Morphological, structural and tribological characterisation of pulsed laser deposited titanium nitride coatings

J.M. Lackner[1,2,3], W. Waldhauser[2], R. Ebner[1,2], B. Major[4], T. Schöberl[5]

[1] Materials Center Leoben, Leoben, Austria
[2] Joanneum Research Forschungsgesellschaft mbH, Leoben, Austria
[3] Institute of Physical Metallurgy and Materials Testing, University of Leoben, Austria
[4] Institute of Metallurgy and Materials Science, Polish Academy of Sciences, Cracow, Poland
[5] Erich Schmid Institute, Austrian Academy of Sciences, Leoben, Austria

Corresponding author:
Dr.Wolfgang Waldhauser,
JOANNEUM RESEARCH Forschungsgesellschaft mbH / Laserzentrum Leoben
Leobner Str. 94, A-8712 Niklasdorf
Tel.: 0043 (0)3842-81260-2311
Fax: 0043 (0)3842-81260-2310
e-Mail: wolfgang.waldhauser@joanneum.at

Abstract

Because of its high hardness and low wear rates titanium nitride (TiN) is the most widespread material for hard coatings. Thin TiN films have been deposited industrially in recent years with various deposition methods. For coating of heat sensitive materials and machine parts at low temperatures down to room temperature only a few deposition techniques can be applied. One of these is the pulsed laser deposition (PLD) method, which was used in this work for the deposition of TiN thin films on three-dimensional shaped substrates.

A Nd:YAG laser of 1064 nm wavelength was applied to vaporize titanium targets in low pressure N_2 atmospheres at room temperature. As substrate materials for the deposition of the TiN films a high speed tool steel (DIN 1.3343) and a corrosion resistant steel (DIN 1.4542) were used. The substrate surfaces were situated parallel (on-axis) and rectangular (off-axis) to the target surface to simulate film deposition on three-dimensional shaped tools. The films were examined by light-microscopy, scanning electron microscopy (SEM), X-ray diffraction (XRD), nano-indentation and pin-on-disk tests. The results indicate, that the PLD method is suitable for deposition of crystalline, strong textured TiN films with a very low surface roughness, with an excellent adhesion to the substrates, with a high hardness and a high wear resistance.

1 Introduction

Titanium nitride (TiN) is a well known coating material for improving the tribological perfomance of tools and machine parts in industrial applications. A significant increase of tool lifetime can be achieved with TiN thin films commonly formed by various chemical vapour deposition (CVD) and physical vapour deposition (PVD) techniques [1]. For the deposition of TiN thin films these methods require elevated substrate temperatures higher than 200 - 500 °C to achieve good adhesion on the substrate and high hardness. This high substrate temperatures inhibit the use of TiN films in many applications where the substrate cannot withstand such high temperatures. Thus there is a high demand for developing low-temperature deposition processes for the growth of TiN thin films, such as pulsed laser deposition (PLD).

In the PLD technique a pulsed laser beam is focussed onto a target in order to evaporate its surface layers under vacuum or low pressure process gas conditions [2]. The vaporized material consisting of atoms, ions and atomic clusters is then deposited onto the substrate. The outstanding advantage of this technique is the possibility to deposit thin films of very high chemical purity and adhesion to various substrate materials at room temperature. Furthermore high rate film growth on surface areas situated perpendicular to the target's surface is also possible by using a low pressure process gas. The application of reactive process gases leads to the opportunity of varying the film stoichiometry in a wide range.

The application of the PLD process for the deposition of TiN thin films was shown by several authors in the last years [3 – 8]. The aim of these works published was the deposition of TiN films for microelectronic, decorative and optical purposes because of their high thermal stability and low electrical resistance. However, the friction and wear behaviour of PLD TiN films has not been reported detailed in literature so far. The goal of the present study is to close this gap and to show the outstanding capability of PLD for deposition of TiN thin films for tribological purposes in industrial applications.

2 Experimental details

2.1 Film deposition

High purity titanium targets were used for the ablation experiments using a pulsed Nd:YAG laser system, which provides four beams of 1064 nm wavelength, 0.6 J pulse energy and 10 ns pulse duration at a repetition rate of 50 Hz [9]. In this multi-spot evaporation system the targets are rotated during the laser irradiation in order to avoid the formation of deep craters. The emitted species were deposited at room temperature (approx. 25°C) onto steel substrates mounted parallel (on-axis geometry) as well as normal (off-axis geometry) to the target surface, see Fig. 1.

