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2007 J. Phys.: Conf. Ser. 59 16

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Industrially-scaled room-temperature pulsed laser deposition of Ti-TiN multilayer coatings

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Abstract. The aim of the current work is the transfer of multilayer design knowledge on the Pulsed Laser Deposition (PLD) technique for industrially-scaled room-temperature growth of titanium – titanium nitride (Ti-TiN) structures. Because almost all PVD and CVD coating techniques require substrate temperatures $> 200^{\circ}\text{C}$ for sufficiently adhering and dense coatings, there is high demand for the development of large-area and high-rate low-temperature vacuum deposition process like the PLD, e.g. for the coating of temperature-sensitive or shape-distortion-sensitive materials and substrates. A pulsed Nd:YAG laser (wavelength: 1064 nm) was used for depositing alternately Ti and TiN layers in Ar and N_2 atmosphere, resp., forming nearly particulate-free, very smooth and dense 1 μm thick coatings. Starting from single layers, in multilayers with thicker individual layers hardness and scratch resistance (critical load in scratch tests) is decreased, but this trend is reversed in multilayers of very thin (< 100 nm) individual layers. In contrast, the compressive growth stress is dropping down continuously in the multilayers of increasing period numbers.

1. Introduction

Besides alloying for the formation of multi-component and multi-phase coatings, the mechanical properties of surfaces can be manipulated by coating with multilayer structures. Such coatings of a great number of thin layer with different elastic, plastic, and tribological properties can possess greater strength, elasticity, plasticity, wear resistance, etc. than thick single-layer coatings [1].

Wear of hard PVD coatings on tools and machine elements is often closely related to sudden or fatigue cracking [2,3]. The life of such components can consequently be prolonged through an improved coating fracture resistance, e.g. by introducing a high density of interfaces (grain or phase boundaries) in the microstructure (found in multiphase ceramic bulk materials but also in multilayer coatings) [4,5]. Reasons for this effect has been suggested to be crack deflection by “weak” interfaces [6] or by differences in the elastic moduli of the layer materials [9], crack-tip shielding by plastic deformation in combination with strong interfaces [7], and favorable gradients in residual stress [8]. One way to improve the coating fracture resistance would thus be to deposit a multilayered structure consisting of alternating thin layers of a hard material (e.g. titanium nitride (TiN)) and a softer, more ductile material (e.g. titanium (Ti)). The Ti layers would theoretically allow extensive plastic deformation at crack tips and, due to a lower elastic modulus compared to TiN, deflect the crack into

the plane of the coating. Consequently, multilayered Ti/TiN coatings should display an improved fracture resistance compared to homogeneous TiN [10]. Additionally, improved hardness, wear and friction increase behavior were experimentally found for Ti-TiN multilayer coatings [11-13].

Until now, there is lack of knowledge about multilayer coating architecture for tribological purposes deposited by the Pulsed Laser Deposition (PLD) technique. The main drawback, complicating the multilayer growth is generally the low level of automating of PLD deposition equipment (mainly laboratory built) increasing the expenditure of time for deposition [14]. Thus, the aim of the current work was to show the successful adaptation and transfer of PVD (sputtered, arc evaporated) multilayer growth attempts to the PLD technique, exemplary on the improvement of single-layer TiN films by a multilayer Ti-TiN architecture. Increasing difficulty was set in the current work by the room temperature PLD coating attempt. Generally, PVD and CVD coating requires elevated substrate temperatures higher than 200–500°C to achieve good adhesion on the substrates and dense microstructures. These high-substrate temperatures inhibit the use of vacuum coatings in many applications, in which the substrates (e.g. pre-stressed tools) or substrate materials (e.g. plastics, compounds) cannot withstand such high temperatures. Thus, there is a high demand for developing low-temperature deposition processes for hard coating materials. One of the most promising candidates for industrially room-temperature coating in the nearest future is the PLD technique, which was recently up-scaled for industrial demands at Laser Center Leoben [15].

