Room-temperature Industrially-scaled Pulsed Laser Deposition of Coatings for Wear-protection, Low-friction and Decorative Applications

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ABSTRACT

Increasing demands on dimension accuracy and, thus, the minimization of distortion during coating – the final manufacturing step of many tools and machine components – as well as the increasing application of high-strength, but low temperature resistant materials – plastics, reinforced polymer compounds as well as light metals – require low-temperature vacuum coating techniques. However, many of the presently used techniques like sputtering, arc and electron beam evaporation, as well as the plasma-assisted CVD techniques are not able to provide coatings at low deposition temperatures (< 100°C) with properties of high- or medium-temperature deposited coatings. In the field of PVD techniques the Pulsed Laser Deposition (PLD) coating technique stands out against nearly all others by its unique feature of pulsed high- and low-energetic plasma flux, enabling even the deposition of tribological and decorative coatings at room temperature with properties, till now only known for elevated deposition temperatures (> 250°C).

The present work emphasizes this feature of the PLD technique based on both scientific investigations of the adhesion strength (Rockwell indentation tests and scratch tests) and the tribological performance (pin-on-disc tests) as well as on the behavior of the coatings in selected industrial applications. The results show generally high critical loads (> 40 N) in scratch tests and adjustable tribological properties (friction coefficients between 0.05 and 1.0) depending on the coating type (TiN, TiCN, TiO2, CrN, CrCN, TiAlN, DLC, etc.). Due to the high wear resistance even in thin films, the room-temperature deposited PLD coatings are ideally for decorative applications of temperature-sensitive materials.

Additionally to the development of tribological and decorative coatings, high efforts were taken in up-scaling of the PLD process from a laboratory coating technique to an industrial applicable one.

INTRODUCTION

Pulsed Laser Deposition (PLD) is a Physical Vapor Deposition (PVD) coating technique for the production of thin films. A huge variety of PVD processes, e.g. thermal evaporation, arc ion plating, magnetron sputtering, thermionic arc deposition, anodic arc deposition and pulsed laser deposition (PLD) are applied today for deposition of thin films [1]. The selection of a coating technique strongly depends on the application, normally the process with most appropriate combination of features is used.

In principle PLD is a young coating technique despite the fact that the first experiments date back to the early 1960s [2]. Main problems of the early days were insufficient beam properties like rather low mean beam power, non-uniform energy distribution or worse power-time profiles of the laser pulses. But this problem can be considered as solved because many powerful pulsed laser sources suitable for PLD are available today.

PLD of course competes with other coating techniques, but it has extraordinary process features, which favour PLD for some new and special applications. Main objective of the present paper is to demonstrate the advantages of the PLD technology on the one hand and to show the possibilities for up-scaling the PLD process from a laboratory coating technique to an industrial one on the other. In addition the properties of different PLD coatings deposited at nearly room temperature are discussed and possible new applications in the field of tribological and decorative coatings which can be exploited by PLD will be outlined.

PLD COATING – STATE-OF-THE-ART

Over the past decades PLD has become a well established laboratory coating process which enables the deposition of a huge variety of thin films with complex chemical compositions for magnetic, electric or semiconductor applications [3-7]. More than 300 different materials (pure metals, alloys, semiconductors, compounds, polymers etc.) have been successfully deposited by means of PLD [8], which indicates the outstanding flexibility of PLD regarding its ability to deposit different types of coatings. This outstanding flexibility in deposition of different materials results from the special process features of PLD, especially from the fact, that a pulsed laser beam is used to evaporate the target material. The high power densities achievable in focussed pulsed laser beams (normally > 10^9 W cm^{-2}) enables the evaporation of all known materials.

Ablated atomic material, both ions and neutrals, are significantly more energetic during PLD than for other thin film deposition techniques. This means that condensing species are energetic enough to stimulate the growing thin film, leading to smoother, denser thin films as a result of increased adatom mobility [9]

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without using substrate heating, which prevents the deposition of high-quality multilayer films. In order to achieve the same effect, other deposition techniques frequently use a substrate heater to thermally energise adatoms or even artificially stimulate adatoms by firing ion beams directly towards the growing thin film. In the field of PVD techniques the Pulsed Laser Deposition coating techniques stands out against nearly all others by enabling even the deposition of tribological and decorative coatings at room temperature with properties, till now only known for elevated deposition temperatures (> 250°C).

