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# Pulsed laser deposition of titanium oxide coatings at room temperature—structural, mechanical and tribological properties

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## Abstract

Titanium oxide (TiO<sub>x</sub>) coatings exhibit extraordinary optical, electrical and tribological properties, but very less is known about coatings deposited at room temperature. In the present work this gap was closed by employing the room temperature pulsed laser deposition (PLD) technique. In order to simulate different deposition conditions, the substrate (AISI M2, molybdenum) surfaces were situated parallel ('on-axis' geometry) and perpendicular ('off-axis') to the pure titanium targets ablated by the Nd:YAG lasers with a wavelength of 1064 nm. The combination of a four-beam PLD evaporator with a suitable movement of the substrates resulted in a high-rate film growth on large surfaces. The coating structure investigated by X-ray diffraction consists of a mixture of monoclinic β-TiO<sub>2</sub> and amorphous TiO<sub>x</sub> phase. The ratio of the amount of the phases, the hardness and the elastic constants strongly depend on the O<sub>2</sub> gas pressure and the target–substrate arrangement applied for deposition. Owing to the very high adhesion and their very smooth surfaces, the TiO<sub>x</sub> coatings exhibit friction coefficients of approximately 0.55 and wear rates of lower than 10<sup>-15</sup> m<sup>3</sup> N<sup>-1</sup> m<sup>-1</sup>, turning out that titanium oxide coatings deposited by means of PLD are very promising candidates for wear protection applications.

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## 1. Introduction

Titanium oxide (TiO<sub>x</sub>) is a widely spread coating material for catalytic, sensoric and microelectronic applications due to its exceptionally physical and chemical properties [1]. The two most important crystalline phases of stoichiometric TiO<sub>2</sub> (rutile and anatase) possess high refractive indices [2], high dielectric constants, high chemical stability and biocompatibility as well as low friction coefficients [3].

At present, mainly ion beam deposition [1], magnetron sputtering [4–6] and arc deposition techniques [2,7] are used for the physical vapour deposition (PVD) of TiO<sub>x</sub> coatings. Very less is known about the deposition of coatings in the titanium–oxygen system by pulsed laser deposition (PLD). Some authors [8–11] presented fundamental work about the PLD of these coatings and

found crystalline anatase and rutile type structures of TiO<sub>2</sub> coatings. These structures are comparable to other PVD TiO<sub>2</sub> coatings, for which Löbl [12] and Szczyrbowski [13] developed a phase diagram dependent on the substrate temperature and the energy of the deposited species: high temperatures and energies favour the growth of rutile, whereas at low temperatures and low energies anatase as well as amorphous films are found.

The high substrate temperatures of at least 300–400 °C necessary in most PVD techniques for high adhesion of the coatings to the substrate and dense coating structures prevent the coating of heat-sensitive substrates like pre-quenched tools or materials like polymers. The PLD technique allows the coating of these materials at room temperature with excellent adhesion strength due to the high ionized vapour (plasma) ablated from the target by the laser beam. Although the PLD technique is a well-developed laboratory deposition process, it has not reached an industrial breakthrough yet [14]. The main obstacle is the availability of large-area deposition

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Table 1

Deposition parameters, thicknesses after 90-min deposition, chemical compositions and mechanical properties of the PLD TiO<sub>x</sub> coatings

Sample/ coating	Deposition arrangement	O <sub>2</sub> gas flow (sccm)	Thickness (μm)	Oxygen content (at.%)	β-TiO <sub>2</sub> phase content (vol.%)	Hardness (GPa)	Elastic modulus (GPa)
TiO <sub>1</sub>	On-axis	10	1.80 ± 0.05	66.8 ± 0.8	20.7	11.16 ± 0.67	208.9 ± 4.9
TiO <sub>2</sub>	On-axis	30	1.60 ± 0.05	69.9 ± 0.8	49.3	6.69 ± 0.08	195.5 ± 3.6
	Off-axis	30	1.45 ± 0.05	71.0 ± 0.8	~0	6.14 ± 0.2	187.2 ± 2.9
TiO <sub>3</sub>	On-axis	60	1.45 ± 0.05	70.3 ± 0.9	20.5	4.25 ± 0.06	154.6 ± 1.5

equipment necessary for coating of large substrates for industrial use (e.g. tools, sheets, foils). To overcome this problem a multi-beam PLD evaporation system was installed at Laser Center Leoben of JOANNEUM RESEARCH Forschungsgesellschaft mbH [15], which was used for the deposition of the TiO<sub>x</sub> coatings. This facility allows high-rate film growth and large-area deposition with a maximum of 5% difference of the growth rate over the full deposition height.

