carbon-carbon (C/C) composites have also been studied by the means of damping capacity [25, 26]. Graphite fabric has been impregnated with phenolic resin for investigating the resonance frequency of the composite specimen and damping ratio at the stage of as cured and after carbonization at 800 °C [25]. The authors observed a decrease of resonance frequency and density, and an increase for damping ratio of the samples after carbonization. The increase of damping ratio after carbonization was attributed to the additional energy-dissipation sites that are developed due to the transverse cracks and increased micro-pores in the carbonized specimen. On the other hand, a later work [20] reported a decrease in damping ratio of the C/C composite materials due to impregnation of nanographite fillers which increase stiffness of the composites by filling the porosities inside the composite material.

Although there is a clear benefit of incorporating nanosized inclusions in composites, the studies are limited to matrix materials made of resins or polymers. A viable method that could generate for instance metal matrix composites (MMCs) with nanosized inclusions is still lacking. Conventional methods that apply heating in the process pose risk of agglomeration and coarsening of nanoparticles, which adversely affect the damping property of materials. For this reason, plasma-enhanced processes instead of thermally activated synthesis methods may be beneficial. Radio frequency PECVD was demonstrated earlier to create a nanostructured and multilayered copper/hydrogenated amorphous carbon coatings [27]. With increased thickness of the films from 56 nm to 205 nm, the elastic modulus decreased from 177 GPa to 100
GPa and its hardness decreased from 13 GPa to 6 GPa. The residual stress in multi-layer samples was found to be well below 1 GPa due to the soft Cu layer that acts as adhesive substrate for a-C:H layers. Another technique, high power impulse magnetron sputtering is becoming widely used in the recent years for creating nanostructured materials coatings with increased growth rate in reference to other conventional methods such as sputtering, evaporation or chemical vapor deposition [28, 29]. The high density plasma and thus the enhanced chemical vapor deposition can produce globular nanocrystalline structures at temperatures of around 200°C [30]. Extremely fast cooling rates at \(10^{13} \text{ K·s}^{-1}\) facilitate non-equilibrium growth of the deposited layers thereby generating nanostructured grains [31, 32].

CrTiN/NiTi coatings synthesized by in situ magnetron sputtering were measured to have loss modulus of 10.91 GPa (elastic modulus=210.6 GPa, loss factor=5.18%)[33]. The high damping capacity of the coating layers were concluded to be due to the toughness of CrTiN, super elasticity of NiTi and strong piezo-electric effect in PZT (lead zirconate titanate) layer that constituting the hetero structure. However, the analysis of damping effect from the internal structure of each layer and the synthesis process condition was lacking.

The aim of this work is to synthesize high dynamic modulus materials with PECVD method combined with HiPIMS technology and analyze the effect of process parameters on the properties of composite coatings. Multi-layered structures of pure copper (Cu) and carbon-nitride doped metal matrix (CuCNₓ) were synthesized by varying the experimental conditions. The micro and crystal structure of the produced coatings were assessed by scanning electron microscopy (SEM), atomic force microscopy (AFM), Raman spectroscopy and X-ray diffraction (XRD), respectively. The process parameters on the coatings structural and mechanical properties were found to correlate. To demonstrate the practical utility of the technology, the best performing coating was applied on the fixture area of a milling tool, and the vibration properties of the structure were compared to an uncoated reference sample.

2. Experimental

2.1 Synthesis of nanostructured composite coatings by PECVD method

The PECVD process combined with HiPIMS is described in details elsewhere [34, 35]. Atoms are sputtered from the cathode surface and then traverse through the
plasma towards the substrate/workpiece. The plasma consists of atoms from the cathode and radicals as well as electrons and ionized species of Ar, C$_2$H$_2$ and N$_2$ [36]. HiPIMS was reported to reach a higher ionization rate and a higher plasma density due to a very high discharge current density at the cathode during the active pulse [37].

The typical current-voltage characteristic of the discharge is shown in Figure 1. In the pulse discharge regime, the plasma is characterized with high plasma density in the order of $10^{18}$ m$^{-3}$ [36]. The plateau discharge is similar to that for a DC magnetron with lower plasma density. Adatoms and admolecules condensed on the surface of substrates are then bombarded by highly energetic ions with an extremely fast ($10^{13}$ K·s$^{-1}$) cooling rate. The low substrate temperature (<200°C) and quick cooling rates favor film growth with nanosize grains [38].

