Chapter 11

Features of the Microstructure of Multilayered (TiAlSiY)N/MoN Coatings Prepared by CA-PVD and Their Influence on Mechanical Properties

Olga Maksakova, Alexander D. Pogrebnjak, Oleksandr Bondar, Vyacheslav Stolbovoy, Yaroslav Kravchenko, Vyacheslav Beresnev and Pawel Zukowski

Abstract Thin nanolayered coatings composed of the consequent alternation of multi-element (TiAlSiY)N and binary MoN layers were deposited by the cathodic arc deposition. The elemental composition, phase structure, microstructure and mechanical properties of the coatings were studied by well-established experimental methods: SEM, EDS, XRD, TEM, and microindentation. It was found that (TiAlSiY)N/MoN coatings had a complex chemical composition, which preferably consisted of a mixture of Ti, Al and Si nitrides. The preferential crystallographic orientation along (200) plane was found for all samples. TEM results showed that investigated coatings composed of ununiform nano-scale multilayered structures with modulation periods ranged from 20 to 32 nm. The maximum microhardness of the deposited coatings reached 1087H_V0.1.

O. Maksakova (✉) · A. D. Pogrebnjak · O. Bondar · Y. Kravchenko
Sumy State University, Sumy, Ukraine
e-mail: maksakova.tereshenko@gmail.com

V. Stolbovoy
National Science Center Kharkiv Institute of Physics and Technology, Kharkiv, Ukraine

V. Beresnev
V. N. Karazin Kharkiv National University, Kharkiv, Ukraine

P. Zukowski
Lublin University of Technology, Lublin, Poland

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11.1 Introduction

Designing of the multilayered films that improving the properties of the coated materials is a difficult task but in case of its successful fulfillment obtained material gained improved hardness, wear resistance, temperature stability and better performance [1–6]. Synthesis of alternating nanoscale layers consisting of various materials is a particularly promising strategy through the design of atomic-scale architectures. The results reported in works [7–23] prove that multilayered coatings of simple-composition, such as TiN/ZrN, CrN/AlN, ZrN/CrN, TiN/NbN, CrN/MoN, TiN/MoN, TiN/CrN demonstrate the significant improvement of mechanical and tribological properties, as well as better thermal and corrosion resistance compared to the monolayer films.

Nowadays, a novel tendency, in which the multielement and multilayered strategies for the synthesis of functional coatings based on transition metal nitrides, metalloids, and refractory elements are combined, starts to develop widely [24–33]. Chen et al. [34] investigated TiAlSiN-based monolayers and multilayered coatings fabricated by the cathodic arc evaporation. It was shown that the deposition method exceedingly enhanced adhesive strength and toughness. According to the results of milling tests, the lifetime for TiAlSiN coated substrates increased by approximately 172%. Tribology experiments did by Çalışkan's [35] indicated that the nanocomposite TiAlSiN/TiSiN/TiAlN multilayered coating had a higher value of load (L_{C3}) at almost 44% and longer functioning time than single layer TiN and TiAlN coatings. The work-team of the manuscript [36] investigated the TiAlN, TiAlSiN and TiAlN/TiAlSiN multilayered coatings deposited by magnetron sputtering. Obtained results pointed out that multilayered composite demonstrated enhanced adhesion strength compared with TiAlSiN. Therefore, a multilayered concept of TiAlSiN-based coatings arises much interest and can be used for the protection of cutting tools and working parts used in different industrial processes, where the high hardness, wear and corrosion resistance, and thermal stability at over 1100 K are required.

It is suggested that the addition of a low amount of Yttrium to the TiAlSiN alloy will improve the high-temperature oxidation resistance. The nitride of TiAlSiY will maintain high hardness as the formation of YO_2 phase at the grain boundaries is possible. This phase blocks inward diffusion of oxygen and outward diffusion of metal components of the coating because Yttrium has a high affinity towards Oxygen [37–42]. Considering all these advantages, the study of TiAlSiYN-based multilayered coatings presents great scientific interest.

The main focus of this work is concentrated on the detailed microstructural research of recently developed multilayered (TiAlSiY)N/MoN coatings and the establishment of the effect of their structural features on mechanical properties.

11.2 Methods and Experiments

11.2.1 Deposition Technology

Cathodic arc deposition (CA-PVD) is a widely applied method for the deposition of nitride-based coatings. The primary advantage of this technique lies in its ability to produce highly ionized plasma. Ion energies of plasma produced by CA-PVD can be further increased or tuned due to a negative potential applied to the substrate. Application of a direct current substrate bias during deposition leads to the formation of coatings with dense structure and well adhesion. However, this technological parameter increases residual compressive stresses of the coatings that influence on mechanical and tribological properties of the coated material [43–45].