During deposition the substrates have been moved with a relative speed of 5.4 cm s^{-1} through the plasma plumes. The ferritic corrosion resistant steel (DIN 1.4542) and the quenched and tempered high speed steels (HSS, DIN 1.3343) substrates, the latter with a hardness of 64 HRC, both with mirror-polished surfaces, have been cleaned ultrasonically in pure acetone and ethanol prior to film deposition. The reaction chamber was evacuated before starting deposition to pressures below $2x10^{-3}$ Pa using a pumping unit consisting of a rotary vane pump and a turbomolecular pump. During deposition the flows of the process gases (Ar, N_2) were adjusted by means of electronic mass flow controllers.

2.2 Film characterization

The surface quality and structure of the films was inspected with light and scanning electron microscopy (Cambridge Instruments Stereoscan 360). Chemical analysis were performed with wavelength dispersive spectroscopy (WDS).

The crystal structures of the deposited TiN thin films were determined by X-ray diffraction (Philips PW 1710 XRD) operated in Bragg-Brentano geometry using Co K_{α} radiation. The X-ray $\sin^2\Psi$ method was used to measure the residual stresses of the first order on the basis of diffraction line shifting.

The hardnesses and Young’s moduli of the films were measured by nanoindentation with Berkovich indenters. The applied maximum loads were 11 mN, the loading rates 20 nm s^{-1} for all measurements. Apart from mechanical investigations this apparatus was also used for atomic force microscopy (AFM).

The dry sliding friction of the TiN thin films at room temperature (25 °C) was evaluated using a CSEM Instruments high-temperature pin-on-disk tribometer with 6 mm 100Cr6 ball-bearing steel balls, partly coated with TiN, as counterparts. All experiments have been carried out on the as-deposited, ultrasonically cleaned thin film surfaces. The applied load was 10 N at a sliding speed of 0.1 m s^{-1}. The relative humidity during measurements was about 60%. The wear tracks were inspected with optical profilometry (Veeco NT-1000) to determine wear mechanisms and wear coefficients.

3 Results and discussion

3.1 Structure, texture and composition of the films

Fig. 2 shows AFM micrographs of the surfaces of thin films deposited on on-axis and off-axis mounted HSS substrates. Due to the higher energy of deposited species as a result of the perpendicular hit of the substrate’s surface, the probability of nucleation and the activation of diffusion on the surface are higher in the case of the on-axis grown film [2], leading to finer nanocluster structures. According to light microscopy only a small amount of defects can be detected in both cases. These defects originate in the ablation process of the target surface, where apart from ions, atoms and clusters also molten particulates (droplets) are ejected [2]. For the films deposited in the on-axis geometry slightly higher densities of droplets (11400 mm^{-2}) were found than for off-axis grown films (10900 mm^{-2}). These nearly pure titanium droplets are round-shaped and smaller than 1 µm. These characteristics were also shown and discussed for PLD SiO_x films earlier [10].

The thicknesses and structures of the TiN films deposited were detected on fracture sections by SEM. Both, on-axis and off-axis grown films (Fig. 3), have a micro-columnare microstructure, comparable to Zone T structures of Thornton’s structure zone model [11]. Due to the lower energy of the deposited species, the micro-columns of the off-axis grown films are larger. The crystallite sizes were found in the range of 10 nm resp. 7.5 nm for the on-axis resp. off-axis grown films by analysis of the {220} XRD peak. By comparing the film thicknesses a significant difference can be found between the films as a consequence of the different deposition arrangements: In contrast to the on-axis deposition geometry the ablated species can only hit the surface of the off-axis placed substrate after scattering with the other atoms in the deposition chamber. So the deposition yield values are significantly smaller in this arrangement leading to film thicknesses of 0.9 µm compared to 1.6 µm of the on-axis grown films [10].

WDS showed in both cases nearly stoichiometric compositions (TiN) of the films. The Ti / N atom ratio was typically 1 ± 0.05 for all investigated films.

Typical XRD spectra for on-axis resp. off-axis grown TiN films are presented in Fig. 4. In these spectra the labeled peaks correspond to the TiN coating and substrate reflections. For both films, the XRD spectra show the face-centered cubic structure of stoichiometric TiN. In contrast to the off-axis grown film the on-axis film shows also peaks of the α-Ti phase with the strongest reflection in the {100} and {110} orientations, the latter coincidences with the {220} TiN reflection. For the TiN phase in both samples the strongest reflections are the {220} and {111} peaks.