![Figure 1 Typical discharge voltage and current curves measured on the cathode during coating deposition [39], redrawn with permission from Springer Ltd.](image)

The coating depositions were carried out in a high vacuum cylindrical chamber (200 cm in length and 100 cm in diameter) equipped with a planar rectangular magnetron cathode (surface area 62×12 cm$^2$) in an unbalanced configuration, i.e. the magnetic strength is lower in the center of the target surface than in the periphery. The target plates (made of pure copper or graphite) were mounted on the cathode and cooled during the process. Prior to the deposition process, the chamber was evacuated to a base pressure of $1.5\times10^{-3}$ Pa. All depositions were carried out at ambient temperature without any external heating of the substrates. For each deposition, the substrates
were mounted on a rotating fixture (~1.3 rpm) at a distance of approximately 10 cm from the target.

Before installing into the chamber, each substrate was cleaned with soap and water followed by ultrasonic-bath cleaning in 2-propanol and acetone for 30 minutes. In situ plasma etch cleaning was performed prior to the main deposition process while biasing the substrate with a medium frequency voltage (±600 V at 100 kHz) in Ar atmosphere (0.8 Pa). Four samples were prepared by sputtering a pure graphite or copper target plate in a reactive plasma atmosphere (~3Pa) with an original gas composition of Ar (~1Pa), N\textsubscript{2} (~1Pa), O\textsubscript{2} (≤ 0.05 Pa) and C\textsubscript{2}H\textsubscript{2} (~1 Pa).

The parameters used for coating deposition, film density and thickness are described in Table 1. Sample A was coated just with one thick layer (CN\textsubscript{x}) while all the other samples were coated with interlayers of copper (Cu) followed by CuCN\textsubscript{x}. Coating density was obtained by measuring the weight of the substrate before and after coating along with the volume of the coating.

### Table 1 Detailed description of coating deposition parameters.

<table>
<thead>
<tr>
<th>Sample</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td>Substrate</td>
<td>Silicon</td>
<td>Silicon</td>
<td>Steel disc</td>
<td>Steel disc</td>
</tr>
<tr>
<td>Coating composition</td>
<td>CN\textsubscript{x}</td>
<td>Cu:CuCN\textsubscript{x}</td>
<td>Cu:CuCN\textsubscript{x}</td>
<td>Cu:CuCN\textsubscript{x}</td>
</tr>
<tr>
<td>Cathode material</td>
<td>Graphite</td>
<td>Copper</td>
<td>Copper</td>
<td>Copper</td>
</tr>
<tr>
<td>Gas composition when depositing different layers</td>
<td>CN\textsubscript{x}</td>
<td>N\textsubscript{2} (~55sccm), Ar (~187sccm) and C\textsubscript{2}H\textsubscript{2} (~29sccm)</td>
<td>n.a.</td>
<td>n.a.</td>
</tr>
<tr>
<td>CuCN\textsubscript{x}</td>
<td>N\textsubscript{2} (~55sccm), Ar (~187sccm) and C\textsubscript{2}H\textsubscript{2} (~29sccm)</td>
<td>N\textsubscript{2} (~25sccm), Ar (~56sccm) and C\textsubscript{2}H\textsubscript{2} (~16sccm)</td>
<td>N\textsubscript{2} (~40sccm), Ar (~49sccm) and C\textsubscript{2}H\textsubscript{2} (~25sccm)</td>
<td></td>
</tr>
<tr>
<td>Cu</td>
<td>n.a.</td>
<td>Ar (~187sccm)</td>
<td>Ar (~56sccm)</td>
<td>Ar (~56sccm)</td>
</tr>
<tr>
<td>Number of layers</td>
<td>1(CN\textsubscript{x})</td>
<td>9(Cu):9(CuCN\textsubscript{x})</td>
<td>32(Cu):33(CuCN\textsubscript{x})</td>
<td>37(Cu):38(CuCN\textsubscript{x})</td>
</tr>
<tr>
<td>Deposition rates (and duration)</td>
<td>CN\textsubscript{x}</td>
<td>8.2 µm·h\textsuperscript{-1} (49 h)</td>
<td>n.a.</td>
<td>n.a.</td>
</tr>
<tr>
<td>CuCN\textsubscript{x}</td>
<td>n.a.</td>
<td>15 µm·h\textsuperscript{-1} (4 h)</td>
<td>6.3 µm·h\textsuperscript{-1} (20 min)</td>
<td>4.8 µm·h\textsuperscript{-1} (20 min)</td>
</tr>
<tr>
<td>Cu</td>
<td>n.a.</td>
<td>6.5 µm·h\textsuperscript{-1} (2 h)</td>
<td>7.2 µm·h\textsuperscript{-1} (15 min)</td>
<td>3 µm·h\textsuperscript{-1} (10 min)</td>
</tr>
<tr>
<td>Density</td>
<td></td>
<td>1.72 g cm\textsuperscript{-3}</td>
<td>3.26 g cm\textsuperscript{-3}</td>
<td>2.99 g cm\textsuperscript{-3}</td>
</tr>
<tr>
<td>Peak power</td>
<td>66 kW</td>
<td>54 kW</td>
<td>100 kW</td>
<td>240 kW</td>
</tr>
<tr>
<td>Peak current</td>
<td>60 A</td>
<td>60 A</td>
<td>100 A</td>
<td>200 A</td>
</tr>
<tr>
<td>Biasing at 100 kHz</td>
<td>None</td>
<td>None</td>
<td>±100 V</td>
<td>±100 V</td>
</tr>
<tr>
<td>Discharge frequency</td>
<td>300 Hz</td>
<td>300 Hz</td>
<td>300 Hz</td>
<td>100 Hz</td>
</tr>
<tr>
<td>Pulse length</td>
<td>400 µs</td>
<td>400 µs</td>
<td>170 µs</td>
<td>150 µs</td>
</tr>
</tbody>
</table>

