

Pulsed laser deposition of advanced titanium nitride thin layers

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Abstract

Titanium nitride thin layers were fabricated by pulsed laser deposition (PLD) using a Nd:YAG laser on both metallic (ferritic steel, pure titanium) and non-metallic (polyurethane) substrates by ablation of pure titanium in nitrogen environment. On-axis and off-axis geometry of deposition was applied. Residual stresses were measured in the TiN phase showing the compressive values in the range of -6 to -8 GPa for the on-axis growth while of approximately -2.8 GPa for the off-axis position. Texture examinations revealed the $\{110\} \langle 112 \rangle$ main texture component in the substrate, while differences were stated in the TiN phase in respect to the geometry of deposition. In the case of on-axis growth, the mostly axial texture with plane $\{110\}$ parallel to surface with tendency to $\{110\} \langle 011 \rangle$ was observed, while in the case of the off-axis growth the very pronounced $\{112\} \langle 223 \rangle$ dominant orientation was stated. Examinations of crystalline size and lattice strain were carried out on the basis of diffraction line broadening. Deposition of the TiN at room temperature on the polyurethane substrate revealed uniform thin layers. Residual stresses showed compressive stresses of approximately -1500 MPa. The measured texture was stated to be close to random. Morphology of deposited layers, examined by means of AFM, revealed similarity to the three-dimensional growth mechanism. © 2003 Elsevier B.V. All rights reserved.

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1. Introduction

Interest in pulsed laser deposition (PLD), as a technology for producing thin layers of complex materials, has been growing exponentially in recent years [1–5]. Condensation from the vapour phase and rapid solidification favours nanostructure formation in the thin layers. The deposition of virtually any material—from pure elements to multicomponent compounds—on various substrates, shows that PLD is a technology suitable for fabrication of thin layers for a wide range of applications. A typical set-up for the deposition of metallic alloys and multilayers consists of a target holder and a substrate holder housed in a vacuum chamber. Ablated targets are struck at an angle of 45° by a pulsed and focused laser beam in an ultra high vacuum chamber. The atoms and ions ablated from the target are deposited on substrates mounted on a heater. High-power pulsed lasers with nanosecond pulses are used as an external

energy source to vaporize materials and to deposit thin films.

1.1. Processes occurring during PLD

A sequence of particular processes occurs during laser ablation from the target and deposition of the ablated material on the substrate surface [4,5], namely: absorption of laser energy intensity (i), target heating (ii), ablation of a material (iii), plasma formation (iv), plasma expansion (v), deposition of particles with high kinetic energy (vi), instantaneous deposition rate connected with laser pulse (vii).

1.2. Applications

One of important advantages of the PLD method is a stoichiometry transfer from the target to substrate and production of multilayered materials. It could also be possible to influence the transferred plume to produce a special environment in the reactive chamber, which yields a layer of a requested phase. The method has

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been applied until now to a wide spectrum of materials [3,4].

Titanium nitride (TiN) coatings have proved their efficiency in increasing the lifetime of cutting tools. Their tribological properties are widely known [6,7] and their use in bioengineering applications as biomaterials has been considered, particularly as a wear-resistant coating for Ti6Al4V orthopaedic implants [7]. The tests undertaken showed that wear was reduced, that the TiN friction coefficient was low and that the TiN presented good chemical stability.

The purpose of this work was to study the titanium nitride coatings fabricated by PLD method. A Nd:YAG laser operating at the fundamental harmonics was used to deposit the TiN on both metallic (ferrite steel and pure titanium) and non-metallic (polyurethane) substrates by ablation of pure titanium in nitrogen environment.

2. Experimental

Thin films of titanium nitride were deposited by means of a Nd:YAG laser operating at the fundamental harmonics (1064 nm) in nitrogen environment in the reactive chamber. High purity titanium targets were used for ablation, effectuated by application of 0.6 J pulse energy (fluence approx. 30 J/cm²), 10 ns pulse duration at a repetition rate of 50 Hz. The deposition on metallic (ferritic steel and pure titanium) and non-metallic (polyurethane) substrates was performed at room temperature. Before deposition was started, the reactive chamber had been evacuated to pressure below 2×10^{-3} Pa by means of a pumping unit, consisting of a rotary vane pump and a turbomolecular pump. During deposition, the flow of the process gases (Ar, N₂) was adjusted by means of electronic mass flow controllers [8].

