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Influence of Nitrogen Partial Pressure and Substrate Bias on the Mechanical Properties of VN Coatings

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Abstract

Vanadium nitride coatings were deposited via magnetron reactive sputtering system with varying nitrogen partial pressures and negative substrate bias to further understand the influence of the sputtering conditions on the microstructure and the mechanical performance. Grazing incidence X-ray diffraction, field emission scanning electron microscopy equipped with energy dispersive X-ray and X-ray photoelectron spectroscopy were used to characterize the microstructure; nano-hardness tester and profilometer were used to measure the mechanical performance. By varying the nitrogen partial pressures from 0.007 Pa to 0.29 Pa, more compact coating with higher hardness (22.9 GPa) was achieved at 0.29 Pa. In parallel, the influence of bias voltage on the residual stress and hardness was significant.

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Open access under [CC BY-NC-ND license](https://creativecommons.org/licenses/by-nc-nd/4.0/).**Keywords:** VN; coating; microstructure; mechanical performance

1. Introduction

High speed and dry cutting poses tougher challenges to the protective coatings, such as low-friction and lubricating in addition to mechanical properties [1]. Intrinsic solid lubricants like DLC, MoS₂, and h-BN often begin to fail their tribological effectiveness at elevated temperatures, in humid atmosphere or due to oxidation. The same happen to other lubricants from chemical reactions between coating and moisture of the ambient atmosphere. In recent years, Magnéli-phase, which is one kind of high-

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temperature lubricious oxide materials with easy moveable shear planes, has attracted increasing interests. [2, 3] These phases exhibit good thermal stability and tribological property [3, 4]. Among these materials, vanadium easily oxidizes at high temperature and its melt forms a lubricant layer [3]. Consequently, a lot of efforts have been made to develop vanadium nitride hard coating, such as TiN/VN, TiAlN/VN, and CrAlVN coatings, to combine high hardness and high temperature lubricant properties into one [1]. Compared with TiN and CrN, studies on the vanadium nitride coatings limited are far behind [5, 6, 7].

In this study, VN coatings were prepared via magnetron reactive sputtering. The influence of nitrogen partial pressure (P_{N_2}) and negative substrate bias voltage (V_b) on the microstructure, and mechanical performance were investigated.

2. Experimental

2.1. Sample preparation

VN coatings were deposited by reactive magnetron sputtering (JGP 560C4, CAS SKY Technology Development Co., Ltd., China). Hot-pressed vanadium target (99.95 at.% in purity, 70 mm in diameter, and 5 mm in thickness) was used. The substrate was silicon wafer (100). The distance between the target and substrate was kept in 60 mm. Before loading, the substrates were ultrasonically cleaned in acetone, ethanol and deionized water in sequence for 15 min, followed by rapid drying with nitrogen blow. Before deposition, the target surface was pre-sputtered in pure argon (Ar) plasma for 10 min.

Two series of VN coatings were fabricated, one in varying nitrogen partial pressure and the other in varying substrate bias (Table 1).

Table 1 Sputtering parameters of VN thin coatings.

Parameter	Conditions
Target/diameter	V(99.95 at%) /70 mm diameter
Substrate	(100) Si single crystal wafer
Substrate temperature	Room temperature
Distance between target and substrate (mm)	60
Base pressure (Pa)	4.4×10^{-4}
Working pressure (Pa)	0.35
Target power density (W/cm^2)	~ 1
Deposition time (h)	2.5
N_2 partial pressure (Pa)	0.007, 0.01, 0.03, 0.6, 0.12, 0.18, 0.23, 0.29
Bias voltage (-V)	0, 50, 100, 150, 200

2.2. Characterization

The crystalline structure was characterized by grazing incidence X-ray diffraction (GIXRD). A D/max2550HB+/PC X-ray diffractometer with Cu $K\alpha$ radiation (15 kV and 10 mA) at a scan rate of $2^\circ/\text{min}$ was employed. The scanning angle was performed from 30° to 90° at a step size of 0.02° and the incident angle was set at 1° . Texture coefficients (TC) of (111), (200), (220) and (311) reflections were determined from the intensities of VN peaks [8]. Assuming no significant micro-strain, the average grain size was estimated by the Debye-Scherrer formula [9].