3.2 Mechanical properties of the films

XRD residual stress measurements revealed compressive stresses σ_{11} of about -8100 ± 850 MPa resp. -2800 ± 255 MPa for the on-axis resp. off-axis grown films (see Table 1). The simultaneously measured residual stresses in the ferritic corrosion resistant steel substrate, showed values in the range of about -260 resp. -150 MPa in rolling and transverse direction of the sheet. These very high compressive stresses in the PLD TiN thin films are in accordance to previous examinations [12] and are caused by the high energy of the deposited species (atoms, ions, clusters) during film growth [2] also leading to micro-columnare structures. In the off-axis grown film much smaller values for the compressive stresses were found because of the lower energy of deposited atoms and ions after their scattering with process gas atoms.

Quantitative information about the adhesion of the TiN thin films to the HSS substrates was achieved by Rockwell indentation method [13]. Because of different thicknesses of on-axis and off-axis grown films different damage characteristics were observed (Fig. 5): In the case of the thicker on-axis deposited film an adhesive strength class HF 2-3 connected to some small break-out areas around the indentation and some short cracks can be found (Fig. 5a), whereas in the thinner off-axis deposited film (Fig. 5b) no cracks and neglectable break-outs (HF 1) are observed.

Ultra-micro-hardness and Young's modulus of the samples were investigated using depth-sensing indentation tests. The calculated hardnesses resp. Young's moduli (Table I) are high compared to other PVD or CVD TiN films [14].

3.3 Tribological properties of the films

The friction and wear behaviour of the films was investigated in pin-on-disk tests as a function of the sliding distance against different counterparts. In the case of the uncoated 100Cr6 steel ball (Fig. 6) high friction coefficients were found for both films in accordance to various PVD and CVD films in literature [1]. The investigations of the wear tracks in the regime of long sliding distances showed very low wear after 200 resp. 1000 m (Fig. 7) sliding distance because of the formation of transfer layers [1]. EDS investigations turned out a very high content of iron transfered from the 100Cr6 counterparts compared to titanium in this transfer layers.

On the other side low friction coefficients were received in TiN/TiN couples in the beginning of sliding (Fig. 8) in accordance to [15]. After this initial phase the friction coeffient increases because of TiN wear debris formation. The examination of the wear tracks in the high friction regime shows only abrasive wear after 90 meters sliding distance and no transfer layer formation (Fig. 9).

Although different wear mechanisms occur in 100Cr6/TiN and TiN/TiN couples, the wear coefficients, evaluated with the Holm wear relationship [1], are very low (about 10^{-15} $m^3N^{-1}m^{-1}$) in all couples (Fig. 10). This phenomenon can be attributed to the high hardness of the films [1]. Slightly higher wear can be found for the off-axis grown films. This could be a reason of the lower compressive stresses and lower hardness of these films.

4 Conclusions

Nearly stoichiometric titanium nitride (TiN) thin films were successfully deposited on high speed steels and corrosion resistant steels at room temperature with a multi-spot pulsed laser deposition (PLD) system for industrial applications. To simulate the deposition on three-dimensional shaped tools the substrates were mounted parallel (on-axis technique) and normal (off-axis) to the target surface. A comparision of the tribological properties of on-axis and off-axis grown films showed similar behaviour. Very low surface roughness and excellent adhesion to the substrate were found for the TiN films, which have all a micro-columnare structure and are strongly textured. Because of very high intrinsic compressive stresses up to 8100 MPa very high hardnesses of the films were measured by nanointendations. Compared to other PVD or CVD coatings deposited at elevated temperatures, very low wear coefficient have been observed for sliding against 100Cr6 ball-bearing steel balls in the ball-on-disk test.

5 Acknowledgement

Financial support of this work by the Austrian Federal Ministry of Traffic, Innovation and Technology, the Austrian Industrial Research Promotion Fund (FFF), the Government of Styria, the Technologie Impulse Gesellschaft mbH in the frame of the Kplus Programme and the European Union is highly acknowledged.