## 2. Experimental

### 2.1. Film deposition

High purity titanium targets were applied for the ablation experiments with 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 [14]. 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 substrates mounted parallel ('on-axis' geometry) as well as normal ('off-axis' geometry) to the target surface [16]. Prior to deposition the substrates—molybdenum and high speed steel (AISI M2, hardness  $\sim 64$  HRC)—were mirror-polished and cleaned ultrasonically in pure acetone and ethanol. To provide homogenous film thicknesses over the whole coated surfaces, the substrates were moved with a relative speed of  $5.4 \text{ cm s}^{-1}$  through the plasma plumes during deposition. The reaction chamber was evacuated before starting deposition to pressures below  $2 \times 10^{-3}$  Pa using a pumping unit consisting of a rotary vane pump and a turbomolecular pump. During deposition the oxygen gas flow was adjusted by an electronic mass flow controller.

### 2.2. Film characterisation

The surface quality and structure of the coatings were inspected by light and scanning electron microscopy (Cambridge Instruments Stereoscan 360). Chemical analysis was performed with energy and wavelength dispersive spectroscopy (EDS—Link systems, WDS—Microspec WDX-3PC).

The phase composition of the TiO<sub>x</sub> coatings was analysed by X-ray diffraction (XRD, Siemens D500) using Cu K $\alpha$  radiation and Bragg–Brentano alignment. The estimation of the phase contents is based on the general assumption of proportionality between diffraction line intensity and phase content [17,18]. The texture analyses were performed using a Philips PW 1710 X-ray diffractometer and Co K $\alpha$  radiation. For the pole figure measurements, step sizes of  $2.5^\circ$  for the polar and azimuthal angles were applied.

The hardnesses and elastic moduli of the coatings were determined by nanoindentation using Berkovich indenters. The maximum loads and the loading rates were set at 11 mN and  $20 \text{ nm s}^{-1}$  for all measurements, respectively. Quantitative information of the coating adhesion to the HSS substrates was achieved by the Rockwell indentation method [19].

The dry sliding friction of the TiO<sub>x</sub> coatings at room temperature ( $25$  °C) was evaluated using a CSEM Instruments high-temperature ball-on-disc tribometer with 6-mm AISI 52100 (DIN 100Cr6) ball-bearing steel balls as counterparts. All experiments were carried out on the as-deposited, ultrasonically cleaned surfaces. The applied load was 10 N at a sliding speed of  $0.1 \text{ m s}^{-1}$ . The relative humidity during the measurements was held at approximately 60%. The wear tracks were inspected by optical profilometry (Veeco NT-1000) to determine wear mechanisms and wear rates.

## 3. Results and discussion

Nearly particulate free and very smooth surfaces (roughness  $R_a \sim 3\text{--}5 \text{ nm}$ ) were found for all TiO<sub>x</sub> coatings in light microscopy and optical profilometry investigations, respectively. SEM investigations of fracture sections of the PLD coatings revealed dense microstructures comparable to very fine grained Zone-T structures of Thornton's structure zone model [20]. The coating thicknesses were found dependent on the O<sub>2</sub> gas flows in the range between 1450 and 1800 nm (Table 1). This dependency on the O<sub>2</sub> gas flow can be attributed to differences in the propagation characteristics of the ablated Ti atoms, ions and clusters, leading to more intensive scattering with the O<sub>2</sub> molecules at the higher O<sub>2</sub> flows during deposition, which are proportional to