### 2.2 Nanostructured composite coating characterization

Microstructure characterization was carried out by using field emission scanning electron microscopy (FESEM, Zeiss Ultra Plus). For cross-section imaging, the samples were embedded in an epoxy resin followed by mechanical polishing (from
coarser sandpapers to final polish with diamond and silica nanoparticles). Crystal phase assessment of the cross sectioning coatings was also evaluated with micro-Raman spectroscopy (Horiba Jobin-Yvon LabRAM HR800, Ar⁺ laser source at λ=488nm) and X-ray diffraction (XRD, Bruker D8 Discover, Cu Kα radiation source). Furthermore, thin cross sections measuring approximately 15µm long, 2µm wide and 10µm deep were extracted from the cross section embedded in epoxy resin using a proprietary in-situ Focused Ion Beam (FIB, FEI Helios dual beam). The thin cross section was attached to a copper Transmission Electron Microscope (TEM) grid using FIB-deposited platinum and a window was thinned to electron transparency using the gallium ion beam via FIB. Finally, TEM (Hitachi HD2700) images were acquired followed by the Energy-dispersive X-ray spectroscopy (EDS, Bruker Quantax EDS) mapping from the same area.

Atomic force microscopy (AFM, Veeco Dimension 3100 SPM) was used to evaluate the surface morphology and roughness of coatings. AFM was operated in intermittent mode in air using conical Si tips with a tip radius of 10 nm and a length of ~20 µm (NSC14/AIBS MikroMash, Tallin, Estonia). The root-mean-squared roughness (RMS) was determined over 80×80 µm² areas for each sample. All AFM images were analyzed using the SPIP 6.3.2 software (Image Metrology, A/S).

