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Nano-crystalline nitride-based coatings produced by pulsed laser deposition

Nanokrystaliczne powłoki azotkowe wytwarzane metodą osadzania laserem impulsowym (PLD).

ABSTRACT

Titanium nitride and chromium nitride thin layers were fabricated by pulsed laser deposition (PLD) using a Nd:YAG laser on ferritic and austenitic steel substrate 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 about –2.8 GPa for the off-axis position. Texture examinations revealed the {110} <112> 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 the plane {110} parallel to surface with tendency to the {110}<011> was observed. In the case of the off-axis growth, the very pronounced {112} <223> dominant orientation was stated. TEM examinations performed on thin foils prepared from the cross-section of deposited Cr/CrN/Cr/CrCN multilayer revealed the nano-crystalline structure comprising CrN and CrCN phases together with an amorphous Cr-based phase. Tribological test showed improvement of wear properties of both deposited coatings.

ABSTRACT (in Polish)

Cienkie powłoki azotku tytanu i azotku chromu zostały naniesione na podłoże ze stali ferrytycznej i austenitycznej przy zastosowaniu metody PLD z wykorzystaniem lasera Nd:YAG. Proces osadzania prowadzono w atmosferze azotu przy równoległym i prostopadłym ułożeniu podłoża do powierzchni tarczy w celu symulacji nakładania warstw na obiekty trójwymiarowe. Pomiar wartości naprężeń własnych ujawnił ściskający charakter naprężeń o wartości –6 do –8 GPa dla przypadku równoległego ułożenia zaś –2.8 GPa dla przypadku gdy materiał pokrywany ułożony był prostopadle do tarczy.
Stwierdzono, iż głównym składnikiem tekstury podłoża jest {110}<112>, natomiast tekstura warstwy była uzależniona od ułożenia podłoża względem powierzchni odparowywanej tarczy podczas nakładania. Dla ustawienia równoległego tekstura miała charakter osiowy z płaszczyzną {110} równoległą do powierzchni i z tendencją do tworzenia tekstury typu {110}<011>. W przypadku gdy podłoże ustawione było prostopadle do tarczy dominował składnik {112}<223>. Badania TEM wielowarstwowej powłoki Cr/CrN/Cr/CrCN ujawniły strukturę nanokrystaliczną dla warstw CrN i CrCN, natomiast warstwy Cr posiadały charakter amorficzny. Test zużycia (pin on disc) wykazał, iż obie analizowane powłoki TiN, jak również CrN znacznie obniżają zużycie.

Keywords: titanium nitride, chromium nitride, morphology, texture, residual stresses

INTRODUCTION

Hard and corrosion-resistance coatings are frequently used to protect and enhance the lifetime of industrial components under high and constant wear loads. Titanium nitride is the standard among the transition metal nitride coatings employed in the industry, but requirements to withstand aggressive environments and to improve oxidation and wear resistance under extreme temperatures has led to chromium nitride [1-5]. Chromium coatings form a passivating oxide layer that does not allow further oxidation; explaining why chromium nitride is believed to be a promising solution to corrosive problems.

Recently, another approach to solve some coating problems has been to design new structures, such as multilayers. The multilayer concept has succeeded in a broad range of applications, and is now being proposed as a promising way to improve the wear-resistance properties of hard coatings. Since good results have been obtained using multilayer structure of Ti/TiN [4], the proposal Cr/CrN multilayer has been given. It has been reported that the combination of hard but brittle CrN and tough but soft Cr in a multilayer structure enhances the wear resistance of each individual material [5]. TiN and CrN films are commonly formed by the techniques of chemical vapor deposition (CVD) and physical vapor deposition (PVD) [1]. These methods, however, require elevated substrate temperatures (exceeding 500^{0}C) to achieve good adhesion between films and substrates. Deposition at elevated temperatures excludes applications where the substrate cannot withstand heating. Thus, there is a high demand for developing low-temperature deposition processes for thin films, such as pulsed laser deposition (PLD) [6,7]. In the PLD technique a pulsed laser beam is focused onto a target in order to evaporate its surface layers under vacuum or low pressure process gas conditions. 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 [8]. 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 [6-12].

The aim of this work was deposition of TiN and CrN in form of mono- and multilayers using PLD method in perspective for tribological application.

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EXPERIMENTAL

Thin films of TiN as well as Cr/CrN/Cr/CrCN were deposited by means of a Nd:YAG laser operating at the fundamental harmonics (1064nm) in nitrogen environment in the reactive chamber. High purity titanium or chromium targets were used for ablation, respectively. The targets were effectuated by application of 0.6 J pulse energy (fluence about 30 J/cm^2), 10 ns pulse duration at a repetition rate of 50 Hz. Ferritic steel for TiN and austenitic steel for Cr/CrN substrates were performed at room temperature. Before deposition was started, the reactive chamber had been evacuated to pressure below 2x10^{-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, N_2) was adjusted by means of electronic mass flow controllers. 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).