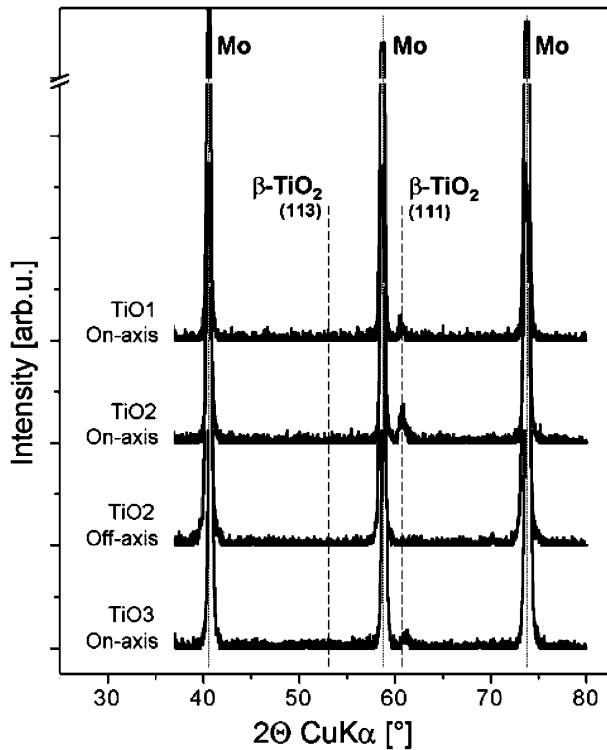


Fig. 1. XRD spectra of the  $TiO_x$  coatings deposited. The peaks found are related to molybdenum (Mo) and  $\beta-TiO_2$  phases of the substrate and coating, respectively.

the total gas pressures. A further decrease of the coating thickness is caused at the same  $O_2$  gas flow by the change of the arrangement of the targets' and substrates' surfaces from a parallel ('on-axis') to a perpendicular ('off-axis') position, in which the scattering of the vapour is nearly indispensable for reaching the substrate surface [21]. Although the scattering of the ablated Ti species strongly influences the deposition rate, the chemical composition is scarcely affected by the scattering processes representing in all coatings nearly stoichiometric  $TiO_2$ . Only a small increase of the oxygen contents  $x$  in the  $TiO_x$  can be found at higher  $O_2$  gas flows as well as in the 'off-axis' grown coating.

The intensity of scattering influences the energy of the deposited species too [21], resulting in differences of the phase composition of the coatings. The XRD spectra (Fig. 1) show besides the peaks originating from

the Mo substrate the reflexions of low intensity related to the coatings deposited in the 'on-axis' target–substrate arrangement. During growth these coatings suffer a bombardment of particles of higher energy increasing the activation of the surface diffusion necessary for crystallisation [21]. In contrast, the energy of the particles deposited onto the 'off-axis' mounted substrate is not sufficient for crystallisation, which can be observed in the missing of XRD reflexions. In the phase analyses the peaks of the 'on-axis' grown coatings were identified with monoclinic  $\beta-TiO_2$  ( $C_2/m$  structure) [22] and lattice parameters given in Table 2. This phase was not found in any PLD and PVD coatings before. In the spectra shown in Fig. 1 in opposite to the (111) reflexions the (311) peak cannot be observed due to the strong  $\{113\}\langle 1-103\rangle$  texture of this phase. Pole figures found in the texture analyses of the 'on-axis' grown coatings (e.g. 'TiO<sub>2</sub>') are shown in Fig. 2a. The comparison with the pole figures of the Mo substrate (Fig. 2b) excludes any influences of the substrate on the coatings' textures.

The estimation of the phase contents based on the diffraction line intensity [17,18] indicates only low contents of crystalline  $\beta-TiO_2$  between  $\sim 0$  and 50 vol.%. The remaining phase volume can be attributed to amorphous  $TiO_x$ . This phase mixture is due to the characteristics of the room temperature PLD technique: a crystallisation of the coatings at the low deposition temperatures ( $\sim 25^\circ C$ ) applied is hardly possible without any activation of the surface diffusion due to the complex lattice structures of stoichiometric  $TiO_2$  phases (rutile, anatase, brookite,  $\beta-TiO_2$ , etc.) [12,13]. The surface diffusion can only be activated by high-energetic atoms and ions ablated from the target. But only medium  $O_2$  gas flows during deposition, which are proportional to the total gas pressures in the vacuum chamber, result in relatively high amounts of crystalline  $\beta-TiO_2$  phase grown. At too low  $O_2$  gas pressures (e.g. coating 'TiO1') the bombardment of atoms and ions during film growth is very high, leading not only to a high activation of surface diffusion but also to a deep penetration of the coatings by the high energy particles, resulting in a part destruction of complex lattice structures [23]. An increase of the  $O_2$  gas pressure to a medium level leads to a decrease of penetration of ions and, thus, to a