The coating thickness, surface and cross-sectional morphology were studied by field emission scanning electron microscopy (SEM, BCPCAS 4800). Energy dispersive X-ray (EDX) attached to the

SEM was adopted to analyze the chemical compositions. X-ray photoelectron spectroscopy (XPS, PHI 5300) was also applied to confirm the element concentration.

The residual stress σ was obtained from the change in the radius of curvature of the Si substrate before and after deposition, using Taylor-Hobson (5P-120) profilometer and Stoney's equation [10]. The hardness of the coatings was determined by nanoindentation (CSEM-NHT) with a Berkovich diamond tip. The indent depth was 70 nm (less than one tenth of the coating thickness to minimize the substrate effect) at a loading speed of 4 nN/min and maximum load of 2 mN.

3. Results and discussion

3.1. Effect of N_2 partial pressure (P_{N_2})

With N_2 partial pressure (P_{N_2}) increasing from 0.007 Pa to 0.29 Pa, the deposition rate of the coatings dropped from 9.5 nm/min to 6.5 nm/min, as shown in Fig. 1. Two reasons are identified: the poor sputtering yield with N_2 compared with Ar; [11] and "target poison" [7, 12]. The N/V atomic ratio of VN coatings with P_{N_2} increasing is plotted in Fig. 2; the ratio increased from 0.58 to 1.09 (EDX, Fig. 2a) due to the increasing concentration of reactive nitrogen ion in the chamber. XPS results confirmed this trend ($P_{N_2}=0.01$ Pa, N/V=0.68; $P_{N_2}=0.18$ Pa, N/V=0.89; $P_{N_2}=0.29$ Pa, N/V=1.09), as shown in Fig. 2b.

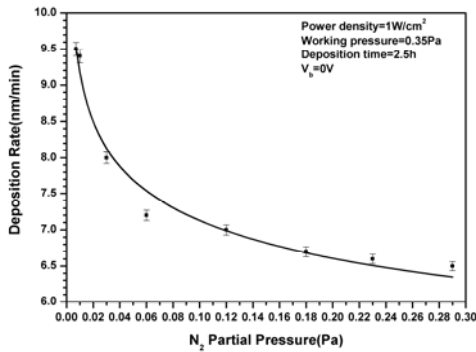


Fig. 1 Deposition rate of VN coatings at different P_{N_2} .

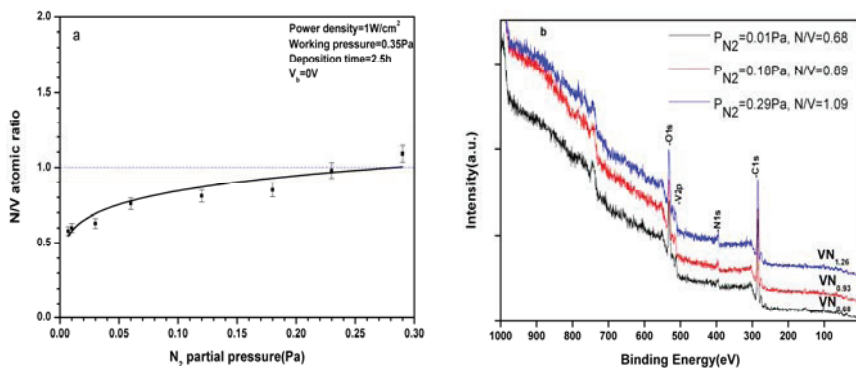


Fig. 2 N/V atomic ratio of VN coatings at different P_{N_2} ; a. EDX, b. XPS.

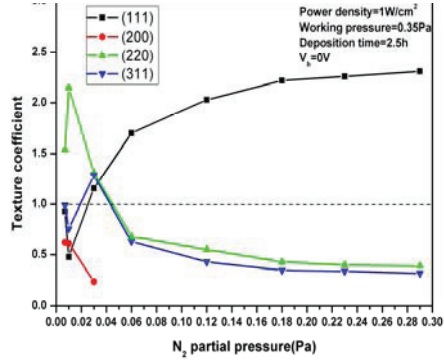
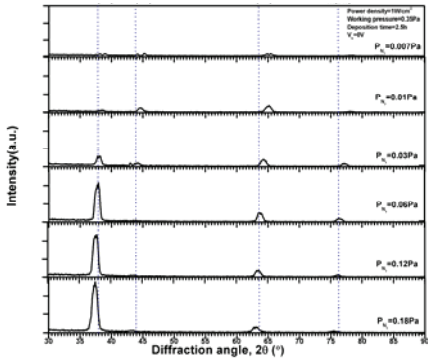


Fig. 3 XRD spectra of VN coatings deposited at different P_{N_2} . Fig. 4 Texture coefficient of VN coatings deposited at different P_{N_2} .