RESULT AND DISCUSSION

To simulate three-dimensional shaped tools, the substrates were mounted parallel (on-axis geometry) and perpendicular to the target surface (off-axis geometry) [9].
The respective AFM micrographs are presented in Fig.1.

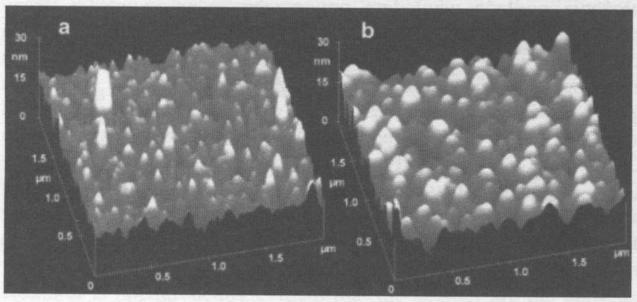

Fig. 1. AFM micrographs of TiN surface layers deposited by means of a Nd:YAG laser in the on-axis (a) and off-axis (b) geometry
Mikrostruktura AFM powłoki TiN (a) podłoże prostopadle do powierzchni tarczy; (b) podłoże równoległe do powierzchni tarczy

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 complete 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.2 and 3.

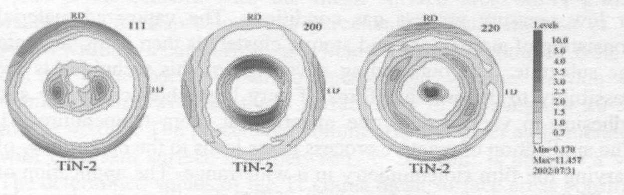

Fig. 2. Pole figures {111}, {200} and {220} of TiN deposited in the on-axis geometry by means of a Nd:YAG laser revealing the {110}<011> texture
Figury biegunowe typu {111}, {200} i {220} powłoki TiN naniesionej na podłoże ułożone równolegle do tarczy, tekstura {110}<011>

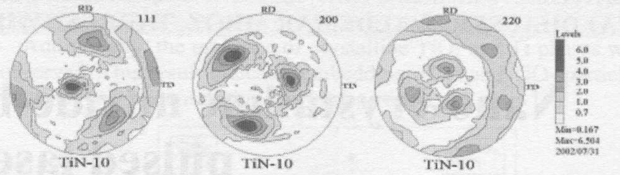

Fig. 3. Pole figures {111}, {200} and {220} of TiN deposited in the off-axis geometry by means of a Nd:YAG laser revealing {112}<223> texture
Figury biegunowe typu {111}, {200} i {220} powłoki TiN naniesionej na podłoże na ułożone prostopadle do tarczy; tekstura {112}<223>

For the study of a possible contribution of substrate texture to the preferred orientation developed in the deposited layers, 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.4.

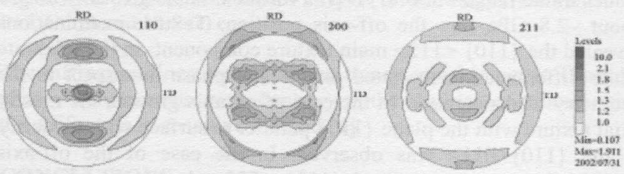

Fig. 4. Pole figures {111}, {200} and {220} of the ferritic steel sheet used as a substrate for TiN, revealing dominant {110}<112> texture which is characteristic for the annealed ferritic steel sheets subjected to the heat treatment after cold-rolling
Figury biegunowe typu {111}, {200} i {220} blachy ze stali ferrytycznej stosowanej na podkładki warstw TiN, dominująca tekstura {110}<112>, która jest charakterystyczna dla blachy ze stali ferrytycznej po procesie walcowania na zimno i wyżarzaniu

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 about –2.8 GPa for the off-axis position. Examinations of tribological properties showed low friction coefficient in TiN/TiN couples in the beginning of sliding (Fig. 5 left). After this initial phase, the friction coefficient increased because of TiN wear debris formation. The wear tracks in the high friction regime revealed only abrasive wear (Fig.5 right).