A Vickers hardness micro indenter (CSM Instruments, Switzerland) was used to characterize mechanical properties. For each sample 12 indents were performed. Load-displacement curves were recorded under linear loading conditions with a maximum applied load force of 5 N, loading/unloading rate of 10 N·min⁻¹ and holding time of 10 s at the maximum indentation depth (hₘₐₓ). The hardness and elastic modulus of the coatings was determined by the Oliver & Pharr method. The creep at maximum static load during the holding time of 10 s was used to identify the damping property [33, 40]. A curve fitting program was used for estimating the creeping of the indenter using equation (1):

\[
d(t) - d(0) = A \times \ln(Bt + 1),
\]

where \( A \) and \( B \) are parameters, \( d(t) \) is the indenter depth at time of \( t \) and \( d(0) \) is the indenter depth at the initial indenter depth at the beginning of the hold period. The estimated parameter \( A \) is then used in equation (2) for calculating the loss factor of the coatings.
\[ \text{loss factor} = GF \times \frac{A}{a(0)}, \]  

(2)

where GF=2 is the geometrical factor for indenters pre-set for the Vickers indenter.

2.3 Model and machining test

The composite with the highest loss factor was selected to be applied as a coating at the location of the fixture clamping on the milling tool (cylindrical rod with a diameter of 20 mm). The coated tool was then compared to an uncoated reference tool by impact model testing and practical machining at an overhang length of 120 mm (L/D=6) while clamped in an HSK 100 tool holder. Model testing was done by using an impact hammer (Dytran ZIEGLER IXYS SN 9117 with a 200 g mass and a plastic tip) and six accelerometers (three Brüel & Kjær type 4508 B with a sensitivity of 929 mV·g\(^{-1}\) and three accelerometers of Dytran model 3225F with a sensitivity of 10.3 mV·g\(^{-1}\)) mounted on the fixture and on the tool, respectively. The model test set up is shown in Figure 2 with the coated tool.

![Figure 2](image)

**Figure 2** (a) schematic view of set up of model testing with a coated tool, (b) coated and the uncoated reference milling tools.

During impact testing, a clamping torque on the nut of nose piece was set at 16 Nm to avoid possible drifting or sliding of the tool due to machining load. Critical stability of the milling tools was tested by Quintana's approach [41] while machining at five spindle speeds (5100 rpm, 5300 rpm, 5500 rpm, 5700 rpm and 5900 rpm) using a slot milling process in the X direction of the milling machine. The inserts were type R390-11T3 08M-PL by SANDVIK with nose radius of 0.8 mm, recommended feed rate of
0.08 mm·min\(^{-1}\) and cutting speed of 345 m·min\(^{-1}\). The hardness of the work piece was measured to be 1.8GPa by ball geometry tip with indentation force of 15.6 Kg. One new cutting edge was used for each set of experiments to avoid process damping caused by the flank wear of inserts [42]. The machining processes started with an axial depth of cut (ap) of 0.2 mm for both types of tools. The consecutive machining operations were arranged to seek for the critical depth of cut, i.e. the minimum of the stability lobes [3]. The axial depth of cut will be increased if tool regenerative chatter is not observed during machining, and will be decreased if chatter occurs.

3. Results and discussion

3.1 Structure and composition of the coatings

The CNx coating layer was deposited by using the mixture of Ar, N2 and C2H2 gases while sputtering off the graphite target (sample A, Figure 3 A1-A3). In the case of Cu:CuCNx composite coatings, CuCNx matrix were deposited by using the same mixture of Ar, N2 and C2H2 gases while sputtering off a copper target plate instead of graphite. In order to add Cu interlayers to the CuCNx matrix, the N2 and C2H2 gases were switched off and just Ar was used (samples B, C and D). The observed horizontal layering formation in sample A (see Figure 3 A1) is due the interruption of deposition overnight which allows the substrate to cool down. While the coating was carried out with low peak power appended with plateau discharge, the plasma density is low and deposition overwhelms etching. The substrate surface is not activated and such layering interface can be observed. The layering structure is more evident in Sample A due to the higher ionization energy of carbon (target material) that reduces the plasma density [43]. At high discharge power and eliminated plateau discharge, the plasma density is high and the substrate is bombarded intensely with energetic particles. Etching on the substrate surface competes with deposition and substrate surface is activated by the heat generated during intense energetic bombardments. A stronger bonding is formed between the substrate surface and adatoms and therefore, horizontal layering structure was not observed in samples C and D. The competing etching phenomenon had also resulted in reduced deposition speed according to Table 1 at higher peak power and reduced plateau discharge.
SEM cross-section micrographs for samples B (Figure 3 B1), C (Figure 3 C1), and D (Figure 3 D1) clearly show the multi-layered structure caused by the periodic deposition conditions. Accordingly, the deposition time and number of layers generates different thickness values for Cu layer and the composite-layer (CuCNₓ) as summarized in Table 2. Additionally, a multi-layered nanostructure within the CuCNₓ layer can be observed for all composite samples (Figure 3 B3, C3, and D3) with periodicity of 200 nm, 85 nm and 65 nm, respectively. Considering the deposition rate for each sample summarized in Table 1, it is clear that the CuCNₓ fine nanostructure is due the substrate rotation speed at 1.3 rpm during deposition process.