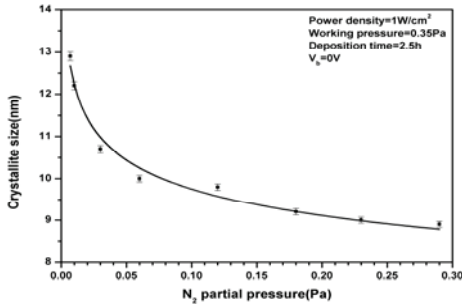


Fig. 5 Crystallite size of VN coatings deposited at different P_{N_2} .

Figure 3 shows the XRD spectra of VN coatings deposited at different P_{N_2} . Only a single phase of fcc-VN with reflections corresponding to (111), (200), (220) and (311) planes are observed. The changes in the preferred orientation as a function of P_{N_2} are qualitatively estimated in terms of texture coefficients (TC), as shown in Fig. 4. With P_{N_2} increased, the coatings show a preferential orientation of (111) plane. In the meanwhile, the grain size decreased from 12.9 nm to 9 nm as P_{N_2} increased (Fig. 5).

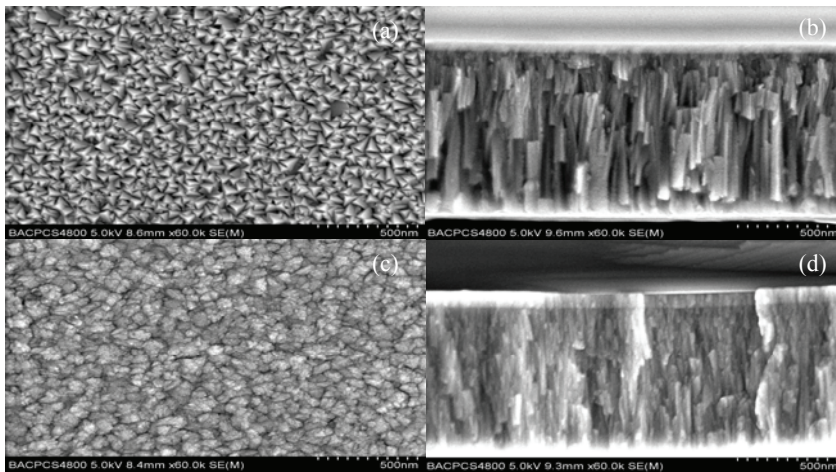


Fig. 6 SEM surface morphology and cross section images of VN coatings deposited at different P_{N_2} ; (a, b) $P_{N_2}=0.03$ Pa, $V_b=0V$, (c, d) $P_{N_2}=0.18$ Pa, $V_b=0V$.

The surface and cross-sectional morphology of VN coatings ($P_{N_2}=0.03$ and 0.18 Pa) were shown in Fig. 6. At 0.03 Pa (P_{N_2}), the surface morphology shows a multi-faced structure and rather rough appearance, while cross-sectional observation also expressed the loose structure. At 0.18 Pa (P_{N_2}), the structure of the coating became compact.

Figure 7 shows the residual stress of VN coatings. When P_{N_2} was lower than 0.03 Pa, the residual stress was very low, and can be neglected due to the loose structure of the VN coatings. With increase of P_{N_2} , a slowly increasing of compressive stress was observed up to -0.4 GPa, as the structure became denser, and the stress induced by sputtering could not be released thus compressive stress increased. Figure 8 shows hardness of VN coatings. The hardness increased from 9 GPa to 23.3 GPa when the P_{N_2} increases from 0.007 Pa to 0.23 Pa, as the crystallite size became smaller, in good agreement with Hall-Petch law [13].

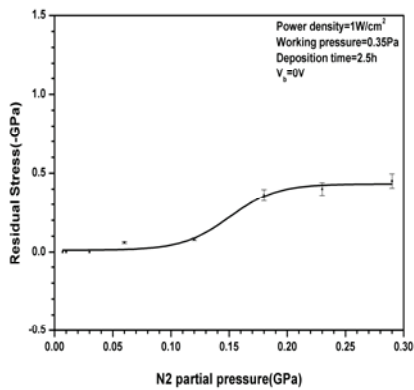


Fig. 7 Residual stress of VN coatings at different P_{N_2} .

