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Large-area high-rate pulsed laser deposition of smooth TiC_xN_{1-x} coatings at room temperature—mechanical and tribological properties

J.M. Lackner[a,*], W. Waldhauser[a], R. Ebner[a,b]

[a]*Laser Center Leoben, Joanneum Research Forschungsgesellschaft mbH, Leobner Strasse 94, A-8712 Niklasdorf, Austria*
[b]*Materials Center Leoben, Franz-Josef-Strasse 13, A-8700 Leoben, Austria*

Abstract

Titanium carbonitride (TiC_xN_{1-x}) hard coatings possess excellent tribological behavior in metal punching and forming as well as high biocompatibility. Because almost all PVD and CVD coating techniques for TiC_xN_{1-x} coatings require substrate temperatures higher than 150–200 °C for reaching sufficient adhesion strength to the substrate surface, there is high demand in the development of large-area and high-rate low-temperature vacuum deposition processes. In the present work, this call was fulfilled by the application of the room temperature pulsed laser deposition (PLD) for TiC_xN_{1-x} coating with various carbon (x) and nitrogen contents.

A pulsed Nd:YAG laser (wavelength: 1064 nm) was used for the vaporization of pure titanium targets in low-pressure N_2/C_2H_2 atmospheres. The highly ionized metal vapor was deposited onto polished substrates (molybdenum, AISI D2 steel), forming a nearly particulate-free, very smooth and dense film structures, which can be hardly reached by using other PVD techniques. The variation of the gas flow during deposition causes a change of the chemical composition and the microstructure of the nearly particulate-free coatings, and, consequently, of the mechanical and tribological properties. The solid solution hardening of the fcc TiN lattice by low contents of carbon increases the hardness and elastic modulus, while higher carbon contents decrease this effect. Furthermore, the maximum in hardness and elastic modulus correspond with the minima in the friction coefficients (~0.2) and Wear rates of both the coated disc and the counterparts (AISI 52100 (DIN 100Cr6) ball-bearing steel balls).
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Keywords: Pulsed laser deposition; PLD; Laser ablation; Titanium carbonitride; TiCN; Tribology

1. Introduction

Over the past decade, the extension of the service life of cutting and forming tools, and mechanical components has been successfully achieved by applying thin hard coatings onto their surfaces. Initially, titanium nitride (TiN) coatings, favored for their high hardness as well as gold-like appearance, were most widely used for Wear and corrosion protection. Due to increasing demands on the surfaces of tools and mechanical components, TiN coatings were superseded by multi-component, multilayered and/or graded coating materials like, e.g. titanium carbonitride (TiC_xN_{1-x}) [1,2]. Ertuerk et al. [3] pointed out that TiC_xN_{1-x} films are solid solutions of fcc TiN and fcc TiC incorporating the advantages and characteristics of both. In contrast to TiN, TiC_xN_{1-x} coatings predominate with their better anti-adhesive [4] and anti-abrasive [5,6] capability.

In recent years, methods based on moderate-temperature CVD processes [7,8] and PVD processes [7,9,10] have been developed allowing the production of hard coatings with improved Wear resistance on temperature-sensitive materials like tempered tool steels. Although the plastics industry call for very low-temperature (<50 °C) vacuum coating techniques, which distinguish by excellent adhesion to the substrate surfaces towards chemical or galvanic coating, the development of such techniques turned out to be very hard. Additional difficulty is caused by particulates (droplets) which result from the target evaporation in many PVD processes (arc, sputtering, etc.). Besides influences of the substrates, thickness of the coatings, deposition sequences

* Corresponding author. Tel.: +43 3842 81260 2305; fax. +43 3842 81260 23010.
E-mail address: juergen.lackner@joanneum.at (J.M. Lackner).

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(in multilayer or graded coatings) and the type of Wear, also the surface morphology of the coating strongly affects the tribological performance of TiC_xN_{1-x} coatings [2].