<table>
<thead>
<tr>
<th>Thickness</th>
<th>Sample A</th>
<th>Sample B</th>
<th>Sample C</th>
<th>Sample D</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total (µm)</td>
<td>350</td>
<td>450</td>
<td>130</td>
<td>110</td>
</tr>
<tr>
<td>Cu layer (µm)</td>
<td>only CNₓ</td>
<td>13±2</td>
<td>1.8±0.2</td>
<td>0.6±0.1</td>
</tr>
<tr>
<td>CuCNₓ layer (µm)</td>
<td>only CNₓ</td>
<td>60±5</td>
<td>2.1±0.2</td>
<td>1.6±0.1</td>
</tr>
<tr>
<td>CuCNₓ nanostructure periodicity</td>
<td>only CNₓ</td>
<td>~200nm</td>
<td>~85nm</td>
<td>~60nm</td>
</tr>
</tbody>
</table>

Figure 3, SEM cross-section micrographs for samples A (A1, A2, A3), sample B (B1, B2, B3), sample C (C1, C2, C3) and sample D (D1, D2, D3). Column #1 shows the multi-layer structure, brighter colors are Cu layers while darker colors are CuCNₓ. Column #2 shows the boundary between Cu and CuCNₓ layers. Column #3 shows high magnification imaging for CuCNₓ nanostructured layer. These columns description does not apply to A1, A2 and A3 since sample A is composed just by CNₓ layer.
TEM-EDS elemental mapping (Figure 4) carried out on cross-sectioned samples reveals the CuCN\textsubscript{x} fine nanostructure is caused by the alternating layers enriched in Cu, C, N, and O in different ratios. The fine Cu-enriched layers (appearing as darker areas in the bright field TEM images) have an approximate composition of \(~50\%\) Cu, \(~38\%\) C, \(~6\%\) N and \(~6\%\) O (by mass) that are alternated with layers reduced in their copper content with an overall approximate composition of \(~30\%\) Cu, \(~45\%\) C, \(~15\%\) N and \(~15\%\) O (by mass) (Figure S1). It is worth pointing out, that both N and O are present in the Cu and C enriched layers. Furthermore, Cu nanocrystals with a size of few nm can be found in both C and Cu enriched fine nanostructures (Figure S2).

![Figure 4 TEM-EDS elemental maps of cross-sectioned Sample D. The lower magnification bright field transmission electron micrograph and the corresponding elemental maps (upper row of panels) display the Cu interlayers and the fine-structured in the CuCN\textsubscript{x} matrix. Higher magnification analyses (lower row panels) reveal the fine structured CuCN\textsubscript{x} composed of layers enriched in Cu and C.](image)

AFM topography analysis (Figure 5) reveals that the surface of the samples is not smooth and has similar morphology for all samples regardless of the deposition parameters. Since the sample cross-section data do not indicate similar rough structuring inside the bulk of the samples, the fractal-like structures are clearly caused by transient conditions after finalizing the deposition of the Cu and CuCN\textsubscript{x} layers.