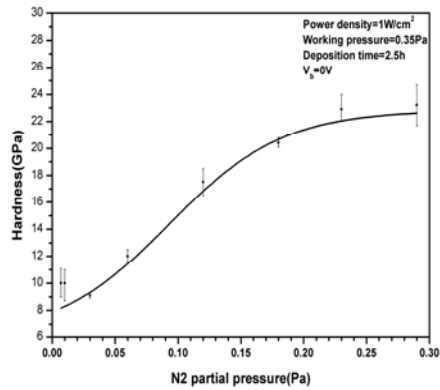


Fig. 8 Hardness of VN coatings at different P_{N_2} .

3.2. Effect of substrate bias voltage (V_b)

With substrate bias voltage (V_b) changed from 0 V to -200 V, the deposition rate of the coatings dropped from 6.7 nm/min to 5.6 nm/min, as shown in Fig. 9. As negative V_b is applied to the substrate,

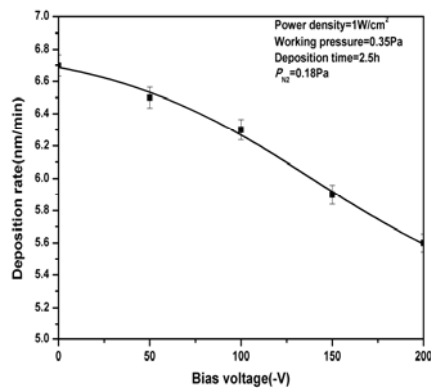


Fig. 9 Deposition rate of VN coatings at different V_b .

positive ions of the plasma are attracted toward the substrate and transfer their kinetic energy to the surface atoms. As the V_b increases, the incident ion energy increases, and as a result, re-sputtering from the deposited surface may take place, resulting in decreased deposition rate [14, 15]. The influence of V_b on the N/V atomic ratio was shown in Fig. 10, similar with the results of [15]. In this process, the N/V atomic ratio increased from 0.85 to 0.98 (EDX, Fig. 10a) as revealed by XPS results ($V_b=0$ V, N/V=0.89; $V_b=-200$ V, N/V=1.02) shown in Fig. 10b. The increase is attributed to the increase of ionized N atoms [16].

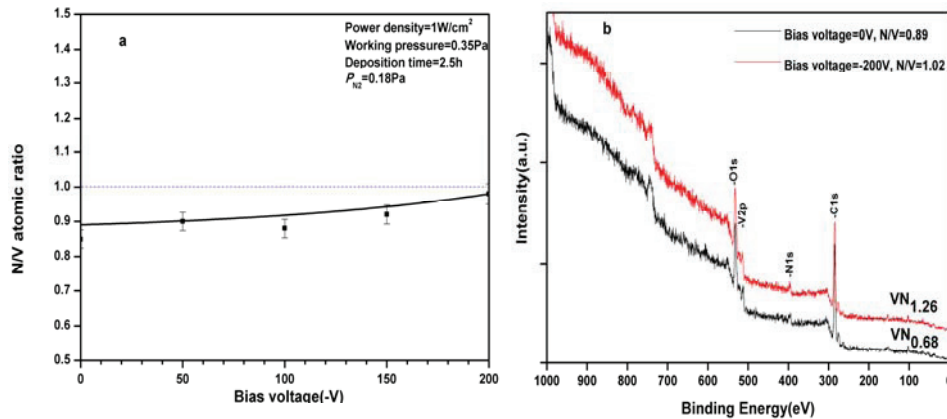


Fig. 10 N/V atomic ratio of VN coatings at different V_b ; a. EDX, b. XPS.