Table 2  
Lattice parameters of the  $\beta-TiO_2$  phase found in the PLD  $TiO_x$  coatings and of the reference  $\beta-TiO_2$  [18]

Sample/coating		a (nm)	b (nm)	c (nm)	$\beta$ (°)
TiO1	On-axis	$12.269 \pm 0.004$	$2.968 \pm 0.001$	$6.072 \pm 0.005$	109.8
TiO2	On-axis	$11.718 \pm 0.040$	$2.956 \pm 0.007$	$5.860 \pm 0.012$	105.2
	Off-axis	Amorphous			
TiO3	On-axis	$12.994 \pm 0.012$	$3.068 \pm 0.002$	$5.799 \pm 0.003$	107.9
$\beta-TiO_2$ [18]		12.163	3.735	6.513	107.3

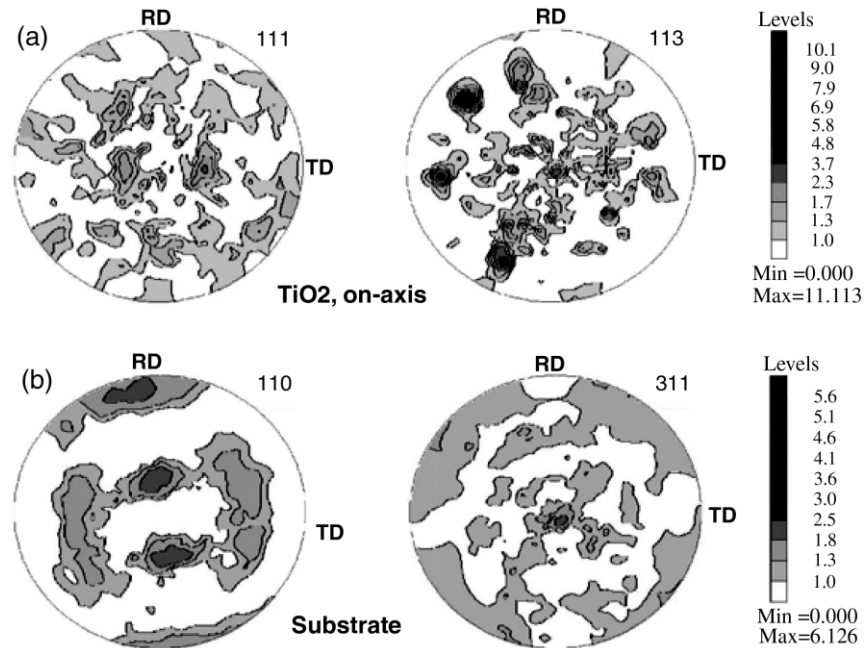


Fig. 2. Pole figures of the (a) (1 1 1) and (1 1 3) reflexions of  $\beta$ -TiO<sub>2</sub> found in the 'on-axis' deposited coating 'TiO<sub>2</sub>' and of the (b) (1 1 0) and (3 1 1) reflexions of the Mo substrate.

maximum of crystalline  $\beta$ -TiO<sub>2</sub> phase, found in the 'on-axis' coating 'TiO<sub>2</sub>'. Too high O<sub>2</sub> gas flows leading to high gas pressures during deposition reduce the energy of the deposited species and, thus, enable the activation of the surface diffusion, resulting in lower contents of crystalline phase. In the case of the 'off-axis' grown coating 'TiO<sub>2</sub>' the energy of the species deposited is too low for sufficient activation of diffusion, leading to its amorphous structure. The higher amount of crystalline phase in the 'on-axis' grown coating 'TiO<sub>2</sub>' further results in a higher compressive stressed lattice, which can be seen in the much lower lattice parameters of this coating in Table 2.