6 References

[1] Holmberg, K.; Matthews, A.: in: Coatings Tribology, Elsevier, Amsterdam, 1994
[2] Chrisey, D. B.; Hubler, G. K.: in: Pulsed Laser Deposition of Thin Films, John Wiley & Sons, New York, 1994
[3] Gu, H. D.; Leung, K. M.: Surf. Coat. Techn. 110 (1998), 153-157
[4] Craciun, V.; Craciun, D.: Appl. Surf. Sci. 138-139 (1999), 593-598
[5] Phani, A. R.; Krzanowski, J. E.: Appl. Surf. Sci. 174 (2001), 132-137
[6] Chowdhury, R.; Vispute, R. D.: J. Mater. Res. 11 (1996), 1458-1469
[7] Auciello, O.; Barnes, T.: Thin Solid Films 181 (1989), 65-73
[8] Biunno, N.; Narayan, J.: Appl. Phys. Lett. 54 (1989), 1519-1521
[9] Ebner, R.; Waldhauser, W.; Lenz, W.: in: Proc. Materials Week 2001, Munich, 2001
[10] Lackner, J. M.; Waldhauser, W.; Ebner, R.; Lenz, W.; Suess, C.; Jakopic, G.; Leising, G.; Hutter H.: Surf. Coat. Techn., (2002), in print
[11] Thornton, J. A.: Journ. Vac. Sci. Techn. 11 (1974), 666-670
[12] Major, B.; Ebner, R.: Appl. Phys. A 69 (1999), 921-923

[13] Jehn, H.; Reiners, G.; Siegel, N.: in: DIN-Fachbericht 39, Charakterisierung dünner Schichten, Beuth-Verlag, Berlin, 1993, S. 210ff
[14] Sedlácek, V. in: Metallic surfaces, films and coatings, Elsevier, Amsterdam, 1992
[15] Franklin, S. E.; Beuger, J.: Surf. Coat. Techn. 54/55 (1992**)**, 459-465

Figure 1: Schematic view of the PLD system for thin film deposition

Figure 2: AFM micrographs of a (a) on-axis and (b) off-axis grown film

Figure 3: SEM micrographs of fracture sections of a (a) on-axis and (b) off-axis grown film

Figure 4: XRD spectra of (a) on-axis and (b) off-axis grown TiN films (α-Fe … ferritic steel substrate (DIN 1.4542))

Figure 5: Comparision of film adhesion evaluated by Rockwell indentations [13] of (a) on-axis and (b) off-axis grown films

Figure 6: Dependence of the friction coefficient on the sliding distance for (a) on-axis and (b) off-axis grown TiN films against uncoated 100Cr6 balls (10 N, 0.1 ms^{-1}, 25°C, 60% humidity)

Figure 7: Wear track after 1000 m sliding against a uncoated 100Cr6 ball of an on-axis grown TiN film (10 N, 0.1 ms^{-1}, 25°C, 60% humidity)

Figure 8: Dependence of the friction coefficient on the sliding distance for (a) on-axis and (b) off-axis grown TiN films against TiN coated 100Cr6 balls (10 N, 0.1 ms^{-1}, 25°C, 60% humidity)

Figure 9: Wear track after 90 m sliding against a TiN coated 100Cr6 ball of an on-axis grown TiN film (10 N, 0.1 ms^{-1}, 25°C, 60% humidity)

Figure 10: Comparision of wear coefficients for on-axis resp. off-axis grown TiN films against (a) uncoated 100Cr6 balls (wear track diameter: 10 mm) and (b) TiN coated 100Cr6 balls (wear track diameter: 7 mm) (10 N, 0.1 ms^{-1}, 25°C; 60% humidity)

Table 1: Surface roughnesses, lattice stresses, Young's moduli and hardnesses of the substrate and on-axis resp. off-axis grown TiN PLD films

Fig. 1: J.M. Lackner et.al.; Morphological, structural and tribological characterisation of pulsed laser deposited titanium nitride coatings