Structure examinations of the deposited layers were performed by means of scanning electron microscopy (SEM Philips XL30), transmission electron microscopy (TEM Philips CM20), atomic force microscopy (AFM) and X-ray diffraction (XRD Philips PW 1710).

3. Result and discussion

Fig. 1 presents the TEM micrographs (bright field) of the cross-section of the TiN deposited thin layer on the ferritic steel substrate. The presented electron diffractions were measured in the three zones of the TiN deposited layer marked as 'a', 'b', 'c', respectively, where 'a' is close to the substrate; 'b' intermediate zone and 'c' is close to the surface of the coating. A fine-grained microstructure (even nano-structure) of the deposited thin layer of TiN was observed in these TEM micrographs. Ring electron diffraction patterns were identified to be caused by the TiN phase. However, the

observed darkness contrast between region 'a' and regions 'b, c' could have be related to varied nitrogen concentrations in the TiN phase at the onset of deposition and during the process of deposition. To simulate three-dimensional shaped tools, the substrates were mounted parallel (on-axis geometry) and perpendicular to the target surface (off-axis geometry). The respective AFM micrographs are presented in Fig. 2.

Texture examinations by means of the XRD method were performed for the above mentioned TiN layers, produced in different geometries. Three pole figures were measured basing on the diffraction lines of the 111, 200 and 220 types in the reflexion mode and the completed pole figures were obtained by re-calculation of the experimental data using a specially dedicated own programme. They revealed differences and the results are shown in Figs. 3 and 4. For the study of a possible contribution of substrate texture to the preferred orientation developed in the deposited layers, an examination of the ferritic steel used as a substrate was performed and the obtained results in the form of pole figures are presented in Fig. 5. The measurements of residual stresses in the TiN phase, performed by means of the XRD method, showed compressive values in the range of -6 to -8 GPa for the on-axis growth while of approximately -2.8 GPa for the off-axis position.

Deposition of the TiN at ambient conditions on polyurethane substrate revealed that the uniform thin layer and diameter of crystallite was related closely to the thickness of the deposited layer, which is presented in Fig. 6. An evident grain growth is visible. It tends to increase together with an increase of the layer thickness. The TiN layers deposited on polyurethane are of diffusive character, which can be inferred from the diffusive shape of the interface layer/substrate (Fig. 7a) and EDX line scan of Ti through the thickness (Fig. 7b).

4. Concluding remarks

Metallic titanium was used as the target. Previous results, presented in Ref. [9,10], showed that the TiN phase was formed independently of the nitrogen flow in the reactive chamber. Even deposition of metallic titanium in argon environment led to the formation of a new tetragonal phase of the Ti(N) type [10]. The obtained electron diffraction patterns of the ring type indicated the presence of a very fine grain or even nanostructure (Fig. 1) in PLD layers. To improve adhesion of TiN, the onset of the process was triggered by deposition of metallic titanium. Duration of this first step of the deposition process was of approximately 2–3 min and led to the formation of a layer with thickness of approximately 0.1 μm and with a grain size slightly higher than that of the subsequently deposited TiN, which could be inferred from the tendency to form spot-type electron diffraction patterns. Even contrast in dark-