Pulsed laser deposition (PLD) is one of the few coating techniques which fulfill the demands of both room-temperature deposition and very smooth coating surfaces [11–15]. By the development of a PLD coater designed for industrial applications at Laser Center Leoben, Austria, the high-rate PLD of almost all known engineering materials in inert or reactive high-vacuum atmospheres is now possible on large-area sheet and three-dimensionally shaped substrates [11–15]. The current work summarizes for the first time the achievements in large-area PLD coating on the example of the structural, mechanical and tribological behavior of TiC_xN_{1-x} coatings.

2. Experimental

2.1. Coating deposition

In the pulsed laser deposition (PLD) technique, a pulsed laser beam is focused onto a target in order to evaporate its surface layers under vacuum or low pressure gas conditions. In the current work, the ablation of the pure titanium (99.9% Ti) was performed by a pulsed Nd:YAG laser system, which provides four beams of 1064-nm wavelength with 0.6-J pulse energy and 10-ns pulse duration at a repetition rate of 50 Hz [11–15]. The vaporized material, consisting of atoms, ions and atomic clusters, is then deposited on the polished AISI D2 tool steel discs of 62 HRC hardness and molybdenum sheet, ultrasonically cleaned in pure acetone and alcohol. The advantage of this technique is the possibility to deposit coatings of high chemical purity and high adhesion to various substrate materials at room temperature [11–15]. The high adhesion—the best adhesion class HF1 on the 6-part scale for the DIN Rockwell indentation test—was also found for the TiC_xN_{1-x} graded multilayer coatings, which were deposited in different C_2H_2/N_2 gas mixtures after evacuation of the vacuum chamber to 3×10^{-3} Pa by the pumping system consisting of a turbomolecular and a rotary vane pump. The thickness of all coatings was set to 1.5 μm and contains an about 0.5-μm adhesive Ti–TiN graded interface and an about 1.0-μm-thick TiC_xN_{1-x} top layer deposited in the specified C_2H_2/N_2 gas mixtures. The multi-beam PLD approach, showed in Fig. 1, allowed large-area coating with low deviation (~5%) of the deposited coating thickness over the used deposition height of ~22 cm [11,12]. The given deposition rates in Fig. 1 reveal the high-rate film growth.

2.2. Coating characterization

The surface morphology of the coatings was investigated by scanning electron microscopy (SEM). This microscope is equipped with an energy dispersive spectroscopic analyzer (EDS) for chemical analysis. X-ray diffraction (XRD) investigations of TiC_xN_{1-x} coatings on Mo substrates were performed on a Bruker AXS D8 Discover diffractometer in grazing incidence alignment using 1° incidence of the primary CuKα X-ray beam. For hardness testing, a Fischerscope H100 nanoindenter was used. The maximum loads applied on the Vickers indenter were 10 mN. Ball-on-disc tests at a sliding speed of 10 cm s^{-1} were performed in the tribological characterization of the coatings on the coated D2 tool steel substrates at room temperature, ambient relative humidity (~60%) and 2 and 10 N load using AISI 52100 (DIN 100Cr6) ball-bearing steel balls of 6-mm diameter as counterparts. The coated discs as well as the balls were cleaned with pure acetone and alcohol prior to testing. Optical profilometry was applied for Wear track and surface roughness inspection as well as for calculating the Wear rates.