![Figure 5 AFM topography images of the coatings. The rough surface is due to post deposition of carbonaceous particles in the transient cooling period of the reactor chamber.](image)
For all produced samples, Raman spectra (collected from the cross-sectioned samples) show two broad bands indicating the presence of amorphous carbon (Figure 6A). After fitting with base line corrected Lorentzian components, the two observed bands are centred around 1560 cm$^{-1}$ (G-band) and 1370 cm$^{-1}$ (D-band) as shown in Table 3. G-band is correlated with the in-plane vibrations of sp$^2$ hybridized carbon, while the D-band is due to defect sites having sp$^3$ hybridization [44, 45]. The intensity ratio of D and G-bands I_D/I_G is observed to be constant with the deposition process peak power. This result indicates that increased deposition discharge power and plasma density have insignificant effect on the formation of defects or on the graphitization of the deposited carbon. The copper interlayers seem to have no influence on the formation of the Cu:CuCN$_x$ layers either. In addition to Raman spectroscopy, XRD patterns of each sample were collected in order to identify any crystal phases in the composites. The reflections in the XRD patterns correspond to (111), (200) and (220) planes of faced-centred-cubic (fcc) structure of copper as well as to cuprous oxide (Figure 6B). This result is in agreement with the measured lattice spacing values of 2.1 Å and 2.4 Å which may be assigned to Cu(111) and Cu2O(111), respectively (Figure S2). In the case of the CN$_x$ layer (sample A), the XRD pattern also show a reflection assigned to silicon (Figure 6B). In this particular case, the XRD pattern can be attributed to the copper pre-layer and the silicon substrate indicating that the CuCN$_x$ coating is amorphous material in agreement with Raman analysis. The average crystal size for Cu was calculated from the peak broadening (by integral breadth method) to decrease from 18 to 13 nm with increasing plasma peak power which has been found earlier associated with the formation of globular nanosized crystal structure [30].
Figure 6 (A) Raman spectra and (B) X-ray diffraction patterns of CN\textsubscript{x} film deposited on a Cu pre-layer (black plots) and multilayered Cu:CuCN\textsubscript{x} coatings synthesized using different conditions (red, blue and green plots). Note: the reflections assigned to Cu in the CN\textsubscript{x} film are due to the Cu pre-metallization layer of the substrate. In the case of the Cu:CuCN\textsubscript{x} coatings, the reflections of Cu are due to the inter-metallization layers and to the Cu inclusions in the Cu:CuCN\textsubscript{x}.

Table 3 D and G peak positions and intensities ratios ($I_D/I_G$) for all samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td>D-peak (cm\textsuperscript{-1})</td>
<td>1366</td>
<td>1377</td>
<td>1378</td>
<td>1377</td>
</tr>
<tr>
<td>G-peak (cm\textsuperscript{-1})</td>
<td>1576</td>
<td>1566</td>
<td>1569</td>
<td>1563</td>
</tr>
<tr>
<td>$I_D/I_G$</td>
<td>0.75±0.08</td>
<td>0.81±0.03</td>
<td>0.73±0.02</td>
<td>0.72±0.03</td>
</tr>
</tbody>
</table>

3.2 Mechanical properties

Figure 7A and B shows the typical loading-unloading curves for CN\textsubscript{x} and Cu:CuCN\textsubscript{x} coatings at 5N load and the corresponding creep tests. The average value obtained for the hardness and elastic modulus are plotted in Figure 7 C and D, respectively. For CN\textsubscript{x} coating, Vickers hardness micro-indentation analysis shows that 35% of the indentation work is due to elastic deformation. No significant changes were observed on the elastic deformation (~32% in average) after Cu inclusions and Cu interlayers were incorporated to the CN\textsubscript{x} matrix. In addition, it was observed that not only the hardness decreased (sample B, Figure 7C), but also the elastic modulus slightly decreased (sample B, Figure 7D). On the other hand, both hardness and elastic modulus significantly improved when peak power was increased and reduced plateau discharge are used in the course of deposition (samples C and D, Figure 7C-D). There is higher plasma density in pulse discharge comparing to plateau discharge [37] which could explain the observed increase for the coating hardness on samples C and D. Although the substrate is known to have possible effect on the hardness and elasticity of thin films [46], the presented coatings with thickness of hundreds of micrometers cannot be regarded as thin films thus we do not expect any direct influence of the steel and Si surfaces on the mechanical properties of our coatings. Furthermore, the maximum indentation depth in our experiments was less than 10% of the coating thickness to make sure the results reflect the true materials properties of the films.