Multi-purpose cathodic arc evaporation system was utilized to deposit multilayered coatings using circular TiAlSiY and Mo targets operated at the cathode currents of 100 and 150 A, respectively.

A composite multi-element cathode had the following elemental ratio Ti—58 at. %; Al—38 at. %; Si—3 at. %, Y—1 at. %. The composite cathode was sintered using the spark plasma sintering unit. The purity of Mo cathode was 99.8%. The nitrogen with a purity of 99.95% was fed into the chamber as reaction gas through the control facility. A constant nitrogen pressure of 0.53 Pa was constantly kept during the deposition process. The coatings were deposited onto a 321S51 steel substrates of 18 × 20 × 2 mm size. The substrates stopped in front of each cathode for 1 min for the deposition of alternating layers. The deposition time for the films was 1 h.

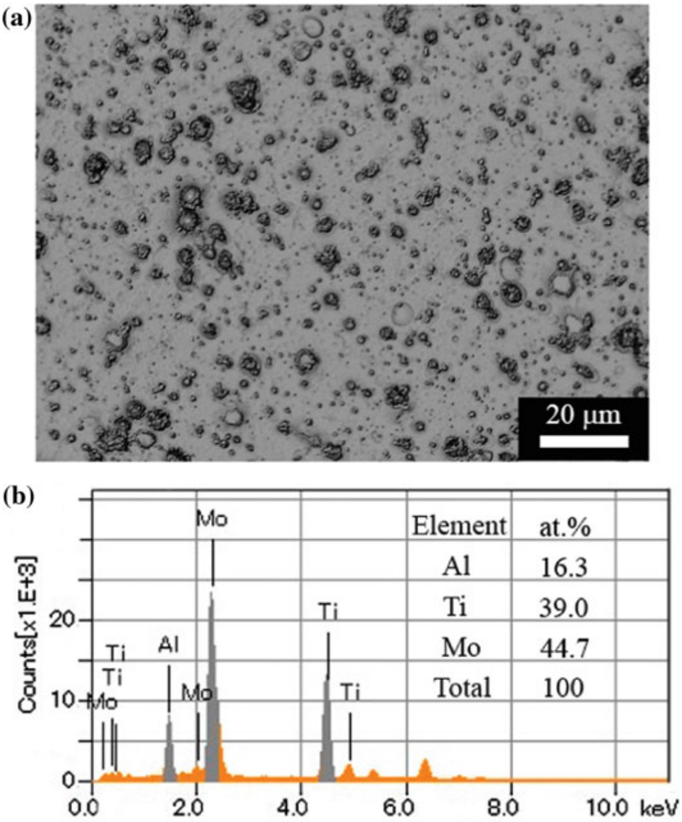
11.2.2 Investigation Methods

The surface of the deposited samples was examined by scanning electron microscope (JEOL) (JEM-7001TTLS). The cross-section of the coatings was prepared and studied by the focused ion beam (FIB) (JEOL JEM-9320). ImageJ program was used to calculate the total and bilayer thickness of experimental composites [46]. The TEM and EDS investigations were conducted using a JEOL ARM 200F operated at 200 keV. The X-ray diffraction (XRD) investigations were carried out using a PANalytical diffractometer equipped with a $CuK\alpha$ X-ray source with PIXcel 3D detector. XRD measurements were carried out in the θ–2θ mode and obtained results were used to determine the phase state, preferred orientation and crystallite size. The hardness tests were carried out using the statistical microindentation method taking into account the area of the tip imprint. The Shimadzu HMV-G Micro Vickers Hardness Tester equipped with a tetrahedral diamond pyramidal tip with an angle of 136° between the opposite faces was used. The delay time after reaching the specified load was 10 s.

11.3 Results and Discussion

11.3.1 Surface Morphology and Elemental Composition

The morphology of the surface of experimental coatings has a rather rough texture due to a large number of drop constituents that can be seen in Fig. 11.1a. This phenomenon is typically observed for CA-PVD products and attributed to the technological process when active gas in the vacuum chamber extensively undergoes a reaction with the evaporated material and forms solid refractory compounds [47–50]. The EDS spectrum of the surface elemental composition of investigated coatings is shown in Fig. 11.1b.



