

DOCTORAL (PhD) DISSERTATION



INVESTIGATION OF NEW COMPOSITION CVD COATING FORMULATIONS IN TERMS OF MECHANICAL PROPERTIES AND CUTTING EFFICIENCY

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1. INTRODUCTION

In metal cutting operations, tool performance directly effects on the manufacturing efficiency, productivity, and the costs. As industrial demand for machined components continues to rise, enhancing the durability and performance of cutting tools has become a critical technological challenge. This dissertation addresses this challenge through a comprehensive investigation of titanium nitride TiN-based coatings deposited by chemical vapor deposition (CVD), with a particular focus on their tribological behavior, oxidation resistance, and wear properties.

This study employs advanced characterization techniques, including scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM-EDS), optical microscopy (OM), X-ray diffraction (XRD), mechanical testing (Vickers microhardness, tribology, surface roughness, adhesion), and thermal analysis (thermal conductivity, infrared imaging, and oxidation testing). This multifaceted approach enables a comprehensive evaluation of different coating systems, including bilayer TiN/TiC, TiCN/Al/TiN, and other TiN-based coatings applied to WC-Co cermet and steel substrates.

Today, with increasing performance requirements for machined components, the application of hard coatings has emerged as a powerful solution to improve the properties of cutting tools against wear and thermal shock under service conditions. For over three decades, depositing hard coatings onto cemented carbide cutting tools has proven remarkably effective in enhancing tool lifetime and cutting performance. The commercial application of these coatings began with the thermal chemical vapor deposition (CVD) process. Currently, hard coatings have evolved into

complex composites consisting of various materials, each fulfilling different requirements, such as excellent adhesion to the substrate with minimal interaction with the workpiece material. The development of hard coatings initially began with the single layer coatings. Subsequently, the variety expanded with the development of hard materials such as TiC and TiN.

This research provides significant contributions by developing more accurate wear testing protocols to enhance the reliability of coating performance evaluations, deeper understanding of oxidation behavior to extend tool life in high-temperature applications, and identifying optimal coating compositions and structures to improve tribological performance.

2. SCOPE & OBJECTIVES OF PRESENT STUDY

This PhD dissertation aims to develop and evaluate the TiN-based CVD coatings that can significantly enhance the performance of cutting tools. The study focuses on the following objectives:

1. Investigation of mechanical properties: Assessing the micro-hardness, wear and tribological properties of the CVD coatings.
2. Characterization of coating structures: Utilizing advanced techniques such as X-ray diffraction (XRD), scanning electron microscopy (SEM), and energy-dispersive X-ray spectroscopy (EDS) to study the microstructure and composition of the coatings.
3. Evaluation of oxidation behavior: Analyzing the oxidation resistance of the coatings at high temperatures to

determine their thermal stability and potential for use in the extreme conditions.

4. Evaluation of coating composition: Experimenting with different CVD coatings to identify the optimal coating thickness, number of layers, and elemental composition that offer the best performance in terms of durability and resistance to wear and adhesion.

3. MATERIALS AND METHODS

All samples presented in the study were produced by Büttner Ltd. (Nagyatád, Hungary) in a newly developed reactor located at their site. Tungsten carbide-cobalt composite and alloy steel were used as substrates for the coatings. The process involved the use of precursors such as titanium tetrachloride (TiCl₄), nitrogen (N₂), hydrogen (H₂), and argon (Ar). Table 1 details the manufacturing parameters for bilayer TiN/TiC CVD-coated samples. These samples were categorized into two groups: sample A and sample B. For sample A, the conditions included a lower temperature and double the pressure relative to sample B. The flow rate of precursor gases was kept nearly constant in standard liters per minute (SLM), and the TiC layer was deposited under the same parameters for both samples.

Table 1: Manufacturing parameters for bilayer TiN/TiC CVD-coated samples.