The creep at maximum static load during the holding time of 10 s (Figure 7B) was used to calculate the loss factor in order to evaluate the damping property of the coatings. The hold period is of importance as it may affect the accuracy of hardness and modulus measurement [47]. The recommended hold period for the coating material is >100 s after which the indentation depth increase due to creep in 1 min is
less than 1% of the total indentation depth. The shortened hold period of 10 s used in the Vickers indentation test leaded to overestimated hardness and modulus of the damping coating in the present study, however up to a certain extent of approximately 5%. The minimum time needed for a creep event [48] is the reciprocal value of parameter B in equation (1) and its value is less than 1.5 s for all of the damping coating samples. Although the holding period of 10 s is short comparing to the recommended holding period, it is enough to make a correct estimation of parameter A in equation (1). The residues of the curve fitting for all points are less than 10 nm which is comparable to the resolution of the indentation depth measurement. This indicates that the parameter A in equation (1) estimated by non-linear curve fitting method and the loss factor calculated by equation (2) are acceptable. The current study focuses more on the comparison study of the damping coatings’ properties than accurate measurement of their exact values. The results clearly show that damping property (loss factor) improved after adding the copper inclusions as compared to the bare CN₅ coating (Figure 7D). The smaller crystal sizes observed when applying higher discharge power further improved the damping since it increased the grain boundary/interface area. Accordingly, the loss modulus (product of elastic modulus and loss factor) for sample D reached the value of 2.6 GPa which can be categorized as a high dynamic stiffness material according to the stiffness-loss map [5, 11].
Figure 7 A, Representative loading and unloading hysteresis for CN (sample A) and Cu:CuCN (sample B, C and D) coatings; B, Creep tests results (dots) and fitting according Eq. (1) (black line); C, Surface micro hardness (blue squares) vs. deposition process discharge peak power (red dots); D, Elastic modulus (blue squares) vs. sample’s loss factor (red dots).

Since the average crystal size of sample D (approximately 13 nm) is smaller than half of the CuCN nanostructure periodicity, the main contributor of the observed damping property improvement is due to the nanosized crystals instead of the interfaces between the alternating layers inside the CuCN layer. However, both the nano size crystals and nano thickness alternating layers are able to improve the composites damping property due to the introduced grain boundaries/interfaces.

3.3 Model and machining testing results

In order to evaluate the coating performance, deposition conditions similar to that of sample D with higher discharge current at 250 A was used to apply a 280 µm thick coating on the surface of a milling tool (elastic modulus of 36±3 GPa, hardness of 2.4±0.2 GPa, and loss factor of 0.07±0.02). Prior machining, impact modal analysis was conducted to compare the dynamic properties of the tooling structure with and without the coating. Model analysis results are summarized in Table 4. Although the coated tool was measured to have 6.5%-29.6% higher damping than that of the uncoated reference tool, its mode mass, mode frequency and mode stiffness are slightly lower than that of the reference tool.

Table 4 Model testing result of the coated and reference tools

<table>
<thead>
<tr>
<th>Model analysis results</th>
<th>Uncoated reference tool</th>
<th>Coated Tool</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>X</td>
<td>Y</td>
</tr>
<tr>
<td>Mass (kg)</td>
<td>0.199</td>
<td>0.107</td>
</tr>
<tr>
<td>Frequency (Hz)</td>
<td>833</td>
<td>908</td>
</tr>
<tr>
<td>Damping ratio</td>
<td>0.042</td>
<td>0.027</td>
</tr>
<tr>
<td>Stiffness (10^8 N/m)</td>
<td>5.5</td>
<td>3.5</td>
</tr>
</tbody>
</table>

Stability limit curve for the tools were experimentally determined for both the reference and the coated tool as shown in Figure 8. The critical stability of the reference tool was found to be <0.05 mm. In contrast, the critical stability limit increased up to >0.2 mm after the damping coating is applied on the clamping region.
of the milling tool. Theoretical stability limits for both the tools are inserted in Figure 8 and they were calculated by the stability lobes diagram method proposed by Gurney and Tobias [49]. Since slot milling was performed in X direction of the milling machine, the movement of the cutting tool was free in X direction and was constrained in Y direction. The modal analysis results of the tools at mode 1 and mode 2 in X direction were used to generate the stability lobes diagrams in Figure 8. The specific cutting force was pre-set at 2000 MPa for regular steel. The presented theoretical stability limit in Figure 8 took the minimum of the stability limit curves of mode 1 and mode 2 in X direction over different spindle speed.