Element	at.%
Al	16.3
Ti	39.0
Mo	44.7
Total	100

Fig. 11.1 Results of SEM with EDS analysis of multilayered (TiAlSiY)N/MoN coatings: surface image (**a**); EDS spectrum and elemental composition (**b**)

The surface topography of the (TiAlSiY)N/MoN coatings, studied using 3D model, ensured the estimation of some surface peculiarities, which include: the average roughness (0.27 μm), the texture aspect ratio (0.86) and the maximum height of droplet constituents (8 μm).

11.3.2 Phase State and Microstructure

The diffraction spectra of the multilayered coatings show a strong (200) preferential orientation and low contribution from (111), (220) and (311) planes of fcc-TiN phase (Fm3 m space group) (ICCD: 04-001-2272) (see Fig. 11.2). The (200) diffraction peak has been shifted toward lower angles comparing with bulk values. It indicates a decrease of the inter-planar distance for (200) plane ($d = 2.1043$ Å) and related with the incorporation of Al to the coating. The broad shoulder of the (200) peak ranged from 45.15° to 50.5° can be assigned to the formation of the solid solutions of (Ti, Si)N and (Ti, Al)N that have generated in a result of the substitution of Si and Al for Ti in TiN lattice [51–53]. It is because the ionic radiuses of Si^{4+} (0.041 nm) and Al^{3+} (0.053) ions are smaller than that of Ti^{3+} (0.075 nm) ion. Additionally, it possibly indicates the formation of highly disordered or even amorphous-like phase in the coatings [37]. The presence of the hexagonal δ-MoN phase (P63mc space group) is submitted by (112) and (211) peaks (ICCD: 00-064-0129).

The average crystallite size calculated using the Scherrer method from (200) reflection is approximately 12 nm. The intensities of other reflections are too low for a correct estimation of the average crystallite size.

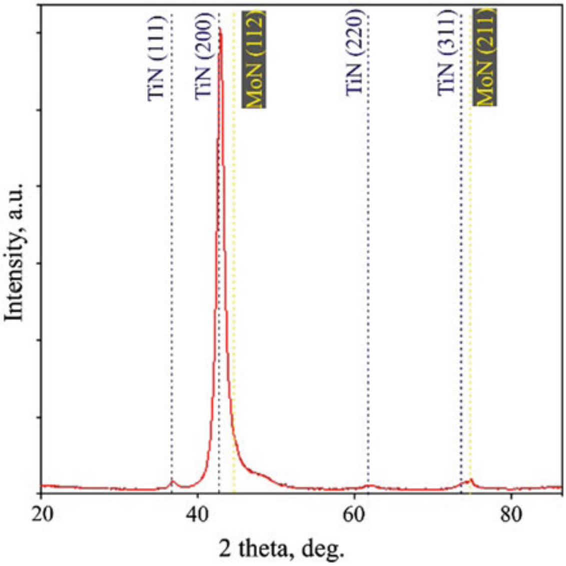


Fig. 11.2 Typical XRD pattern of multilayered (TiAlSiY)N/MoN coatings

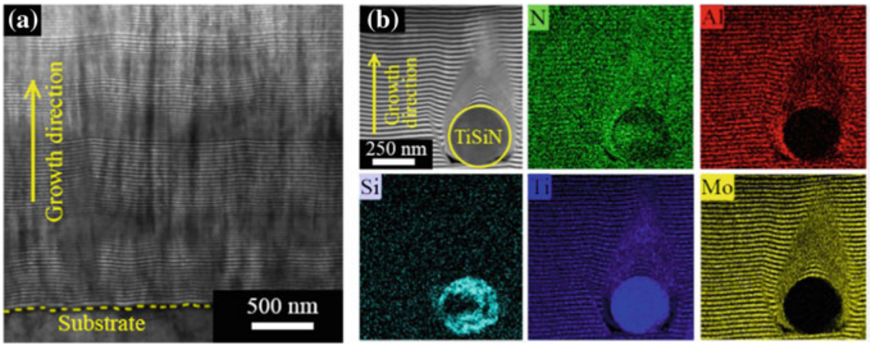


Fig. 11.3 TEM images of the cross-sectional view of multilayered (TiAlSiY)N/MoN coatings: coating-substrate zone (**a**); TEM-EDS elemental mapping of the surface zone (**b**)

The microstructure of the layers and interfaces, as well as elemental composition of (TiAlSiY)N/MoN coatings, have been analyzed from cross-section analysis by means of TEM and EDS. As shown in Fig. 11.3a distinct interface can be seen at the boundary between the steel substrate and the first nitride layer being deposited. The micrographs suggest that the appearance of the MoN layers is darker compared with the lighter contrast of the multi-element (TiAlSiY)N layers. This is because of the higher atomic number of MoN layers [37, 54, 55]. The total thickness of the experimental coatings is approximately 7 μm.