Samples	Layers	Time (h)	Temperature (°C)	Pressure (mbar)	SLM H ₂	SLM CH ₄	SLM N ₂	SLM TiCl ₄
A	TiN	3.00	980	100	4.10		4.10	8.20
	TiC	2.00	1000	80	9.24	1.00		8.22
B	TiN	3.00	1020	50	3.50		4.50	8.00
	TiC	2.00	1000	80	9.24	1.00		8.22

Table 2 summarizes another TiN-based CVD coating examined during the experimental work and their abbreviations. The titanium nitride-based coatings were produced with varying manufacturing parameters, including the volumetric flow rate of precursors, temperature, and pressure. Tungsten carbide cobalt cermet and steel were used as substrates for the coatings. Nine different samples of titanium nitride-based coatings were examined during the work, with thicknesses ranging from 0.3 to 8.6 μm . For the WC-Co substrate coated with titanium carbide and titanium nitride layers, the main goal was to study the effect of the titanium carbide layer on tool life, similar to the sample containing the aluminum oxide support layer. The purpose of examining the steel sample was to study the tribological properties of the coating with sub-micrometer thickness.

Table 2. The abbreviations and the type of other TiN-based coatings.

Sample	Layer type	Substrate	Thickness (μm)		
			Layer 1	Layer 2	Layer 3
TiN1	single layer	WC	0.3-0.6		
TiN2	single layer	WC	0.7-0.9		
TiN3	single layer	WC	1.8-2.8		
TiN4	single layer	WC	2.9-3.8		
TiN5	single layer	WC	5.8-7.2		
TiN6	single layer	WC	6.3-7.8		
TiC/TiN	two-layer	WC	1.2-1.4	1.5-3.1	
TiCN/Al/TiN	multi-layer	WC	8.1-8.6	2.2-3.1	0.9-1.1
TiCN	single layer	ST	0.5-0.7		

3.1 Morphological and characterization measurements

Morphological and characterization analyses were conducted to evaluate the structural and elemental properties of the coatings. These analyses are critical for understanding the surface and internal features, providing insights into performance and potential applications.

3.1.1. Preparation the samples for measurements

The preparation of samples for scanning electron microscopy and energy-dispersive X-ray spectroscopy involved careful cleaning to ensure optimal imaging quality. Samples were cleaned in an ultrasonic bath containing ethanol and acetone to remove contaminants and enhance resolution for back-scattered electron imaging. Cross-sectional samples were embedded in epoxy resin (NXMET XF40) and polished to achieve a smooth surface, crucial for clear visualization of internal structures. This preparation ensured high-quality images and accurate data, facilitating comprehensive analysis of the CVD coatings.

3.1.2 Scanning electron microscopy

SEM and EDS were utilized to investigate the surface morphology, microstructure, and elemental composition of the coatings. The SEM analysis was conducted using a FEI/Thermo Fisher Apreo S scanning electron microscope under high vacuum conditions with an accelerating voltage of 20 kV. SEM utilizes an electron beam with energies between 100 eV and 30 kV, focused on specific points of the sample surface, causing the emission of various particles. The signals produced by electron-material interactions are detected by different detectors, with the beam moving across the surface to generate a time-varying signal

corresponding to the detected signal intensity, producing a grayscale image on the display. Each pixel in the image represents a specific point on the sample.

Depending on the detector used, different material properties can be visualized. Secondary electron (SE) detectors provide surface morphology images, while BSE detectors offer atomic number contrast images. Additionally, EDS detectors allow for local compositional analysis by measured the energy and intensity of characteristic X-rays induced by the electron beam, facilitating both qualitative and quantitative analysis. EDS detectors also enable elemental mapping, determining the composition at each pixel and displaying elements in different colors for visual interpretation. SEM can operate in scanning transmission electron microscopy (STEM) mode to examine samples smaller than 200 nm. This mode, analogous to light microscopy using transmitted light, produces a true magnified image from electrons passing through the sample. The highest resolution achievable with SEM is 1-2 nm.

EDS analysis was performed to determine the elemental composition of the coatings used an EDAX AMETEK Octane Elect Plus Energy Dispersive X-ray Analyzer, operating at an accelerating voltage of 20 kV with a data collection time of 180 seconds.

3.1.3. Optical microscopy (OM)

In this study, optical microscopy (OM) was employed to examine the microstructure and surface features of the CVD-coated samples. The analysis was performed used a Keyence VHX-2000 digital light microscope, which provides high-resolution images with significant depth of field, allows for detailed observation of the coatings' surface morphology.

3.1.4. X-ray diffraction (XRD) measurement

The measurements were performed using a Philips PW 3710 diffractometer with CuK α radiation (50 kV, 40 mA). The scan rate was set to 0.02° 2 θ /s over a range of 10 to 70 degrees 2 θ , employing a curved graphite monochromator. Data collection and analysis were facilitated using X'Pert Data Collector software and High Score Plus 5.0 software, respectively. Phase identification and quantitative phase analysis were conducted using the Rietveld method, with reference to the 2021 Powder Diffraction Files (PDF-2 2021) from the International Centre for Diffraction Data (ICDD).