The decrease of the energy of the deposited atoms, ions and clusters reduces the mechanical properties of the coatings. Hardness as well as reduced elastic modulus were found strongly dependent on the gas flow used for deposition (Table 1) and slightly lower than that found for arc deposited coatings [2]. In spite of the large differences in the mechanical behaviour for all coatings, very high adhesion strength to the substrate surfaces was found. All coatings deposited reached the best adhesion class HF 1 on the six-part scale (HF1–HF6) in the Rockwell indentation tests [19] performed. Only a few cracks, but no delaminated areas, were found in the light microscopy investigations of the indentations' surroundings.

The tribological behaviour investigated in ball-on-disc tests against DIN 100Cr6 (AISI 52100) ball-bearing steel balls at room temperature and a relative humidity of 60% was found very dependent on the deposition

conditions too. During sliding two distinct stages of the evolution of the friction coefficients can be distinguished: (1) The first stage during the run-in period is characterised by high friction coefficients of up to 0.8–1.0. Optical profilometry investigations showed a flattening of the surface roughness, the formation of wear debris and the growth of a transfer layer on the TiO<sub>x</sub> coated disc surfaces. (2) After approximately 20–50 m of sliding the steady-state phase is reached and the friction coefficients drop down to 0.55–0.74 (Fig. 3a). The coating 'TiO1' with the highest hardness and elastic modulus possesses the highest friction (~0.75) in this stage, whereas all other coatings show nearly equal friction coefficients of approximately 0.55. These differences in the friction behaviour can be attributed to the growth of transfer layers on the coating surfaces, shown in the optical profilometry images in Fig. 4. In the case of the coating 'TiO1' (Fig. 4a) a transfer layer of low thickness and high porosity can be observed, whereas for all other coatings the layer is up to six times thicker and very dense (e.g. 'on-axis' grown coating 'TiO<sub>2</sub>' in Fig. 4b). Thus, in the latter case the sliding of the 100Cr6 ball occurs at any time on the transfer layer. EDS investigations of the coatings' wear tracks revealed Ti, Fe, Cr and O in the transfer layer. No indications of the incorporation of worn substrate material (AISI M2) in the transfer layers were found due to the absence of W, Mo, V or Co peaks in the EDS spectra.

The occurrence of these two very different wear phenomena can be attributed to the delamination of the TiO<sub>x</sub> coatings due to the high friction loads in accor-

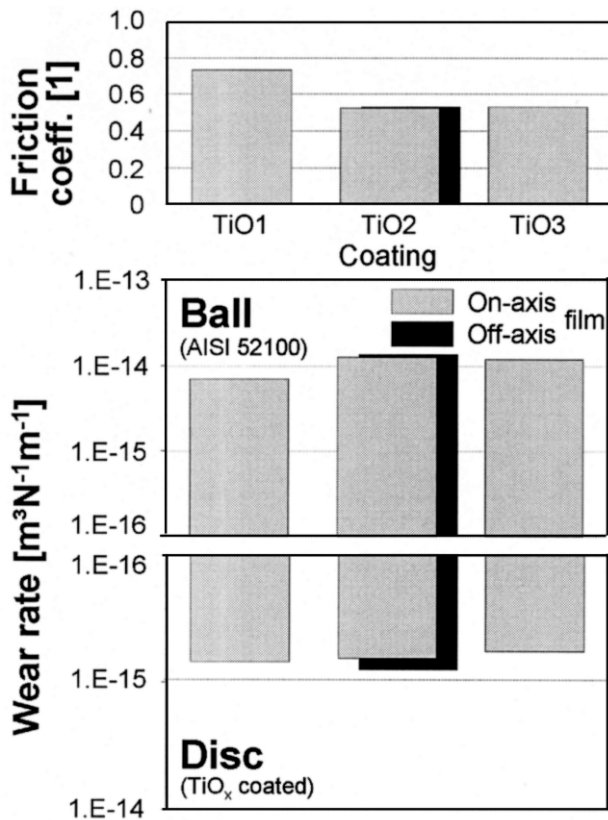


Fig. 3. (a) Friction coefficients and (b) ball and disc wear rates of the PLD TiO<sub>x</sub> coatings against DIN 100Cr6 (AISI 52100) ball-bearing steel balls (tribological parameters: sliding distance: 200 m, friction force: 10 N, sliding speed: 0.1 m s<sup>-1</sup>, temperature: 25 °C, relative humidity: 60%).