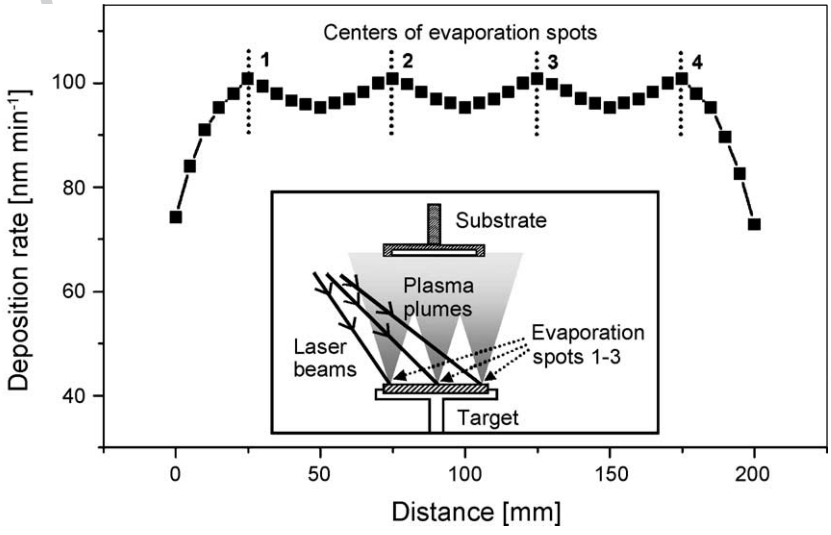

Fig. 1. Principle of the multi-beam pulsed laser deposition approach (insert) and deviation of the deposition rate of TiC_xN_{1-x} (5 sccm C_2H_2, 25 sccm N_2) over the deposited area.

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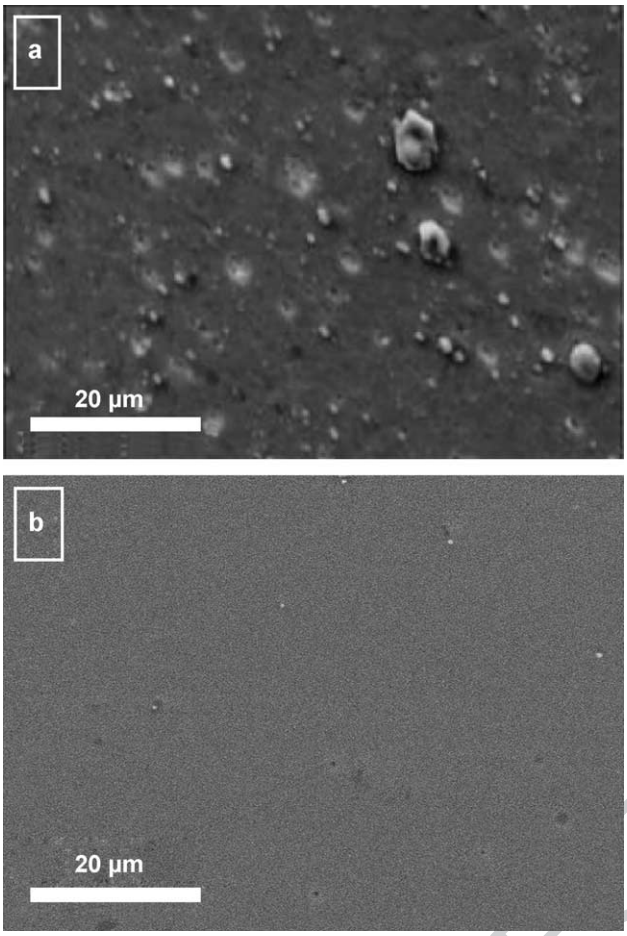

Fig. 2. Surface morphology of graded TiN–TiC_xN_{1-x} coatings found in SEM investigations: (a) unfiltered cathodic arc coating (3.2 µm thick, supplier: Ion Bond) [2], (b) PLD coating (1.5 µm thick).