3.2 Mechanical tests

3.2.1 Vickers micro-hardness test

Vickers microhardness test is a widely used non-destructive method to determine the hardness of CVD-coated samples. In this study, a diamond pyramid indenter was applied to the sample surface under a predetermined force.

Microhardness was measured for both coated and uncoated (reference) samples by used a Vickers microhardness tester (Wolpert 402 MVD, Fritz Müller GmbH, München, Germany) with a load of 0.2 kgf. The hardness values were averaged from five readings per specimen. The indentation diameter was used to calculate the penetration depth of the diamond pyramid, allowed for the distinction between the hardness of the coating and that of the substrate.

3.2.2 Tribological test

The tribological behavior of the coatings was evaluated through dry-sliding experiments conducted by used a TRB3 type tribometer (Anton Paar GmbH, Buchs, Switzerland) in ball-on-disc configuration, based on ASTM standards G99-05 and G133-05. In these tests, the coated samples were evaluated against two different counterface materials: steel, using an Anton Paar 100Cr6 steel ball, and zirconia, using a Fritsch zirconium oxide grinding ball, which complies with the manufacturer's datasheet (composition: ZrO_2 : $\geq 94.2\%$, HfO_2 : $\geq 1.0\%$, MgO : $\leq 3.5\%$ and other: 1.3%). The diameters of the steel and zirconia balls were 6 mm and 5 mm, respectively. All experiments were conducted at a controlled temperature of $25^\circ C$ in ambient air with a relative humidity of $46 \pm 3\%$.

The experimental parameters were systematically maintained, with the maximum sliding speed set at 15.71 cm/s, the normal load fixed at 20 N and stroke length about 10 mm. Throughout the tests, the coefficient of friction (COF) was continuously recorded in relation to the sliding distance, providing valuable data on the frictional performance of the coatings. After the completion of each test, the wear tracks on the samples were carefully cleaned with alcohol to remove any loose wear debris. Subsequently, wear tracks measured by profilometer to evaluate the extent of wear. Additionally, SEM, EDS, and optical microscopy were used to analyze the wear tracks.

To quantitatively compare the wear resistance of the CVD coatings, the wear volume (V^P , mm^3) was calculated according to the standards mentioned above, by used the following equations:

$$V_P = (\pi h / 6) [3D^2 / 4 + h^2] \quad (2.1)$$

$$h = R - [R^2 - (D^2 / 4)]^{1/2} \quad (2.2)$$

Where:

V_P : wear volume, or volume loss (mm^3), h : height of the removed material from the ball (mm), D : diameter of the wear scar on the ball. R : original ball radius (mm).

3.2.3. Surface roughness measurement

Surface roughness measurements were conducted to quantify the surface texture of TiN-based coatings utilized in the present study. The analysis was performed using a Taylor Hobson/AMETEK Surtronic S128 surface profilometer (GmbH, Leicester, England). Surface roughness parameters, including average roughness (R_a), root mean square roughness (R_q), and maximum peak-to-valley height (R_z), were determined to characterize the topographical features of the coatings.

3.2.4. Adhesion test (scratch test)

A modified scratch test was conducted to evaluate the adhesion of the CVD-coated samples. The test was performed by using a TRB3 tribometer (Anton Paar GmbH, Buchs, Switzerland). In contrast to the standard scratch test, where the normal load gradually increased, this modified method applied a constant normal force of 5 N throughout the test. (Different forces (1 N, 2 N, 5 N and 10 N) were initially tested on a CVD-coated sample to determine the optimal load, and 5 N was the most suitable). The stroke length was fixed at 10 mm. The diamond indenter (stylus) marks on the coated surface were examined via a scanning electron microscope to observe coating failures.

3.3 Thermal analysis measurements

3.3.1 Thermal conductivity measurement

The thermal conductivity of the coated samples was determined by used a CTherm TCi™ device. Measurements were conducted with the heating element set to 150°C, employed a 3-second heat pulse and a total measurement time of 7 seconds. For each sample, five parallel measurements were performed to ensure accuracy. Distilled water was utilized as the contact agent to facilitate effective thermal transfer during the measurements.