Figure 1 shows the main components of a PLD coating system. It consists at least of the following components which are: vacuum chamber, vacuum pumping unit, gas supply unit, pulsed laser source, beam guiding system and target manipulation. More sophisticated systems might also contain units for substrate manipulation, substrate cleaning, substrate heating, and activation systems to modify the vapor on its way from the target to the substrate.

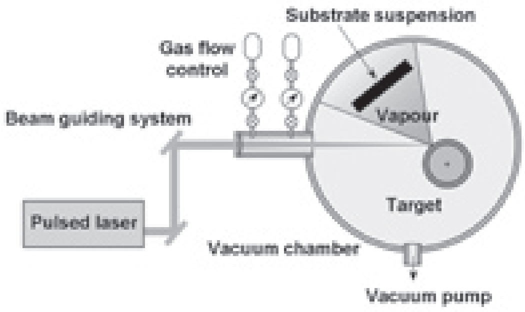

Figure 1: Principle of PLD coating.

Different types of pulsed laser sources are used for PLD [10]. The most common laser sources for PLD are excimer lasers with radiation in the ultra-violet, but also pulsed Nd:YAG lasers with radiation ranging from the near infrared to the ultraviolet radiation or even pulsed CO_2 lasers with infrared radiation are applied. Most of the actually used PLD systems are located at research laboratories and many of them are more or less home-built. Such systems are suitable for doing fundamental research in this area, but their applicability for coating industrial parts is very limited.

INDUSTRIAL SCALE-UP OF PLD

Although possessing the above mentioned outstanding process features PLD has not found its way into the mainstream of coating technologies. A part of the reluctance of industry to adopt PLD is probably based on the perceived costs of producing coatings at useful rates coupled with the high costs of lasers and the lack to deposit large-area films suitable for modern planar processing lines. Due to the rapidly decreasing costs for high-power laser systems (high repetition rate as well as high average output power) in the last years, this argument is diminishing more and more.

In contrast, the lack of knowledge to deposit large-area films industrially-scaled and reproducibility limits the commercial use of PLD. The weak point of the PLD technique is the point (or spot) target vaporization compared to the "linear" vaporization in evaporation or sputtering techniques. To overcome this disadvantage various strategies can be applied to achieve coatings with uniform thickness [11]. Most promising are (a) moving of the substrates relative to the evaporation spot along complex curves, (b) a focusing of the laser beam in a line, and (c) the application of a well defined multi-spot evaporator.

Multi-spot PLD evaporation is based on the optimized superposition of plumes, which are simultaneously ablated from several evaporation spots and allow the imitation of a line evaporator (see insert in Figure 2). Applying this concept thickness variation in the coatings can be kept lower than 5%. Figure 2 shows a typical variation of the deposition rate determined from coatings made from a four-spot PLD evaporation source. The deposition rate is only slightly lower in the overlapping zone, but it decreases rapidly to the left and to the right. The uniformity of the thickness achievable by superposition of plumes is sufficient for many applications [12].

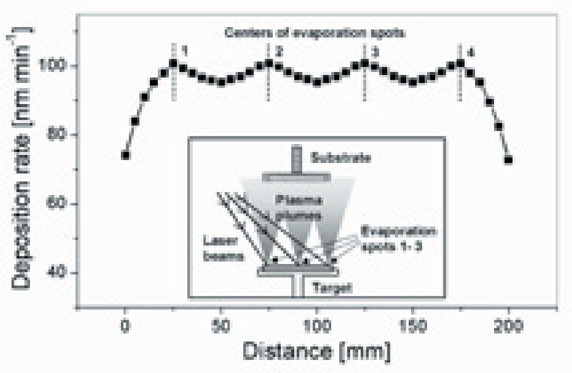

Figure 2: Experimentally determined deposition rates determined from titanium coatings produced by the four-spot PLD evaporation source at Laser Center Leoben, JOANNEUM RESEARCH Forschungsgesellschaft mbH (principle: see insert, target-substrate distance: 100 mm).

The coating of three-dimensional shaped workpieces can be realized by rotating of the substrates and by the use of higher process gas pressures during deposition, allowing more intense scattering in the plume.