3. Results and discussion

3.1. Coating morphology

In contrast to arc evaporated or magnetron sputtered TiC_xN_{1-x}, the PLD technique allows the deposition of very smooth and nearly particulate-free (droplet-free) hard coatings. This is shown in Fig. 2 by the comparison of a typical unfiltered cathodic arc film [2] and the PLD film. The particulates usually originate in the evaporation processes and are ejected besides the (partly) ionized vapor from the target [16]. In magnetron sputtering processes, these particulates are caused by chipping of either hard layers formed during sputtering of metallic targets with the reactive gas atmosphere (e.g. N_2, hydrocarbon compounds) or sintered grains from ceramic targets. In arc evaporated coatings, the particulates (droplets) originate from the push-out of molten target material at too high vapor pressures in the interaction zone of the arc and the target. Although both phenomena can also be found in pulsed laser ablation processes, the avoidance of particulates (droplets) is much easier for many target materials [17]. Besides the laser wavelength, the main influence on the droplet formation in PLD is the laser fluency on the target surface: A too high laser fluency results in high droplet density and rough coating surfaces, while a too low fluency (just higher than the evaporation threshold) prevents high-rate film growth and leads to inefficient deposition rates. Thus, the optimization process for the laser fluency is a golden mean between high-rate and high-quality film growth.

The average densities of particulates found on the arc and the PLD films were found to be about 22,000 and 800

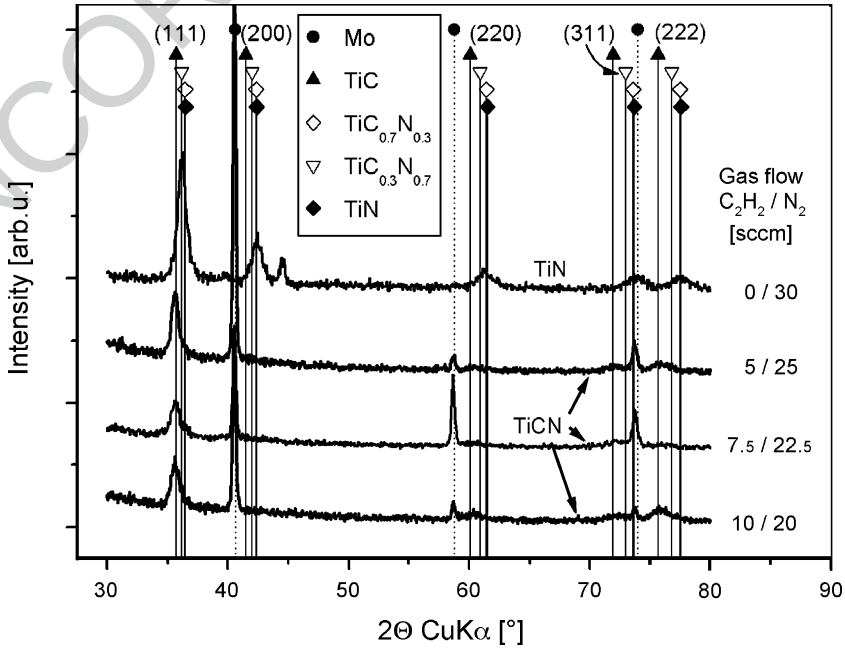

Fig. 3. XRD grazing incidence (1.0°) patterns of PLD TiC_xN_{1-x} and TiN coatings grown in atmospheres of various C_2H_2/N_2 gas flow mixtures on Mo substrates.

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droplets per mm^2 coating surface and μm coating thickness, respectively. The average area covered with droplets is about 100× higher for the arc (~60.4%) than for the PLD films (0.52%). Thus, the roughness was found to be about 28× lower for the PLD (R_a=4 nm) than for the arc coating (R_a=110 nm).

3.2. Microstructure

Due to the high energetic plasma, the microstructure of room-temperature PLD coatings [11–15] is mainly found to be of the Zone-T structure type of Thornton's structure zone model [18]. Such a structure was found too in the SEM