The microstructure of (TiAlSiY)N/MoN composites consists of columnar grains with an average of width ranges from 40 to 120 nm. They are oriented in such a way that the longer axes of the grains are parallel to the growth direction of the coating. The columnar microstructure is typical of the coatings deposited at low temperature and low gas pressure in CA-PVD process. Evident straight and sharp interfaces between (TiAlSiY)N and MoN layers are identified. It is pronounced due to the immiscibility of (TiAlSiY)N and MoN layers. The samples do not display any inter-lamella cracking indicating good adhesion. The thin layers of both deposited condensates have minor disparity expressed as the insignificant imperfection of the thickness of the layers in cross-sectional images. The modulation period extracted from the TEM image is ranged from 20 to 32 nm. Spherical defects start to appear in the bulk of the coating close to the surface. Their average size is approximately 350 nm and elemental composition mostly consists of Ti, Si and N elements (see Fig. 11.3b).

The SAED patterns indicate that nanocomposite coatings have polycrystalline structures with a preferred δ-TiN phase (NaCl-type structure). The separation of some diffraction rings becomes extremely difficult to fulfill in electron microscopy, due to the small differences in the inter-atomic spacing. There is no indication of rings corresponding to the appearance of Si_3N_4 that could indicate the formation of solid (Ti, Si)N in the investigated area.

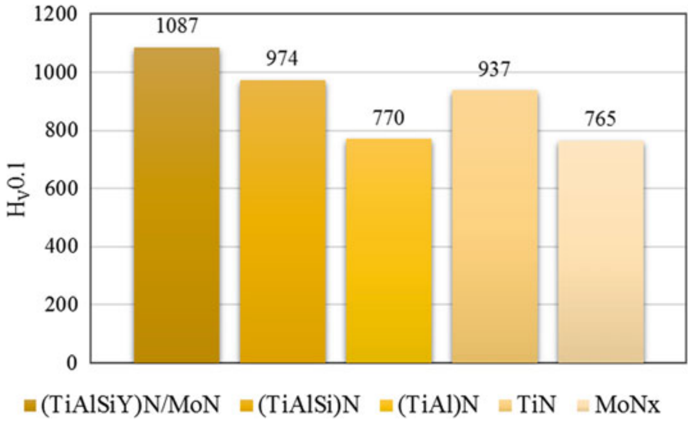


Fig. 11.4 Values of Vickers microhardness of experimental multilayered (TiAlSiY)N/MoN coatings and monolayer coatings based on constituent elements [60–63]

11.3.3 Microhardness

It is known that multilayered hard coating formed on the steel surface definitely increases the hardness of the coated material. In particular, multilayered (TiAlSiY)N/MoN coatings show considerably enhanced hardness (see Fig. 11.4) due to the several factors, which are: multilayered strengthening, which promotes impeding dislocation motion across the interfaces and the difference in elastic modulus of the layers [56, 57]; Hall-Petch strengthening, based on the increasing of volume fraction of grain boundaries with high interfacial energies [58]; Orowan strengthening, which acts in structures with nanometer modulation wavelength [59].

For all experimental coatings, it was observed a strong tendency of decreasing intensity and broadening of the width of the TiN (200) peak, which is in the result of the diminution of the grain size or the residual stress induced in the crystal lattice [64–68]. It is also suggested that the Si incorporation reduced the crystallites size and the residual stress and, hence, has ensured the hardening of nanolayered (TiAlSiY)N/MoN coatings.

11.4 Conclusions

(TiAlSiY)N/MoN multilayered coatings were successfully fabricated by the cathodic arc deposition onto steel substrates under the following deposition condition: arc currents applied to the evaporators were 100 A for the multi-component TiAlSiY cathode and 150 A for molybdenum one; constant substrate bias was-200 V and working gas pressure was 0.53 Pa. The obtained composites had fairly linear layers and well-defined interfaces between layers. The general coatings thickness was approximately 7 μm, while the bilayer thickness varied from 20 to 32 nm. The main phase of TiN had the preferential crystal growth of (200) plane. The average crystallites size was approximately 12 nm. The hardness measurements showed that multilayered (TiAlSiY)N/MoN composites exhibited improved hardness when compared with the MoN_x, TiN, (TiAl)N or (TiAlSi)N films, that reached the value of $1087H_V0.1$.

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