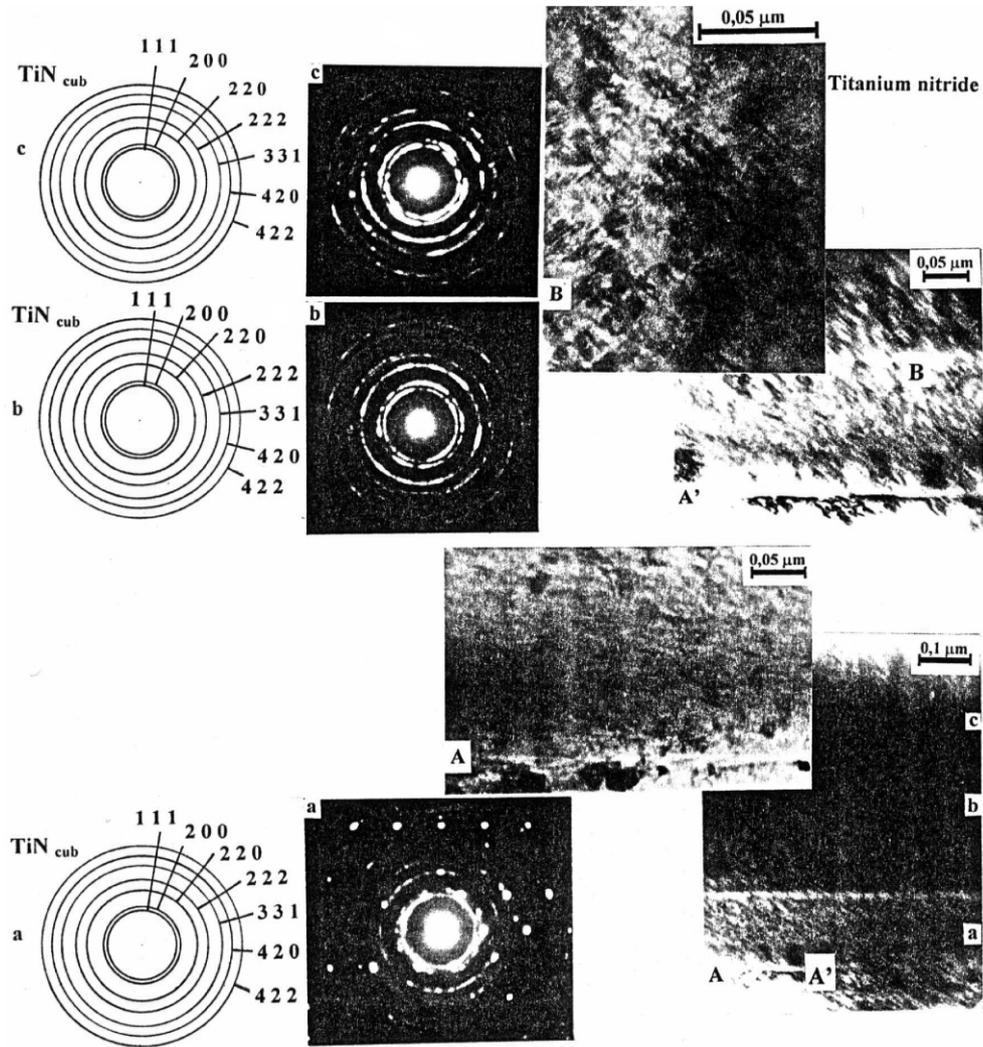


Fig. 1. TEM micrographs of the cross-section of the TiN thin layer deposited on the ferritic steel substrate by means of a Nd:YAG in the on-axis geometry.

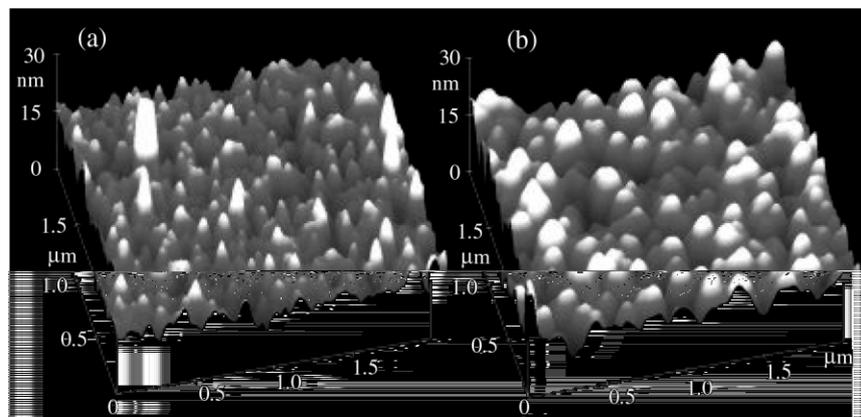


Fig. 2. AFM micrographs of surface layers deposited by means of a Nd:YAG laser in the on-axis (a) and off-axis (b) geometry.