2. Experimental

High-purity titanium targets were used for the ablation experiments in Ar and N₂ atmosphere for Ti and TiN deposition, resp., 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 [15]. By the application of this multi-spot evaporation system the large-area coating is possible with low deviation (~ 5 %) of the coating thickness over the used deposition height of ~ 22 cm [16]. To provide homogenous film thicknesses over the whole surface area, the substrates were moved with a relative speed of 5.4 cm s⁻¹ through the plasma plumes during deposition. The emitted species were deposited at room temperature (~ 25 °C) in the turbo-molecular pumped chamber onto mirror-polished, ultrasonically-cleaned ferrite steel (AISI 630 HT) and (100) orientated silicon wafer substrates mounted parallel to the target surface. The concept for PLD Ti-TiN multilayer deposition was based on totally 1 μm thick coatings with $x(\text{Ti}+\text{TiN})$ multilayer periods ($x = 1, 2, 4, 8, 15$). The half of the multilayer period, the single layer thickness in the periods (individual layer thickness, for a schematics see the insert in figure 2a), was set equal for Ti and TiN.

The coating characterization was limited on structural and mechanical properties, which are known to be changing drastically in multilayer architecture. The phase composition of the TiN coatings was analyzed by an X-ray diffractometer (Philips PW 1710 XRD) in Bragg-Brentano alignment, working with CoK 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 hardness was measured by nanoindentation using a Berkovich indenter. The applied maximum loads were 20 mN, the loading rates 20 nm s⁻¹ for all measurements. Scratch testing was performed using a CSEM scratch tester fitted with a Rockwell “C” diamond (120° cone with a 200 μm hemispherical tip), moved under increased load (0.5 – 30 N) on the coatings. The critical loads for detachment were detected by acoustic emission. After scratching the failure modes were characterized using light microscopy.

3. Results and discussion

The mechanical behavior was found to be highly dependent on the coating structure because hardening mechanisms as well as crack propagation control mechanisms are dependent on the density and quality of interfaces between the alternating single layers – the phase boundaries. The change of the deposition conditions in order to grow the next layer requires the nucleation of new grains at the interface. The frequent renucleation effectively controls the grain size as revealed by Huang et al. [17] for Ti-TiN multilayers. The grain size decreases as the multilayer period is reduced. As no discrete

layers are observed for nominally low multilayer period thicknesses (a few nanometer) no renucleation occurs and the grain size is relatively high [18, 19].

Decreasing the grain sizes leads in the PLD coatings inevitably to their amorphization. This lost of crystallinity due to the frequent renucleation is revealed in figure 1, summarizing XRD spectra of industrially-scaled PLD Ti-TiN multilayer coatings of a total thickness of 1 μm and various multilayer period thicknesses. As higher the number of multilayer periods is (and, thus, as thinner the multilayer period and the individual layers are), the lower is the overall diffraction intensity of the coating, evidencing the low crystallinity.