HYBRID PULSED LASER DEPOSITION (HYBRIDPLD)

Hybrid coating technologies involve simultaneous or successive applications of different processing techniques, which allow the modification and deposition of complex film structures such as graded or multilayer films in one deposition plant. Since the process of material ejection at the target surface using PLD is not that sensitive to the background gas or other system parameters, it is relatively easy to incorporate other accessories such as an electron or ion gun, DC, middle-frequency (MF) or radio-frequency (RF) sources (for biasing) or even (magnetron) sputtering or arc deposition systems in PLD systems.

Based on the principle of multi-beam evaporation from a static target position onto moved substrates (Figure 2) an industrially-scaled PLD coating facility was built at Laser Center Leoben in the last years. The system, shown schematically in Figure 3, comprises the hybrid coating approach (thus, HybridPLD), allowing simultaneous deposition from several coating sources:

- PLD coating is performed from rotating metallic targets using a pulsed Nd:YAG laser system of four laser beams of 1064 nm wavelength, operating at a repetition rate of 50 Hz and providing 10 ns pulses of 600 mJ pulse energy.
- Additionally, magnetron sputtering (bias-supported) from a 400 mm high rectangular sputter target provides a second high-rate coating technique in the HybridPLD equipment. By using pulsed DC sputtering the reactive deposition of a wide range of metals is possible.
- A linear ion source completes the available coating techniques, allowing substrate cleaning and activation as well as plasma-assisted chemical vapor deposition (PACVD) at low substrate temperatures.

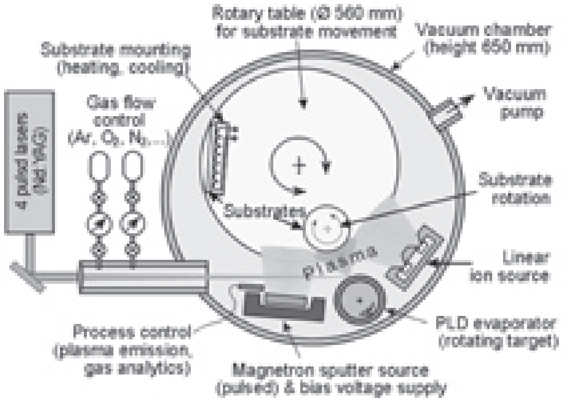

Figure 3: Industrially-scaled hybrid PLD coater including an ion source, pulsed DC magnetron sputtering, substrate biasing, plasma diagnostics, substrate heating and substrate rotation (*Hybrid*PLD coater, JOANNEUM RESEARCH Forschungsgesellschaft mbH, Laser Center Leoben).

To achieve reproducible coatings, the plasma analysis equipment contains a plasma emission monitor for plasma spectroscopy and a time-of-flight mass spectrometer for gas analysis. Stabilized laser power is reached by the application of laser power meters. These devices allow the creation of reproducible reactive deposition in oxygen, nitrogen, hydrocarbon atmospheres by all three available coating techniques. Additionally, inert gas atmosphere (argon) allows the deposition of pure metals.

The deposition of the evaporated species takes place on moveable and rotating substrate manipulators mainly at room temperature, but, if necessary, substrate heating is possible. The whole equipment was designed for industrially-scaled coating and possesses a large vacuum recipient (height of coating area: 400 mm, diameter of substrates up to 560 mm), and is a very versatile tool for the development of coatings as well as for job lot coating (see Figure 4). Pumping is performed by a combination of a rotary vane pump and a turbomolecular pump, allowing recipient background pressures down to the 10^{-5} Pa range.

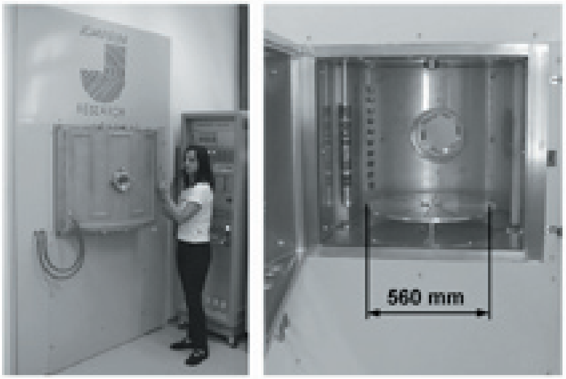

Figure 4: *Hybrid*PLD coater at Laser Center Leoben, JOANNEUM RESEARCH.