3.3.2 Thermal camera

A thermal camera (Trotec XC300, Trotec GmbH, Heinsberg, Germany) was used to monitor temperature distribution and capture thermal images of the coated samples during dry-sliding experiments against steel and zirconia balls.

3.3.3 Oxidation tests

The cyclic oxidation experiment was performed under ambient atmospheric conditions. The samples were entered into a specified furnace (Ivoclar Programat P80) after the temperature inside the furnace reached to 800°C (thermal-shock), the procedure of oxidation process was as the following:

During first five cycles, oxidation time was 2 minutes per a cycle. The sixth cycle had an oxidation time of 10 minutes. Finally, the seventh cycle was 20 minutes. The cumulative duration of the oxidation process was 40 minutes. Post-cooling, the oxygen content of the samples determined by used energy-dispersive X-ray spectroscopy (EDS) after every single oxidation cycle.

4. NEW SCIENTIFIC FINDINGS

1. I have experimentally demonstrated that steel counterparts exhibit significant adhesion to the coating surface within a critical time of 20–60 seconds during ball-on-disc testing, while zirconia counterparts show no adhesion effects. Moreover, I have established that using zirconium oxide effectively eliminates the heating of components when processing similar material systems (*Jakab et al., 2023*).
2. Through a novel approach, I have analyzed the oxidation behavior of CVD bilayer TiN/TiC coatings at 800°C, quantitatively demonstrating that the oxygen content increases to over 68% after 40 minutes, accompanied by a significant decrease in carbon and nitrogen due to their interaction with oxygen. XRD analysis confirmed the transformation of TiN into rutile-TiO₂ after 20 minutes (*Ali et al., 2024*).
3. The oxidation process significantly affected the mechanical properties of CVD bilayer TiN/TiC coatings, particularly in terms of hardness degradation and volume loss, as detailed below:

Statement 3a:

Oxidation at 800 °C led to a marked reduction in Vickers microhardness, decreasing by 78.15% and 57.80% for sample A and sample B respectively, after 40 minutes. This decline is attributed to oxide formation, increased porosity, and crack development caused by the release of gaseous by-products (*Ali et al., 2024*).

Statement 3b:

Tribological performance was similarly affected. Dry sliding tests conducted using a zirconia counterpart at a sliding speed of 15.71 cm/s and an applied normal load of 20 N revealed a significant increase in volume loss. Specifically, the volume

loss increased from $2.04 \cdot 10^5$ to $4.15 \cdot 10^5 \mu\text{m}^3$ for Sample A, and from $1.42 \cdot 10^5$ to $7.31 \cdot 10^5 \mu\text{m}^3$ for Sample B (*Ali et al., 2024*).

4. Through observation of the oxidized surfaces of CVD TiN/TiC coatings, I have demonstrated a color change from gold/yellow to greyish-black during oxidation process. This color transition can serve as a visual indicator for evaluate the oxidation stages and identifying damage in coated cutting tools with same elemental composition (*Ali et al., 2024*).
5. Through comparative analysis, I have established that the stability of TiN-based CVD coatings—defined by their structural integrity and wear resistance—is primarily dominated by surface roughness and hardness. These factors play a more significant influence on wear volume than coating thickness (*Osamah Ali et al., 2024*).

5. PUBLICATION LIST

Published articles related to thesis research

1. **Gyurika, I., Ali, O., & Jakab, M.** Determination of Research Guidelines and Establishing of Test Framework for the Development of New CVD Coating Formulations and New Approach Coating Equipment, Indexed in Springer Nature and Scopus. In *STUE* (2022), Vol. 536, pp 420–431. doi.org/10.1007/978-3-031-20141-7_39
2. **Ali, O., & Gyurika, I.** Recent Advances in Development and Characterization of CVD Multilayer Composite Coatings-A Comprehensive Review. Indexed in Springer Nature Switzerland and Scopus. In *ICTM* (2022), Vol. 657, pp 63–75. doi.org/10.1007/978-3-031-36201-9_6
3. **Jakab, M., Ali, O., Gyurika, I., Korim, T., & Telegdi, J.** (2023). The Tribological Behavior of TiN/TiC CVD Coatings under Dry Sliding Conditions against Zirconia and Steel Counterparts. *Coatings*, 13. doi.org/10.3390/coatings13050832. IF= 2.9, CiteScore: 5.0
4. **Ali, O., Gyurika, I., Korim, T., & Jakab, M.** (2024). A novel approach to investigate oxidation behaviour and mechanical properties of CVD bilayer TiN/TiC coatings. *Processing and Application of Ceramics*, 18, 213–223. doi.org/10.2298/PAC2402213A. IF5=1.4, CiteScore: 2.2
5. **Ali, O., & Gyurika, I.** (2024). Oxidation Behaviour of TiC/TiN Coatings Deposited by Chemical Vapor Deposition (CVD): Mechanisms, Structures, and Properties. *Archives of Advanced Engineering Science*, 1–12. doi.org/10.47852/bonview AAES42022613
6. **Osamah Ali, István Gyurika, Tamás Korim, & Miklós Jakab** (2024). Comparison of Wear and Friction Properties of Titanium-Nitride Based Coatings, *Hungarian Journal of*