Figure 11 is the XRD spectra of VN coatings deposited at different V_b . The coatings grown without bias have a preferred orientation of (111) plane; and under weak ion-irradiation conditions at -50 V, -100 V and -150 V contain predominantly a mixture of (111) and (200) orientations with a small volume fraction of (220) orientation. The coatings deposited at high bias voltage of -200 V have a dominant (111) texture. The changes in the preferred orientation as a function of the bias voltage are qualitatively further estimated in terms of coefficients (T_C) of texture as shown in Fig. 12. Meanwhile the crystallite size tends to decrease from 0 V to -150 V, and then increases as the substrate bias voltage ranges from -150 V to -200 V, as shown in Fig. 13. As more defects will be generated on the surface of growing coating with the increase of incident ion energy the nucleation sites will increase [17], as a result the crystallite sizes of

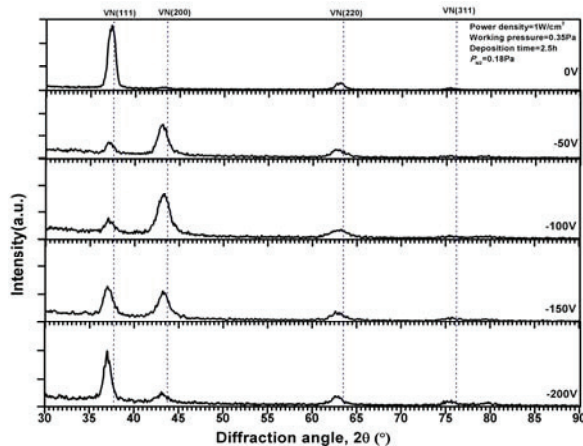


Fig. 11 XRD spectra of VN coatings deposited at different V_b with $P_{N_2}=0.18$ Pa.

the coatings decrease. Further increasing the substrate bias voltage to -200 V , because of high energy ions bombardment on the coatings will induce higher temperature which would promote crystallite size.

The surface morphology and cross section images of VN coatings deposited at -150 V and -200 V were shown in Fig. 14. At V_b of -150 V , the crystal structure is equiaxial; at -200 V , the structure became columnar, with smoother surface as a result of re-sputtering.

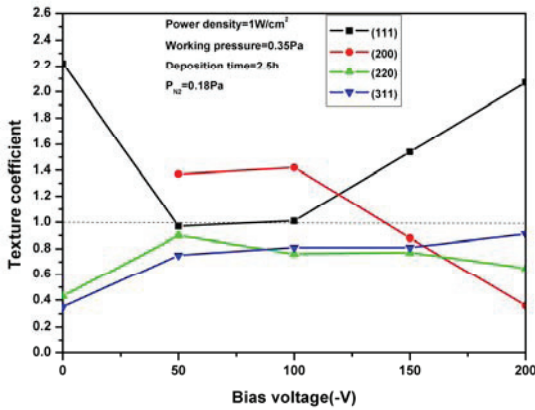


Fig. 12 Texture coefficient of VN coatings deposited at different V_b .

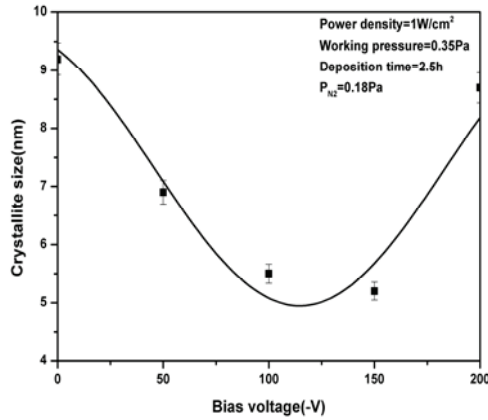


Fig. 13 Crystallite size of VN coatings deposited at different V_b .

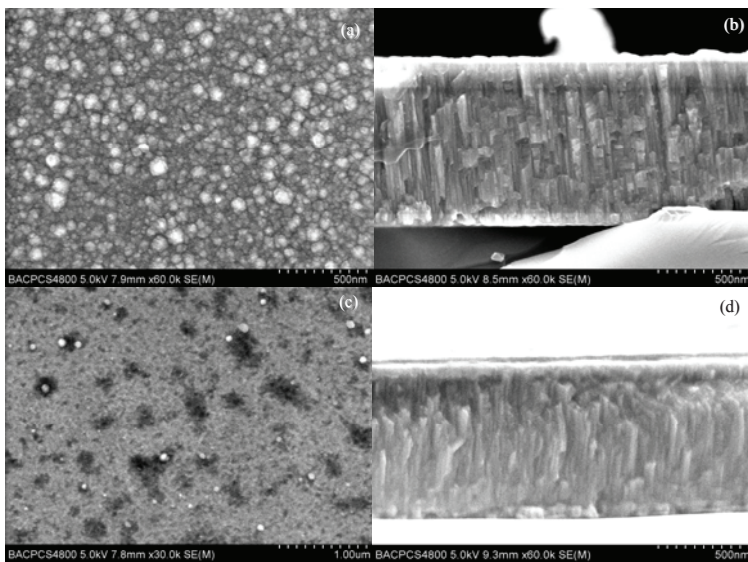


Fig. 14 SEM surface morphology and cross section images of VN coatings; (a, b) $P_{N_2} = 0.18\text{ Pa}$, $V_b = -150\text{ V}$, (c, d) $P_{N_2} = 0.18\text{ Pa}$, $V_b = -200\text{ V}$.