PROPERTIES AND APPLICATIONS OF PLD COATINGS

At present mainly ion beam deposition, magnetron sputtering, and arc deposition techniques are used for industrial wear protection coating of tools and machine parts. However, the high substrate temperatures of at least 300 to 400°C necessary using these techniques for sufficient adhesion of the coatings on the substrate as well as for dense coating structures prevent the coating of heat sensitive substrates like prequenched tools. The PLD technique allows the coating of these materials at room temperature with excellent adhesion strength due to its specific deposition conditions.

Figure 5 compares the adhesion of room-temperature DC magnetron sputtered and PLD metal and hard coatings on hard tool steel substrates. The applied test method for determining the adhesion of thin coatings for tribological purposes after DIN [13] is based on the indentation of a Rockwell C indenter (diamond cone) into the coated substrate (Figure 5a). The indentation results in plastic deformation of the substrate material under the coating with a material flow to all edges of the indent, forming bulgings there. The coating on the surface of the substrate has to follow this deformation or cracks. The higher the plasticity of the coating and the toughness of the interface is, the lower is its tendency to form cracks. The amount of the cracked or delaminated area is the basis for the quantification of the adhesion which is described by so-called adhesion test classes (HF 1 – HF 6) (Figure 5b).

In Figure 5c for a room-temperature PLD titanium nitride (TiN) coating with a 200 nm thick PLD adhesive interface some cracks are apparent in the highest deformed region surrounding the indent, which are running through the coating perpendicular to the substrate. A high fracture toughness of the interface stops the elongation to the cracks, preventing its deflection from the interface. For the PLD TiN coating of adhesion test class HF 1-2 delaminations of the coating are not evident.

The failure of a room-temperature unbiased magnetron sputtered Ti coatings on a non-activated substrate surface occurs by full delamination of the coating, impressively revealing the very low fracture toughness of the abrupt steel-Ti interface (Figure 5d).

Figure 5e shows that changing the interface type from the abrupt interface, occurring for coatings sputtered under these conditions, to the pseudodiffusion type by using a 200 nm thick PLD titanium interface below the TiN sputtered coating prevents fully the formation of cracks and delaminations. The results confirm that PLD hard coatings deposited at room-temperature and sputtered hard coatings with a thin metallic PLD interlayer show excellent adhesion on steel substrates. The critical loads in scratch tests of these coatings are higher than 40 N.

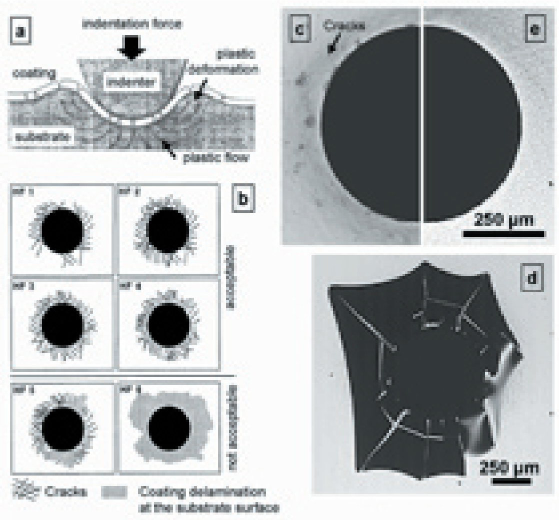

Figure 5: (a) Explanation of the DIN thin coating adhesion test principle [13] based on the Rockwell-C hardness test on polished hard steel substrate materials. (b) Evaluation of the indents surroundings (occurrence of cracks or delaminations) for the quantification of the adhesion test class HF. (c-f) Light microscopical images of the DIN adhesion test indents of room-temperature deposited coatings on tool steels of 60 HRC hardness: (c) 1.5 μm thick PLD TiN layer on 200 nm thick PLD Ti adhesive interface, (d) 1.5 μm thick DC magnetron sputtered Ti layer, (e) 1.5 μm thick unbiased DC magnetron sputtered TiN layer on 200 nm thick PLD Ti adhesive interface.