As a new cutting edge is used for each of the machining test and the cutting speed is relatively high for process damping phenomenon [42], the increased machine tool dynamic stiffness was the main reason for the increased critical stability limit. The critical stability limit is inversely proportional to the negative minimum real part of the machine tool structure’s transfer function [50] expressed as:

$$a_{p_{cri,lim}} = -\frac{1}{2 \times k_c \times \min(\text{real}[G(w)]) \times \mu}$$

(3)

Where $a_{p_{cri,lim}}$ is the critical stability limit expressed in depth of cut, $k_c$ is the specific cutting force [51], $G$ is the transfer function of a machine tool structure, $w$ is the angular frequency and $\mu$ is the overlapping factor determined by the machining parameters. A machine tool structure vibrating at a certain mode can be modelled as:

$$m\ddot{x} + (k + i\eta k)x = F$$

(4)

Where $m$ is the mode mass, $\ddot{x}$ is the acceleration, $k$ is the static stiffness, $\eta$ is the loss factor, $\eta k$ is the dynamic stiffness (product of loss factor and static stiffness), $x$ is the displacement and $F$ is the excitation force. The transfer function [$G(w)$] can be defined as:

$$G(w) = \frac{x}{F} = \frac{1}{(-mw^2 + k) + i\eta k} = \frac{-mw^2 + k}{(-mw^2 + k)^2 + (\eta k)^2} - i \frac{\eta k}{(-mw^2 + k)^2 + (\eta k)^2}$$

(5)

and the negative minimum real part of $G(w)$ can be expressed as:

$$\min(\text{real}[G(w)]) = -\frac{1}{2\eta k}$$

(6)
when \(-mw^2 + k = -\eta k\). The critical stability limit can be expressed:

\[ ap_{\text{crit,lim}} = \frac{\eta k}{k_e \times \mu} \]  

(7)

The critical stability limit is directly proportional to the dynamic stiffness of the machine tool structure. The critical stability of the milling tool was observed to increase from <0.05 mm to >0.2 mm by the damping coating and therefore the dynamic stiffness of the cutting tool was increased by at least 300%.

The sound signal frequency band indicates that both the 1\textsuperscript{st} and 2\textsuperscript{nd} modes are excited under chatter condition in X or Y direction suggesting that the coating improves tool performance (since it is embedded in the regions where the vibrations strain energy concentrates for the 1\textsuperscript{st} and 2\textsuperscript{nd} modes).

Although the coating was observed to improve the critical stability limit of the machining tool by at least 300%, the modal analysis result did not show any significant difference between the coated and reference tools. This is due to the reason that the grain boundary relaxation phenomenon is strongly dependent on excitation energy/strain [7, 12], and the excitation energy is probably not sufficiently high in the course of our impact testing experiments to trigger the internal friction damping phenomenon of the composite coating.
4. Conclusions

High power impulse magnetron sputtering technology was utilized to synthesize high loss modulus composites with high elastic modulus. High density plasma discharge produced by high peak power and eliminated plateau discharge helped in the formation of composite materials with reduced average crystal size thus increased internal grain boundary surface area. An introduction of Cu inclusions in the CN$_x$ material to form CuCN$_x$ nanocomposites and multi-layered Cu:CuCN$_x$ composites was found to increase both the loss factor and elastic modulus of the coatings deposited on steel and Si surfaces.

Comparing our results to the properties of poly(methyl methacrylate) [48], a polymer often used in damping applications, the Cu:CuCN$_x$ composite has similar loss factor
(7.7% versus 7.2%), substantially higher hardness (2.3 GPa versus 0.4 GPa), higher elastic modulus (34 GPa versus 4 GPa) and higher loss modulus (2.6 GPa versus 0.3 GPa). The results suggest an immense potential for generating high loss modulus materials and resolving critical engineering applications subjected to severe vibrations. To demonstrate this, the composite with the highest loss modulus was applied on the clamping region of a milling tool, and according to machining tests, the critical stability limit of the tool could be increased by at least 300%. Such an improvement will result in a radically higher machining capability and significant economic impact in industrial applications.

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References