Conference oral presentation related to thesis research

1. I. G. Gyurika, **O. I. Ali** and M. Jakab, “Determination of Research Guidelines and Establishing of Test Framework for the Development of New CVD Coating Formulations and New Approach Coating Equipment,” *STUE Conference Proceedings*, vol. 536, pp. 420–431, 2022.
2. **O. I. Ali** and I. G. Gyurika, “Recent Advances in Development and Characterization of CVD Multilayer Composite Coatings — A Comprehensive Review,” in *Proc. Int. Conf. Integrated Computer Technologies in Mechanical Engineering – Synergetic Engineering*, Kharkiv, Ukraine, Nov. 18, 2022.
3. **O. I. Ali** and I. G. Gyurika, “A Review of Techniques Utilized for Tests of Extraordinarily Hard Chemical Vapour Deposition Coatings,” in *Proc. Int. Congr. Contemporary Scientific Research*, Gaziantep, Türkiye, Nov. 2–3, 2022.
4. **O. I. Ali**, I. G. Gyurika and M. Jakab, “The Tribological Behavior of TiN/TiC CVD Coatings under Dry Sliding Conditions Against Zirconia and Steel Counterparts,” *Materials Science Day XXIII of PhD Students*, Veszprém, Hungary, Nov. 20, 2023.
5. **O. I. Ali** and I. G. Gyurika, “Investigating the Microstructure and Properties of CVD Coatings for Cutting Tools Based on Cermet,” in *Proc. 7th Int. Conf. Innovative Studies of Contemporary Sciences*, Tokyo, Japan, Apr. 21–23, 2023.
6. **O. I. Ali** and I. G. Gyurika, “Advances of TiCN CVD Coatings for Enhanced Cutting Tool Performance,” in *Proc. Int. Conf. Global Practice of Multidisciplinary Scientific Studies-IV*, Turkish Republic, Apr. 28–30, 2023.

7. **O. I. Ali** and I. G. Gyurika, “Mechanical Characterization of Advanced Chemical Vapor Deposition Coatings for Cutting Tool Applications,” in *Proc. Int. World Energy Conf.*, Turkish Republic, Dec. 4–5, 2023.
8. **O. I. Ali** and I. G. Gyurika, “Microstructural Enhancement of CVD Coatings for Machining Applications,” in *Proc. Int. Conf. Trade and Logistics Symposium-II*, Bursa, Türkiye, May 10, 2024.
9. **O. I. Ali** and I. G. Gyurika, “Improvement Characterization of CVD Coatings for Machining Applications,” in *Proc. 7th Int. Antalya Scientific Research and Innovative Studies Congr.*, Antalya, Türkiye, May 11–13, 2024.
10. **O. I. Ali** and I. G. Gyurika, “A Comprehensive Analysis of Physical and Chemical Vapor Deposition Methods for Advanced Hard Coatings in Cutting Tools,” in *Proc. 8th Int. Conf. Global Practice of Multidisciplinary Scientific Studies*, Dubai, Sept. 25–29, 2024.
11. H. Al-Ethari, **O. I. Ali** and S. F. Namah, “Influence of Warm Forming on Characteristics of Cu10wt%Sn Cast Alloy,” in *Proc. Int. Scientific and Technical Conf. Integrated Computer Technologies in Mechanical Engineering – Synergetic Engineering*, Kharkiv, Ukraine, Dec. 23, 2024.