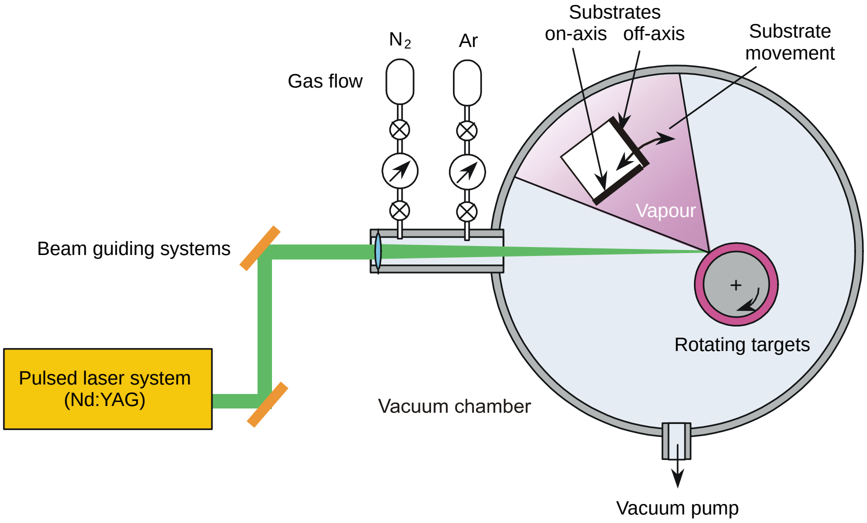

Fig. 2: J.M. Lackner et.al.; Morphological, structural and tribological characterisation of pulsed laser deposited titanium nitride coatings

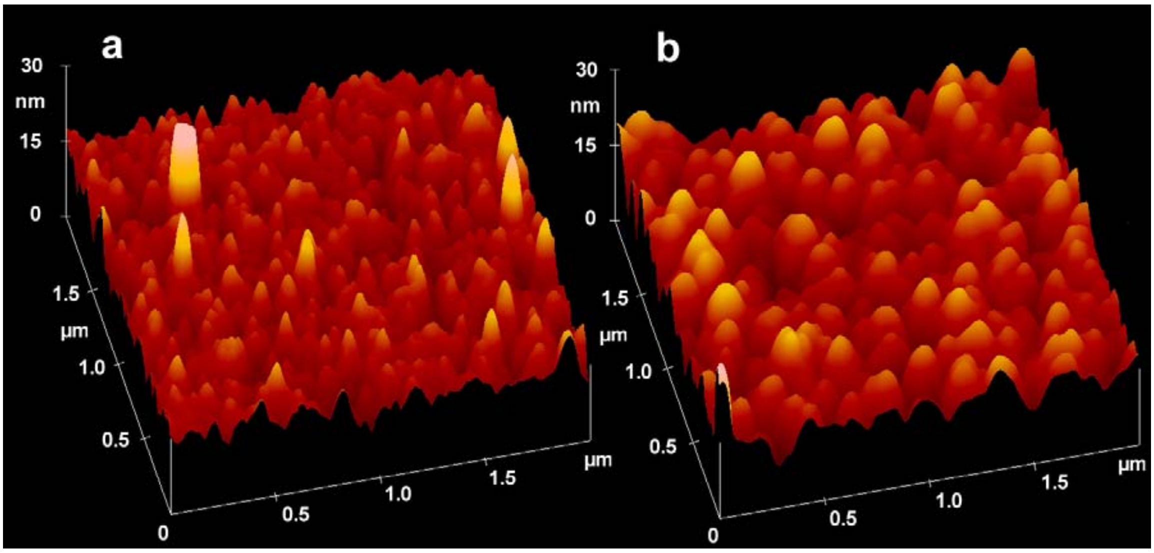

Fig. 3: J.M. Lackner et.al.; Morphological, structural and tribological characterisation of pulsed laser deposited titanium nitride coatings