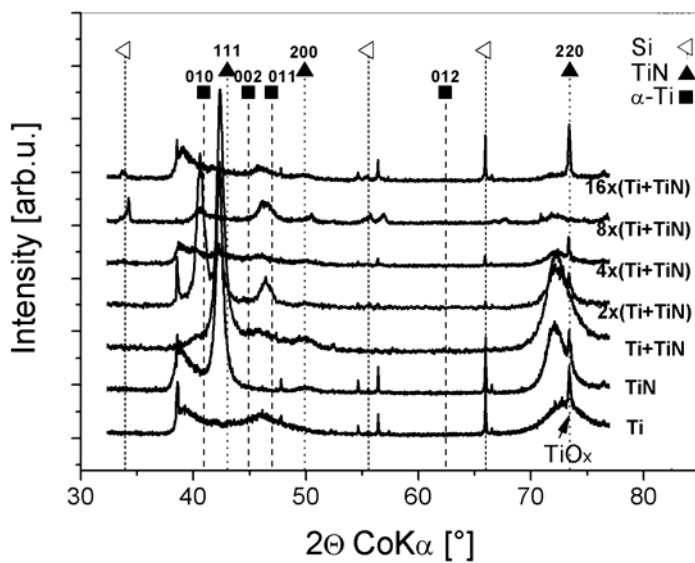


Figure 1. XRD spectra of 1 μm thick Ti-TiN multilayer coatings with a different number of multilayer periods (and for comparison 1 μm thick pure Ti and TiN single-layers). The occurring peaks are assigned to α -Ti, TiN and silicon (substrate). Until now, the reason for the occurrence of the high number of small sharp peaks in the spectra was not definitely solved.

The TiN (111) orientation, possessing the lowest lattice strain energy of all TiN planes [20,21], is getting totally lost in very thin TiN individual layers. The preferred formation of this orientation is generally found in high stressed films. Thus, the lost of the (111) orientation allows the conclusion, that the lattice distortion is drastically decreasing in these layers. A confirmation of this behavior can be found in the increasing TiN (220) peak – the TiN lattice orientation of the lowest surface energy [22-24]. Diminishing lattice distortion let expect higher near-equilibrium arrangement of atoms in the crystallographic film structure. A shift to higher diffraction angles (to the near-equilibrium state) seems to be found for the broad (220) TiN peak, resulting in much lower compressive stressing of the TiN layers. However, an interpretation of this peak is questionable due to the coincidence with the broad peak of the Ti (evident in the Ti single layer too) at similar diffraction angles. This peak is labeled TiO_x because of the good coincidence with Anastase and Rutile diffraction lines – two crystalline types of TiO_2 – and results from preferred incorporation of oxygen from the rest gas atmosphere at the room temperature PLD [3, 25].

The reduction of lattice distortion normally results in the decrease of the residual compressive stress of the coating. Such behavior was hence found for the TiN layers in the multilayers too. Figure 2a presents very obviously, a drop-down of residual stresses in TiN from -11.9 GPa in the 1 μm thick single-layer to about -3 GPa in the multilayer of 15 periods (individual layer thickness: about 32 nm). Bull et al. [18] stated that the presence of any un-reacted Ti in the coating would be expected to reduce the residual stress, since Ti has a lower yield stress than the titanium nitride and could allow stress relaxation by plastic deformation. Stress fields building up in the growth of the highly ordered TiN layer are transferred to the subjacent layer – the Ti layer, deforming it and increasing its compressive stress level compared to the Ti single-layer. Although a decrease of the multilayer period thickness decreases both the stress in the TiN as well as in the Ti layer, the low stress level of the Ti single-layer

coating was found only in the multilayer with the highest number of multilayer periods investigated. Deriving from this finding, it is evident that starting from the Ti-TiN bi-layer, higher number of multilayer periods diminishes the stress in the multilayer.