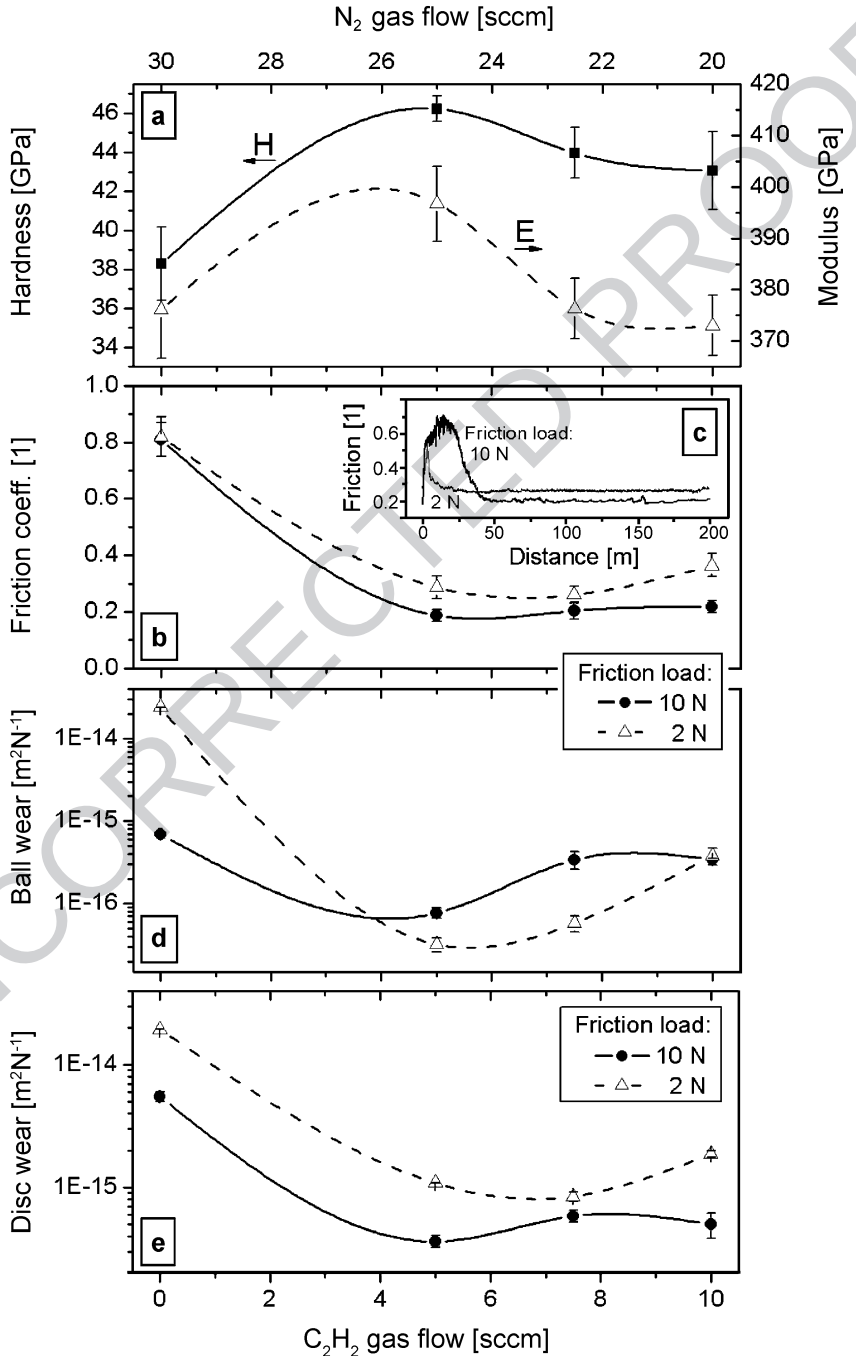

Fig. 4. Mechanical and tribological properties of the TiC_xN_{1-x} (TiN) coatings in dependency on the C_2H_2 and N_2 gas flow during deposition: (a) Hardness and elastic moduli, (b) evolution of the friction coefficient during sliding at different friction loads (Deposition parameters of the coating: 5 sccm C_2H_2, 25 sccm N_2 gas flow), (c) friction coefficient in the ball-on-disc tests, (d) wear rate of the uncoated AISI 52100 (DIN 100Cr6) ball counterpart, (e) wear rate of the TiC_xN_{1-x} coated discs. (Tribological testing parameters: sliding distance: 200 m, sliding speed: 0.1 ms^{-1}, friction load: 2 and 10 N, temperature: 25 °C, relative humidity: ~60%).