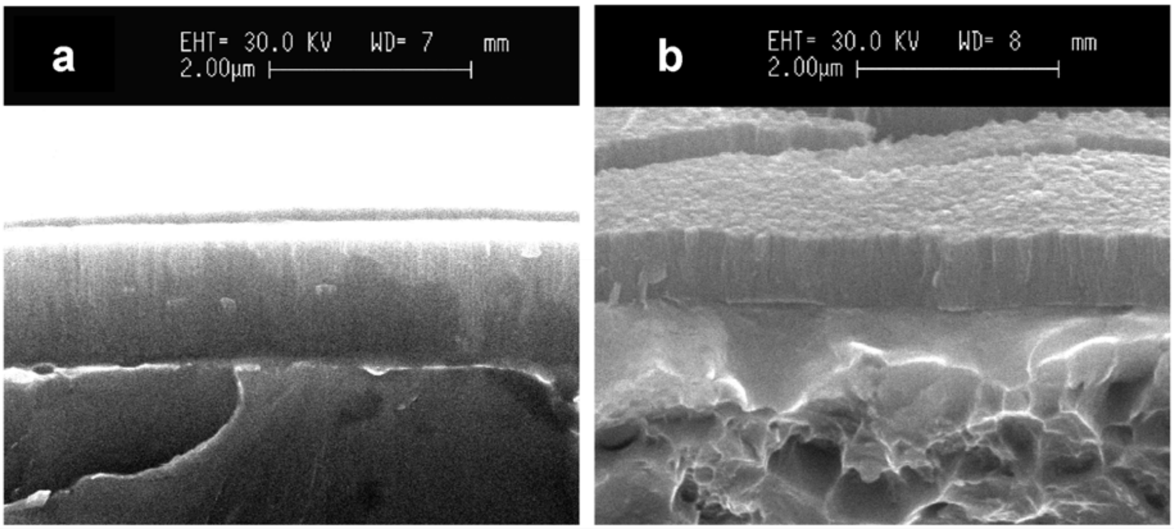

Fig. 4: J.M. Lackner et.al.; Morphological, structural and tribological characterisation of pulsed laser deposited titanium nitride coatings

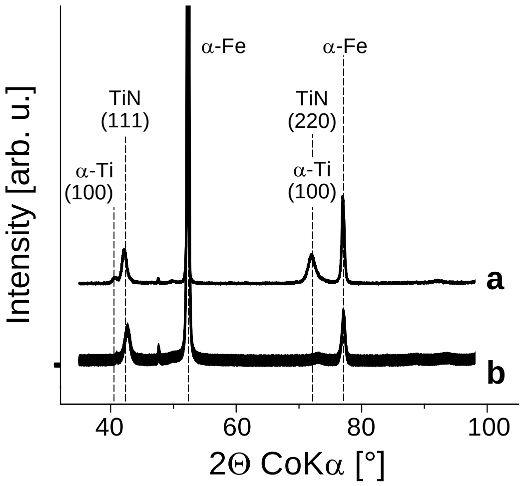

Fig. 5: J.M. Lackner et.al.; Morphological, structural and tribological characterisation of pulsed laser deposited titanium nitride coatings

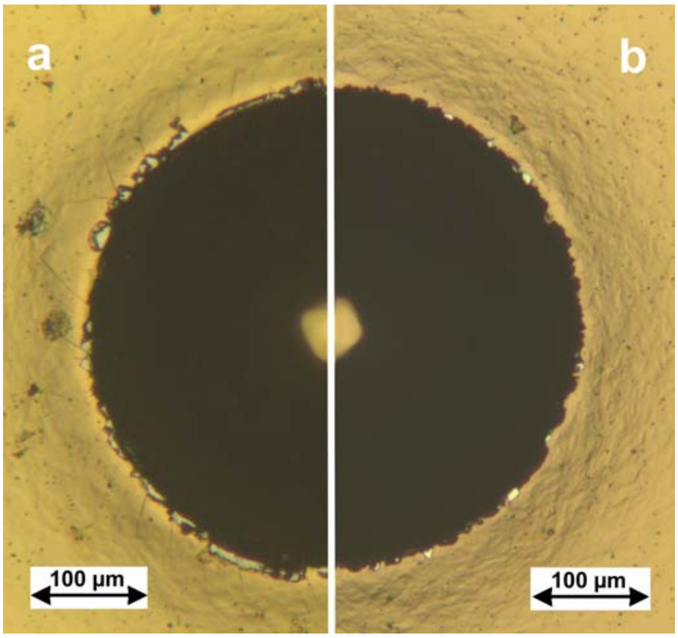

Fig. 6: J.M. Lackner et.al.; Morphological, structural and tribological characterisation of pulsed laser deposited titanium nitride coatings

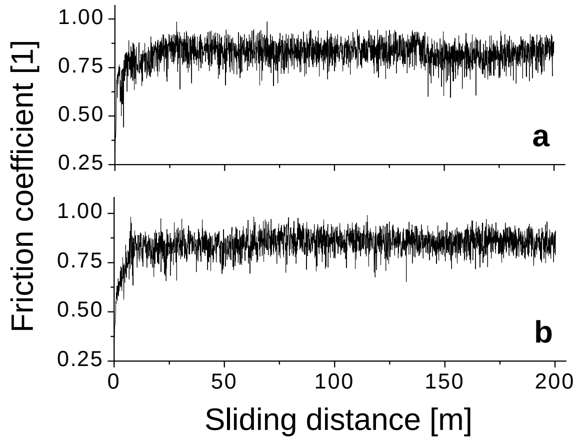

Fig. 7: J.M. Lackner et.al.; Morphological, structural and tribological characterisation of pulsed laser deposited titanium nitride coatings