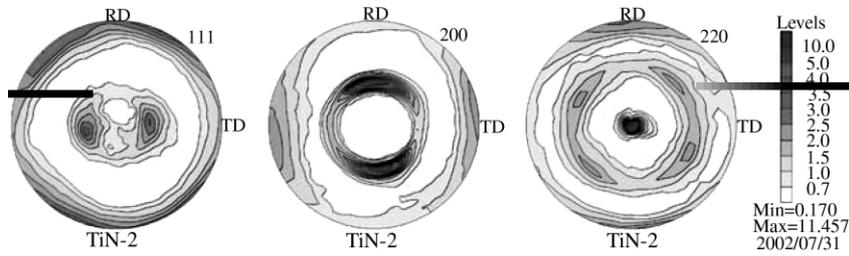


Fig. 3. Pole figures {111}, {200} and {220} of TiN deposited in the on-axis geometry by means of a Nd:YAG laser revealing the {110} <011> texture.

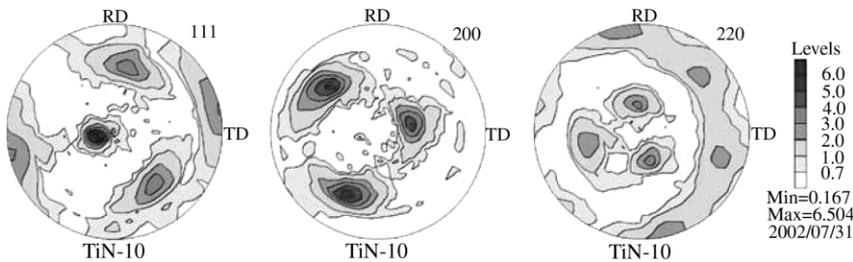


Fig. 4. Pole figures {111}, {200} and {220} of TiN deposited in the off-axis geometry by means of a Nd:YAG laser revealing {112} <223> texture.

ness may indicate the presence of a variation in nitrogen concentration through the thickness of the deposited layer. AFM micrographs showed that both microstructure and texture were different, depending on the applied geometry of deposition. In the on-axis position—due to higher energy of deposited species, which resulted from hitting the substrate surface at right angle—the probability of nucleation and the activation of diffusion on the surface was higher, which led to finer structure. In the case of the off-axis deposition geometry, in contrast to the on-axis one, the ablated species could hit the surface only after scattering caused by a collision with the other atoms in the deposition chamber. Differences in the mechanism of deposition led also to changes in the film thickness, which was about two times smaller in the case of off-axis, compared to the on-axis grown films. The differences in texture were more pronounced (Figs. 3 and 4). The deposition conditions in the off-axis geometry led to the formation of a texture, where a well

developed crystallographic axis was observed beside the preferred crystallographic plane. It was hard to state that there was any correlation between the texture of the substrate and the type developed in the deposited layers.

Examination of the TiN layers fabricated at room temperature on polyurethane substrate showed a correlation between the increase of grain size and of the layer thickness. An increase of the layer thickness was achieved by using a higher number of laser shots while the other deposition parameters were constant. Morphology observation of the cross-section of broken samples revealed a good adhesion which was inferred from the smooth interface layer/substrate, and more evidently from the change of concentration of titanium on line scan.

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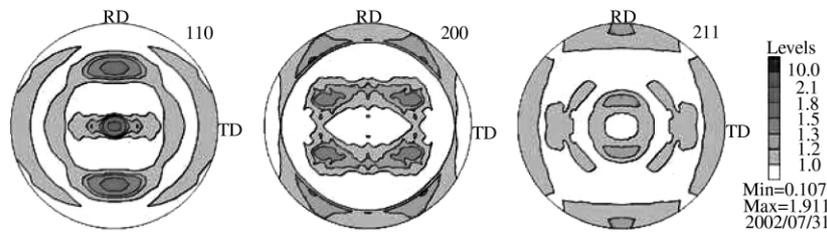


Fig. 5. Pole figures {111}, {200} and {220} of the steel sheet used as a substrate, revealing dominant {110} <112> texture which is very characteristic for the annealed ferritic steel sheets subjected to the heat treatment after cold-rolling.