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investigations of cross-sections of the TiC_xN_{1-x} coatings. The microcrystalline structures grown at the low substrate temperatures are evident too in the broad peaks of the XRD patterns (Fig. 3), comparing TiN and TiC_xN_{1-x} coatings deposited at various N_2/C_2H_2 gas mixtures. The change of the chemical composition of the coatings can be concluded from the increasing shift of the diffraction peaks to lower angles at higher C_2H_2 flows during deposition. This behavior is well known for TiC_xN_{1-x} materials, which possess as well as pure TiN and TiC the NaCl-type fcc lattice structure [3]. Stress measurements, performed only for the pure TiN coating, revealed compressive stresses up to about −8 MPa [19], which cause the full peak shift for the TiN coatings from the position of unstressed TiN. Thus, it seems clear, that also a part of the shift to the lower diffraction angles of the TiC_xN_{1-x} coatings is caused by compressive stresses. The crystallinity of the coatings, which are all (111) textured, seems to decrease with increasing C_2H_2 flows, possibly indicating the incorporation of hydrogen atoms during growth.

3.3. Mechanical and tribological behavior

The replacement of nitrogen atoms by carbon atoms leading to distortion of the fcc lattice results in the increase of hardness and elastic modulus of the coatings (Fig. 4a). Starting from pure TiN, low contents of carbon strengthen the lattice by solid solution hardening, while too high C contents (resulting from high C_2H_2 flows during deposition) result in a decrease of both mechanical properties. Possibly, the decrease of crystallinity affects the lost of hardness of these films.

The addition of carbon atoms to the TiN coating strongly influences the tribological behavior: As shown in Fig. 4b–e, the friction coefficients and Wear rates are drastically decreased in the TiC_xN_{1-x} coatings of the higher hardness. A decrease of hardness increases the Wear rates again, found in the coatings deposited in atmospheres of higher C_2H_2 flows. The little higher disc Wear rates in the tests with 2 N friction load are mainly caused by the Wear calculation method of Holm, in which the Wear rates are defined as the proportion of lost volume to sliding distance and load [20]. In comparison to other low friction coatings like DLC, the same order of magnitude of the ball and disc Wear rates was found for the TiC_xN_{1-x} coatings [21]. Although the investigations have not been finished, the decrease in friction seems to be caused by the formation of carbon-rich transfer layers. Comparing the optical profilometry images of TiN and TiC_xN_{1-x} (Fig. 5a and b), the sliding behavior of the AISI 52100 (DIN 100Cr6) ball-bearing steel ball is very different. While for TiN (Fig. 5a), rough Wear track surfaces are usually found, which are caused by the transfer of steel counterpart material to the TiN surface during Wear, the TiC_xN_{1-x} Wear tracks are characterized by smooth grinding structures and the absence of asperities. On the counterparts to the TiC_xN_{1-x} coatings,