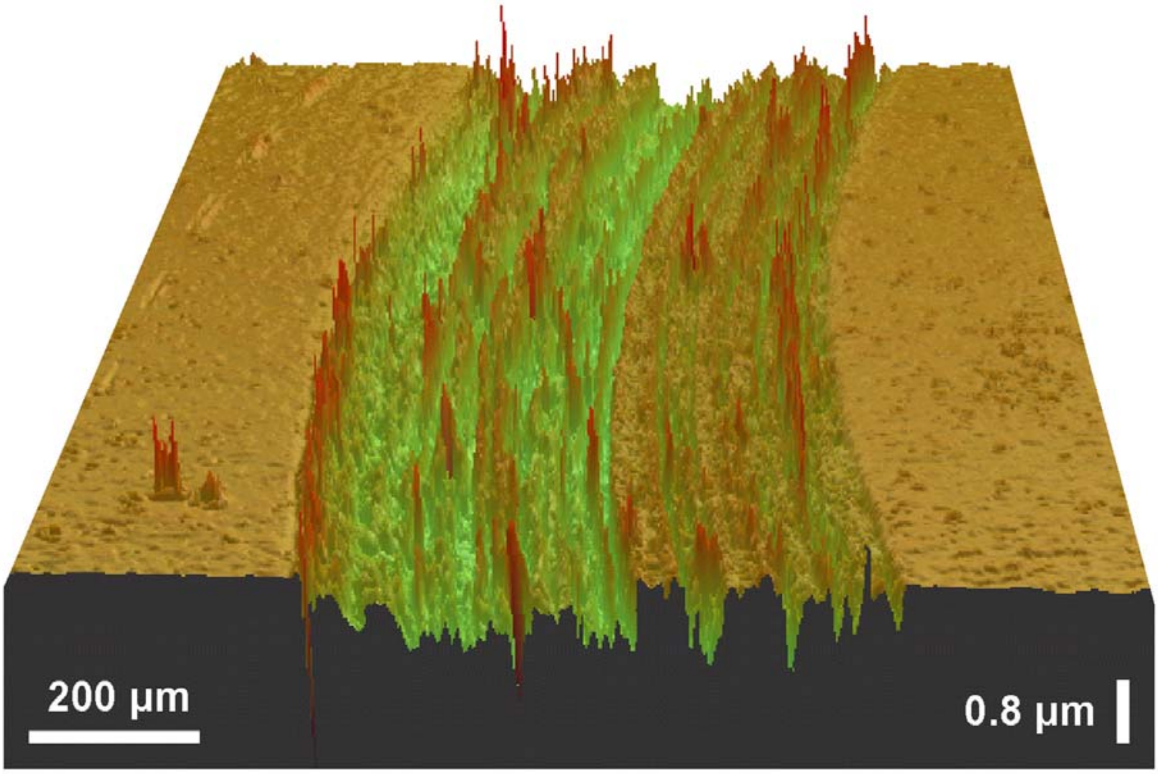

Fig. 8: J.M. Lackner et.al.; Morphological, structural and tribological characterisation of pulsed laser deposited titanium nitride coatings

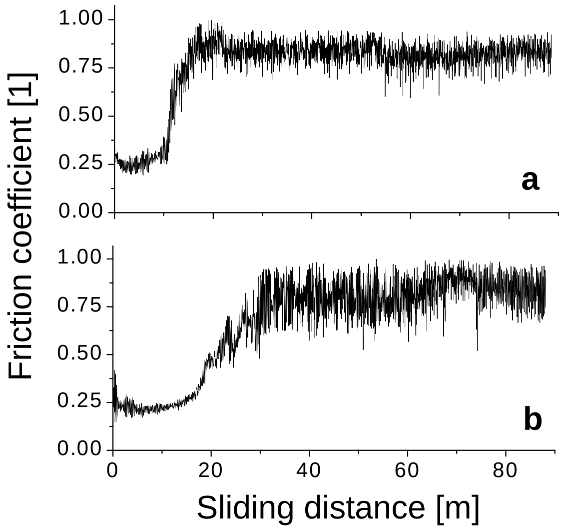

Fig. 9: J.M. Lackner et.al.; Morphological, structural and tribological characterisation of pulsed laser deposited titanium nitride coatings