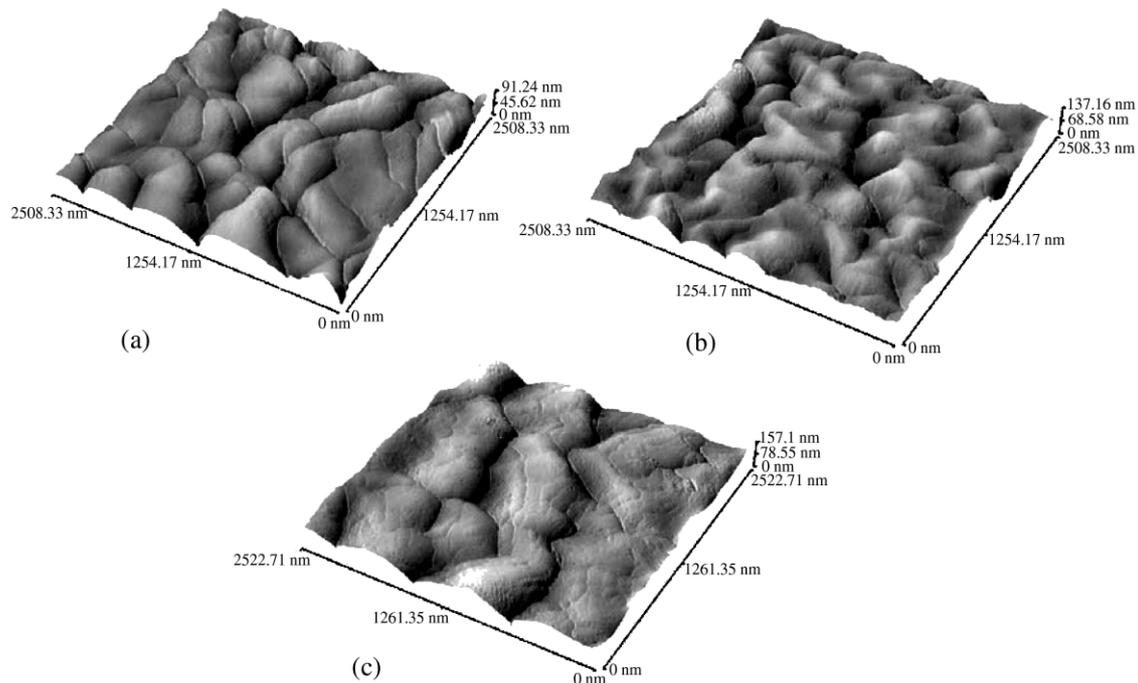


Fig. 6. AFM micrographs of the surface layers deposited on the polyurethane substrate by means of a Nd:YAG laser at the fluence 3 to 50 W/cm² in nitrogen environment with the layer thickness of 0.5 μm (a); 1 μm (b) and 3 μm (c).

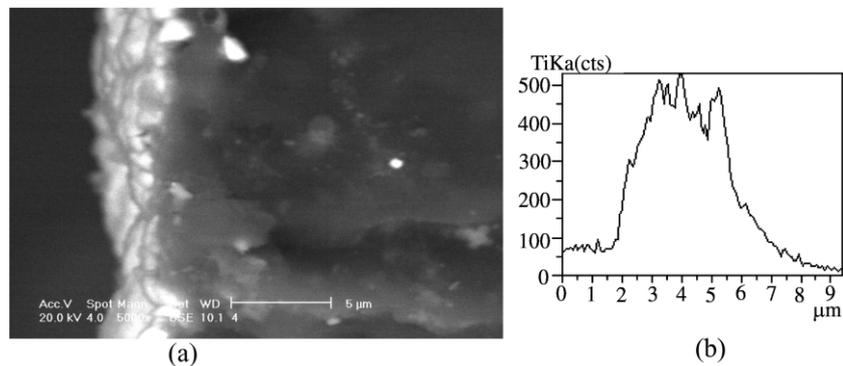


Fig. 7. SEM micrographs of the cross-section of the broken polyurethane samples with the TiN layer deposited by means of a Nd:YAG laser, with the thickness of 1 μm (a) and the EDX line scan analysis through the thickness (b).

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