The tribological behaviour investigated by pin-on-disc tests for a wide variety of coating materials deposited at room temperature by PLD is shown in Figure 6. Based on the excellent coating adhesion and on microstructures comparable to films deposited at some 100°C higher temperatures the friction coefficients and wear rates of room temperature deposited PLD films are similar to conventional PVD coatings. Both basic types of tribological coating materials – (a) hard coatings and (b) solid lubricants – were successfully deposited by PLD.

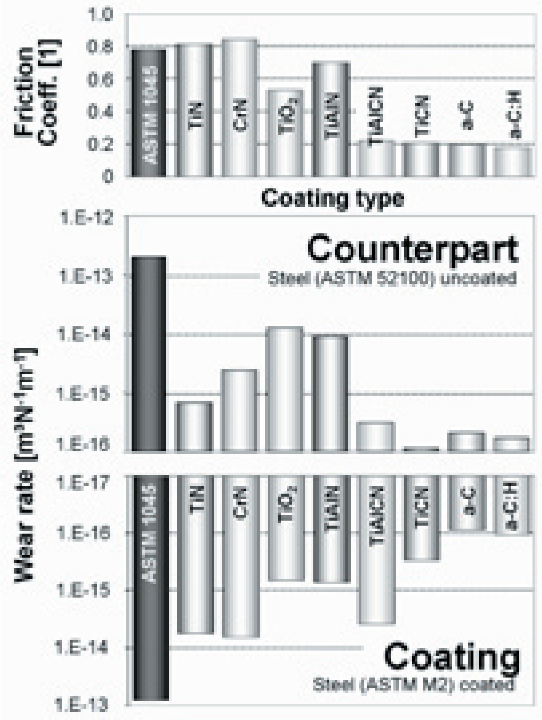

Figure 6: Friction and wear behaviour of hard coatings deposited by the room-temperature PLD technique and tested in the pin-on-disc test. Tribological test parameters: Substrate for coating: ASTM M2 steel, hardened and tempered (~ 63 HRC hardness), mirror-polished surface; Counterpart: ASTM 52100 ball-bearing steel balls, hardened and tempered (~ 60 HRC hardness), mirror-polished surface; Friction load: 10 N; Hertzian pressure: ~ 2 GPa; Sliding distance: 200 m; Atmosphere: 25°C, 60% relative humidity.

The class of hard coatings is characterized by rather high friction coefficients such TiN, chromium nitride (CrN), titanium oxide (TiO_2), and titanium-aluminum nitride (Ti,Al)N, protecting surfaces from abrasion and erosion wear. Thus, their field of applications is mainly the wear protection of tools.

Solid lubricants and hard coatings forming solid lubricant films on their surfaces during the tribological contact, like titanium carbonitrides (Ti(C,N)), titanium-aluminium carbonitrides ((Ti,Al)(C,N)) or hydrogen-free (a-C) and hydrogenated (a-C:H) diamond-like carbon (DLC), possess rather low friction coefficients due to easy slip on their surfaces. These low-friction coatings are qualified for the use in mechanical components like bearings. The color palette of these coatings includes gold, silver, gray, violet, brown and black. Therefore these films are candidates for decorative applications, too. However PLD is in competition with other PVD coating techniques. PLD coatings are excellent candidates for applications where low substrate temperatures (< 100°C) during coating are absolutely necessary.

CONCLUSIONS

Pulsed Laser Deposition (PLD) has been demonstrated as a suitable coating technique for a wide range of coating materials, e.g. metals, oxides, nitrides and carbides. It exhibits outstanding process features which can be the basis for innovative applications in future. The most relevant process features of PLD are the low possible substrate temperatures (20 - 100°C) and the resultant low thermally induced distortion of substrates, the avoidance of thermally induced microstructural changes in the substrate material and an excellent film adhesion. The *Hybrid*PLD coating system designed and built-up at Laser Center Leoben of JOANNEUM RESEARCH Forschungsgesellschaft mbH is a step of industrial scale-up of Pulsed Laser Deposition. The application of a multi-beam approach, the overlapping of several laser plumes allows the increase of thickness homogeneities and high-rate coating. Large-area coating was realized by substrate movement. Potential fields of application are wear-resistant, low-friction and decorative coatings for temperature sensitive substrates. The future of advanced coating leads to hybrid coating techniques, combining several different e.g. PVD and CVD techniques in order to fit their advantages together.

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