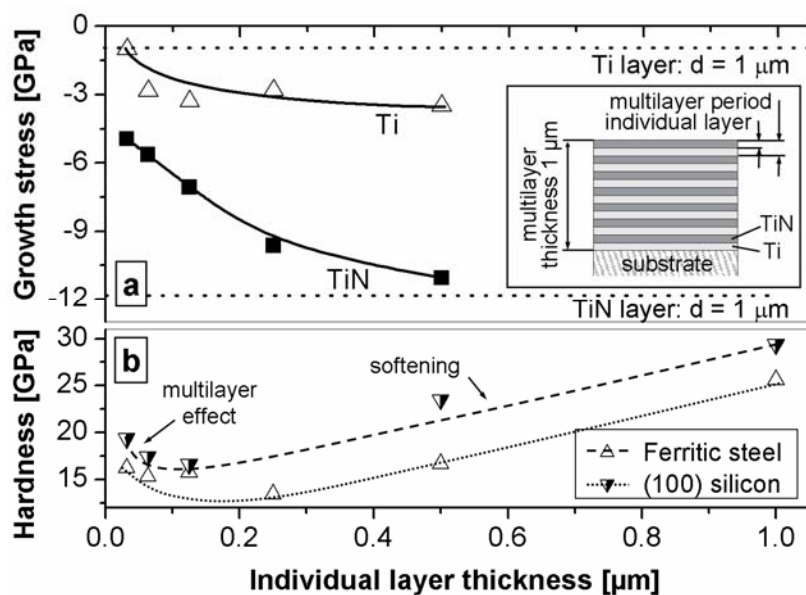


Figure 2. (a) Residual growth stress of PLD Ti-TiN multilayers (total film thickness: 1 μm) measured by the XRD $\sin^2 \Psi$ method in dependency on the individual layer thickness of Ti (and TiN). (b) Hardness of the PLD Ti-TiN multilayer coatings in dependency on the individual layer thickness. The values are given for comparatively softer ferritic steel and hard silicon substrates, revealing the accuracy of the trend in hardness evolution in the multilayer.

Generally, the reduction of the compressive stress level in coatings goes hand in hand with the decrease in hardness. Dislocation propagation would be easier in a low-stressed layer compared to a high-stressed one [18]. Additionally, the integration of a softer component (metallic Ti) in the hard TiN constrains the deformation in the better deformable layer [26]. Both phenomena explain the hardness decrease (softening) in the multilayers of a low number of Ti-TiN periods (larger individual layer thickness), shown in figure. 2b. Grain refinement by renucleation is scarcely found in these coatings of ≥ 0.25 nm individual layer thickness – all adequate XRD peaks of TiN and Ti are scarcely changing their width (figure. 1).

However, the trend of coating softening is inverted at individual layer thicknesses lower than 0.125 μm due to the more complicated dislocation movement. As shown in figure 2b, the hardness is increasing by the Hall-Petch hardening effect: Dislocations are piling-up near or at the interface at very low deformation, if the difference in the dislocation energy between the adjacent layers is high enough and, consequently, the dislocations in one layer are not able to penetrate the interface. The maximum of hardness by Ti-TiN multilayer design was found by several authors to be between 5 and 20 nm period thickness (2.5 to 10 nm individual layer thickness) [17,19]. Such a low thickness was not reached by the deposited PLD multilayers of the current work. Underneath this critical thickness, hardness decreases generally drastically, because the dislocation formation is hindered, comparable to ultra-fine grained materials and competitive deformation mechanisms (e.g. boundary sliding accompanied by short-range diffusion) are preferred.

The critical load for coating detachment was tested by scratch tests and follows a similar trend as the hardness (figure 3). Additionally, the minimum in hardness is corresponding to the minimum of the resistance to delamination (critical load), but presents also the change of the failure mechanism:

(1) According to Bull et al. [18], multilayer coatings of lower individual layer thickness show much less evidence for through-thickness cracking in the scratch tracks at the same loads at which coating of thicker individual layers are failing. Propagating through-thickness cracks are deflected at the interfaces and do not destroy the coating [27]. Thus, the stress distribution is less severe in these multilayers [28]. However, if the stress is too high and exceeding the critical load, complete failure of

the multilayer coating by detachment occurs. The mechanism of failure is buckling (see figure 3-1), which is triggered by compressive stresses in the coating generated ahead of the moving indenter. Localized regions containing interfacial defects allow subsequently the lateral spreading of buckles by the propagation of interfacial cracks [29], mostly leading to the extensive coating delamination.