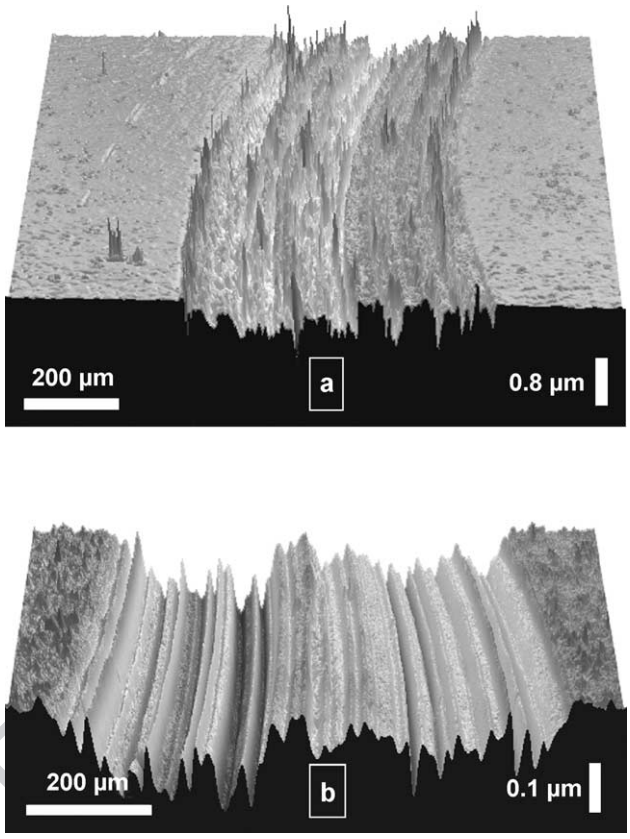

Fig. 5. Optical profilometry images of the wear tracks of (a) a TiN coating deposited at 30 sccm N_2 and (b) a TiC_xN_{1-x} coating (5 sccm C_2N_2, 25 N_2) sliding against uncoated AISI 52100 (DIN 100Cr6) pins at 10 N friction load. (Further tribological testing parameters: see description of Fig. 4).

thin transfer films consisting of mainly carbon and titanium atoms were found in EDS investigations. Thus, the low friction behavior of the PLD coatings seems to be caused by the missing of sticking of the steel counterpart material on the anti-adhesive TiC_xN_{1-x} coating surfaces and, thus, the change from steel/steel transfer layer to carbon-rich transfer layer/TiC_xN_{1-x} coating contacts. Similar phenomena were found for TiC_xN_{1-x} coatings deposited by other PVD and CVD techniques [2].

The friction coefficients were found to be lower for the lower friction force (2 N) applied in the ball-on-disc tests. The dependency of the friction coefficient on the sliding distance for a TiC_xN_{1-x} sample in Fig. 4c reveals a further phenomenon: The run-in period is longer and reflected by higher friction coefficients for the higher friction load (10 N). This high friction during run-in (also for 2 N) confirms the absence of lubricant carbon layers, whose formation goes hand in hand with the decrease of the friction coefficient. Longer run-in sliding distances reveal a more difficult formation of the lubricant layers, which could be caused by the too high shear forces during the contact removing grown lubricant layers from the counterpart surface. The high friction coefficients result in high initial Wear of the coating and counterpart increasing the contact area [20]. As a reason, the Hertzian pressure and the shear forces decrease prevent-

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ing the delamination of the lubricant carbon transfer layers from the coating and the counterpart. At the lower friction load (2 N), the same processes are running faster and the steady-state friction period is reached after shorter distances. The little higher friction coefficient at lower friction load reflects either the more difficult displacement of Wear debris out of the Wear track or the rougher surface of the Wear track found in the profilometry investigations.

4. Conclusions

The pulsed laser deposition (PLD) technique was applied in the current work for large-area and high-rate titanium carbonitride (TiC_xN_{1-x}) film growth on steel and molybdenum substrates at room temperature. The optimization of the laser fluency of the four Nd:YAG laser beams for titanium target ablation allows the growth of very smooth, nearly particulate-free (droplet-free) coatings in C_2H_2/N_2 gas mixtures. The variation of the C_2H_2/N_2 ratio resulted in significant changes of the microstructure, the mechanical and the tribological properties: While TiN coatings deposited in pure N_2 atmospheres possess high friction coefficients (~0.8) in the sliding contact of uncoated AISI 52100 (DIN 100Cr6) counterparts due to the formation of steel transfer layers on the coated disc, the TiC_xN_{1-x} coatings enable a drop of the friction coefficients to 0.2. The pin and disc Wear rates of TiC_xN_{1-x} follow this drop, resulting in a reduction of both values to a 10th of the TiN/steel sliding pair. Furthermore, the hardness is influenced by the replacement of nitrogen by carbon atoms in the fcc lattice due to solid solution hardening. The variation of the friction load affects the run-in behavior of sliding due to load phenomena in lubricant transfer layer growth.

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