dance to Lapastolle et al. [4]. The coating ‘TiO1’ with a high hardness level withstands the friction load better than the other coatings, resulting in a smoother surface of the wear track. Thus, the counterpart (100Cr6 ball) suffers lower abrasive wear, leading to the lower ball wear rates (Fig. 3b). In contrast, the wear rates of the TiO<sub>x</sub> coated discs are nearly independent of the coating investigated due to the nearly equal lost coating volumes in the wear tracks used for calculation.

#### 4. Conclusions

Titanium oxide (TiO<sub>x</sub>) coatings were deposited by means of a four-beam PLD evaporation system from pure Ti targets in O<sub>2</sub> atmosphere at room temperature onto high speed steel (AISI M2) and molybdenum substrates. In order to simulate different deposition conditions the target and substrate surfaces were mounted in a parallel (‘on-axis’ geometry) and a perpendicular (‘off-axis’) arrangement. The coatings possess very smooth surfaces and consist of nearly stoichiometric titanium dioxide. Owing to the various O<sub>2</sub> gas flows used (which are proportional to the total gas pressures

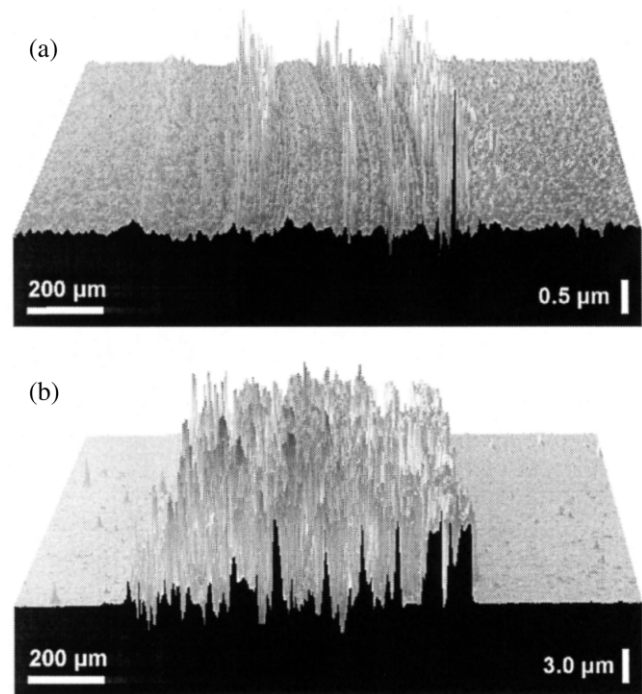


Fig. 4. Optical profilometry images of the wear tracks of the TiO<sub>x</sub> coated discs (a) ‘TiO1’ and (b) ‘TiO2’ sliding against DIN 100Cr6 (AISI 52100) ball-bearing steel balls (tribological parameters: sliding distance: 200 m, friction force: 10 N, sliding speed: 0.1 m s<sup>-1</sup>, temperature: 25 °C, relative humidity: 60%).

during deposition), the structural as well as mechanical and tribological properties of the coatings depend on the energy of the deposited atoms, ions and clusters. The higher the energy, the higher the hardness and the lower the counterpart (AISI 52100/DIN 100Cr6 ball) wear in the ball-on-disc tests. The crystallographic structure was found as a mixture of monoclinic β-TiO<sub>2</sub> and amorphous TiO<sub>x</sub> phases. The highest amount of crystalline β-TiO<sub>2</sub> was found in the coatings deposited in medium O<sub>2</sub> gas pressure atmospheres. Owing to the low energy of the deposited species a low surface diffusion activation necessary for crystallisation of the coatings leads in case of the ‘off-axis’ mounted substrate to fully amorphous coating structures.

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