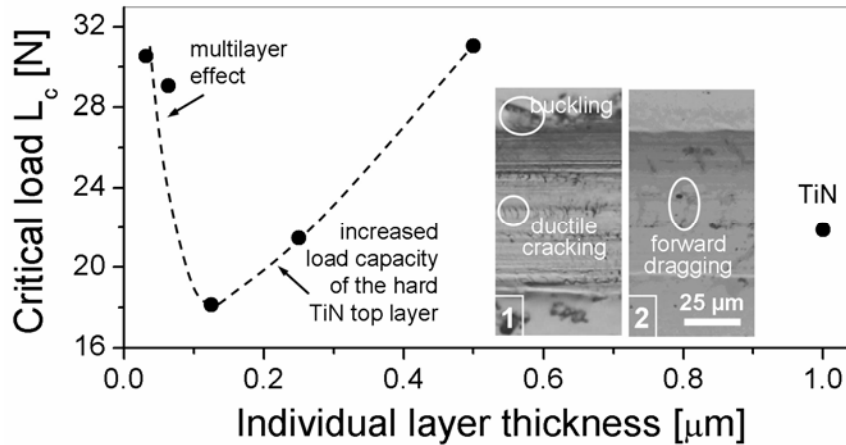


Figure 3: Dependency of the critical load of PLD Ti-TiN multilayer coatings on ferritic steel on the individual layer thickness in the scratch test and failure types at the critical load depending on the layer thickness: (1) Buckling of the 16x(Ti+TiN) multilayer (individual layer thickness: 32 nm): Main feature of the occurring buckle are the curved cracks extending to the edges of and beyond the scratch track and the possibility to chipping of the coating along these cracks. Passing of the scratch stylus over the failed region crushes the coating into the surface of the scratch track and erases most of the traces, except the delamination occurring outside the scratch track. (2) Tearing and peeling failure of a 2x(Ti+TiN) multilayer (individual layer thickness: 250 nm). This failure mechanism is characterized by an apparent forward dragging with suddenly increasing friction coefficients.

(2) In contrast, the failure characteristics for the Ti-TiN multilayers of higher individual layer thickness are strongly different. Additionally, this failure type is found for the Ti and TiN single layer coatings. While shearing in the soft Ti layers is disabled for the lower individual layer thickness, this larger thickness allows quite large shear deformation. Hence, the softer Ti layers dissipate most of the introduced energy by means of shear deformation [30, 31]. The higher the individual layer thickness is, the higher is the critical load due to increased load capacity of the covering TiN layer. This shear deformation is apparent by the forward dragging structures in the images of the scratch tracks (e.g. figure 3-2). This tearing and peeling failure results in the formation of well visible curved cracks across the scratch track [18]. Uncovering the softer multilayer component (Ti) leads to a sudden increase of the friction coefficient, because the Ti coating is relatively sticky and adheres strongly to the scratch diamond. The cracks occurring during scratching are scarcely stopped by interfaces and run through the coating down to the coating-substrate interface. Only the high adhesion of the room-temperature deposited PLD coatings (pseudodiffusion interfaces) prevents a total delamination of the coating under quite low loads.

4. Conclusions

The current work showed that the application of multilayer design by the industrially-scaled Pulsed Laser Deposition (PLD) technique for room-temperature coating is highly advantageous. High numbers of alternating Ti and TiN layers drastically reduces the compressive film growth stress, which could enable the coating of softer, deformable surfaces by the room-temperature PLD. Additionally, the toughness of the coatings expressed by the critical load in the scratch test is significantly improved by the Ti-TiN multilayer architecture compared to TiN single layer coatings.

As a lack of the investigated multilayer system, the hardness of the multilayers is generally lower than for the TiN single layer. Thus, future work will have the aim to enhance hardness without worsening the compressive stress and toughness level.

5. Acknowledgements

Financial support of this work by the Austrian Federal Ministry of Traffic, Innovation and Technology, the Austrian Industrial Research Promotion Fund (FFG), the Government of Styria, the Technologie Impulse Gesellschaft mbH in the frame of the Kplus Programme, the Austrian-Polish Exchange Service, and the European Union is highly acknowledged. The following colleges at Laser Center Leoben and the Institute of Metallurgy and Materials Science of the Polish Academy of Sciences are highly acknowledged for the very useful discussion, coating deposition and coating characterization: Dr. W. Waldhauser, Prof. Boguslaw Major; Mr. D. Hufnagel, Ms. R. Berghauser; DI L. Major, DI R. Major.

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