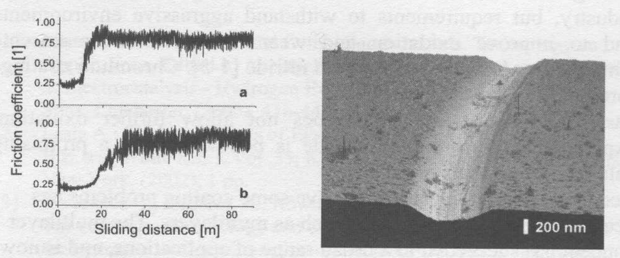

Fig.5. SEM micrograph of a wear track after sliding against a TiN coated 100Cr6 ball on an on-axis grown TiN film (righ side) and a dependence of the friction coefficient on a sliding distance for (a) on-axis and (b) off-axis grown TiN films against TiN coated 100Cr6 balls
Mikrostruktura SEM ścieżek zużycia warstwy TiN po teście tarcia kulką 100Cr6 pokrytą TiN i zależność współczynnika tarcia od długości drogi testu (a) wynik testu zużycia warstwy nałożonej równolegle do powierzchni tarczy (b) wynik testu zużycia warstwy nałożonej prostopadle do powierzchni tarczy

Formation of the nano-crystalline structure comprising CrN and CrCN phases together with an amorphous Cr-based phase was stated in the deposited multilayers Cr/CrN/Cr/CrCN (Fig.6).

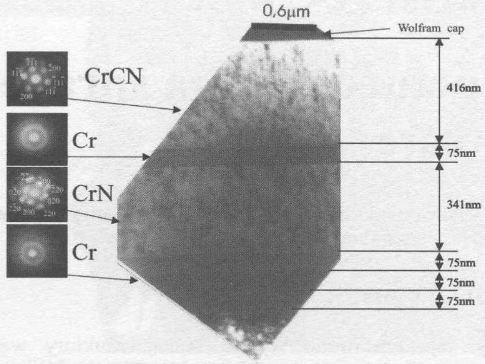

Fig.6. TEM micrograph of the cross-section of Cr/CrN/Cr/CrCN multilayer deposited by means of a Nd:YAG laser in the on-axis geometry together with electron diffractions obtained from the deposited layers and austenite substrate

Mikrostruktura TEM i dyfrakcje elektronowe z przekroju poprzecznego wielowarstwowego materiału Cr/CrN/Cr/CrCN nałożonego przy zastosowaniu lasera Nd:YAG, gdy podłoże podczas nakładania ułożone było równolegle do powierzchni tarczy

The coating has a nano-structure character within individual layers were hardly to be observed. The performed tribological test revealed improvement of the properties, similar to those observed for the TiN coating, however, an increase of the friction coefficient was shifted to the longer sliding distances (Fig.7).

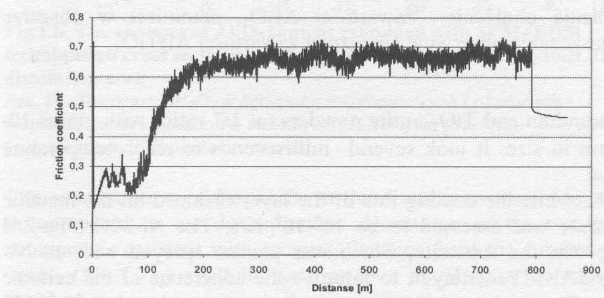

Fig.7. Dependence of the friction coefficient on a sliding distance for on-axis grown of CrN film against TiN coated 100Cr6 balls

Zależność wartości współczynnika tarcia od drogi testu dla przypadku gdy podłoże podczas nakładania warstw ułożone było równolegle do powierzchni tarczy. Test zużycia prowadzony był za pomocą kulki 100Cr6 pokrytej warstwą TiN.

CONCLUDING REMARKS

Metallic titanium was used as the target for deposition of TiN. Previous results [10,11] 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 [11]. Morphology (Fig.1) and the obtained electron diffraction patterns of the ring type (Fig.6) indicated the presence of very fine grains or even nanostructure in the PLD layers. To improve adhesion of TiN or CrN, the onset of the process was triggered by deposition of metallic titanium or chromium, respectively. Duration of this first step of the deposition process was of about 2-3 minutes and led to the formation of the layer with thickness of about 0.1 μm and with a grain size slightly higher than that of the subsequently deposited, which could be inferred from the tendency to form spot-type electron diffraction patterns. 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 a 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 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. 2 and 3). The deposition conditions in the off-axis geometry led to the formation of the texture, where a well developed crystallographic axis was observed beside the preferred crystallographic plane. It was stated that there was poor correlation between the texture of the substrate and the type developed in the deposited layers. TEM examinations performed on the thin foils prepared from the cross-sections of multilayered Cr/CrN/Cr/CrCN coating revealed the the nano-crystalline structure comprising CrN and CrCN phases together with an amorphous Cr-based phase. The columnar growth by the kinetic mechanism seemed to occur during formation of this layer. Both titanium and chromium nitrides coatings improved the tribological properties while the increase of the friction coefficient was shifted to the longer sliding distances for chromium nitride coatings.

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