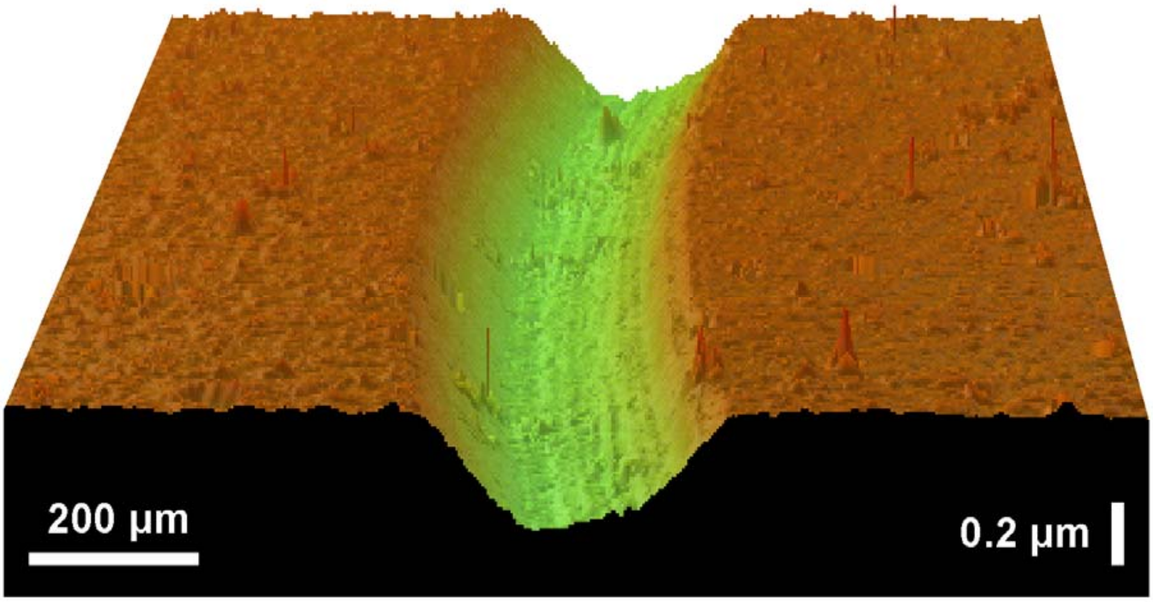

Fig. 10: J.M. Lackner et.al.; Morphological, structural and tribological characterisation of pulsed laser deposited titanium nitride coatings

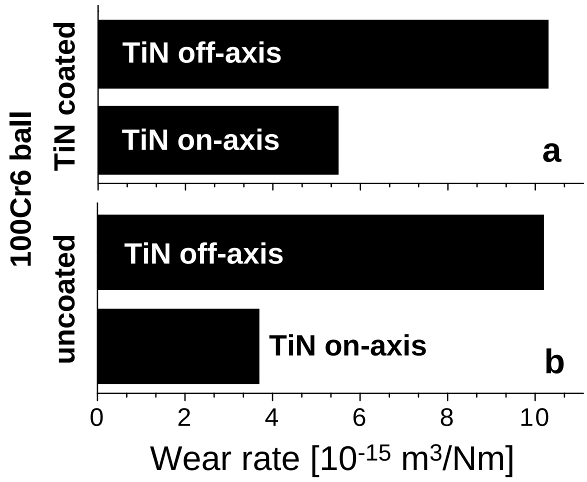

Table 1: J.M. Lackner et.al.; Morphological, structural and tribological characterisation of pulsed laser deposited titanium nitride coatings

Substrate	Surface roughness R_a [nm] 1.3343	Lattice stress σ_{11} [MPa] 1.4542	Young's modulus E [GPa] 1.3343	Hardness H [GPa] 1.3343
Substrate	8.20 ± 0.8	Radial: 260 Transverse: 150	202 ± 4	11.8 ± 0.5
TiN film (on-axis grown)	7.41 ± 0.7	-8100 ± 850	311 ± 8	26.5 ± 1.0
TiN film (off-axis grown)	7.10 ± 0.7	-2800 ± 255	248 ± 7	16.9 ± 0.8