The surface morphology and cross section images of VN coatings deposited at -150 V and -200 V were shown in Fig. 14. At V_b of -150 V , the crystal structure is equiaxial; at -200 V , the structure became columnar, with smoother surface as a result of re-sputtering.

Figure 15 shows the residual stress of VN coatings with varying V_b . When V_b increased from 0 V to –150 V, there is a rapidly increase of compressive stress from –0.36 GPa to –1.69 GPa due to increased bombardment of incident ions; but from –150 V to –200 V, the residual stress slowly reduced to –1.62 GPa, suggesting temperature's annealing effect at energetic bombardment. Fig. 16 plots hardness of the VN coatings at different substrate bias voltage. The increase of hardness from 20.4 GPa to 24.5 GPa with the bias from 0V to –200 V is due partly to the increased compressive stress and partly to the denser structure.

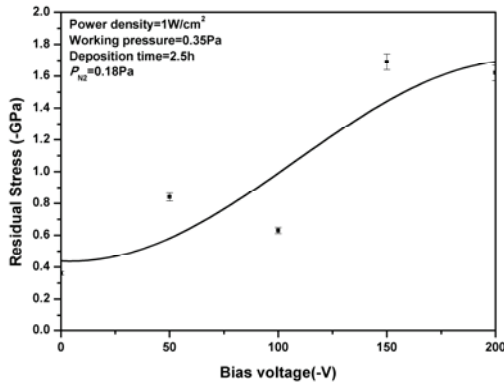


Fig. 15 Residual stress of VN coatings at different V_b .

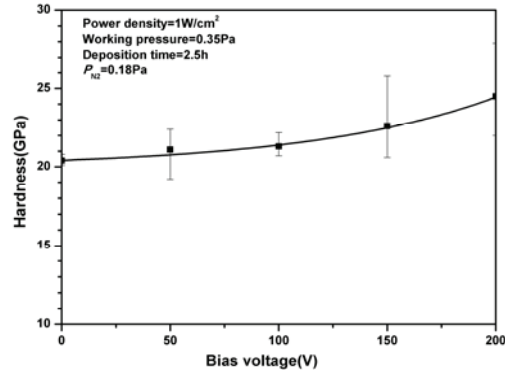


Fig. 16 Hardness of VN coatings at different V_b .

4. Conclusions

In reactive magnetron sputtering of VN coatings, increasing of the nitrogen partial pressure (from 0.007 Pa to 0.29 Pa) brings about denser coatings with higher hardness (22.9 GPa). Increasing of substrate bias voltage generates more residual stress in the coating (–1.62 GPa at –200V), and at the same time slightly further enhances the density of the coating and the hardness.

References

- [1] P.H. Mayrhofer, P.Eh. Hovsepian, C. Mitterer, W.-D. Münz. Calorimetric evidence for frictional selfadaptation of TiAlN/VN superlattice coatings. *Surface and Coatings Technology*, 2004; 177-178: 341-347.
- [2] Münz W-D.. Large-scale manufacturing of nanoscale multilayered hard coatings deposited by cathodic arc/unbalanced magnetron sputtering. *MRS Bull*, 2003; 28:173-179.
- [3] Paul H. Mayrhofer, Christian Mitterer, Lars Hultman, Helmut Clemens. Microstructural design of hard coatings. *Progress in Materials Science*, 2006; 51: 1032-1114.
- [4] Storz O, Gasthuber H, Woydt M. Tribological properties of thermal-sprayed Magnéli-type coatings with different stoichiometries (Ti_nO_{2n-1}). *Surface and Coating Technology*, 2001; 140: 76-81.
- [5] H. Gueddaoui, G. Schmerber, M. Abes, M. Guemmaz, J.C. Parlebas. Effects of experimental parameters on the physical properties of non-stoichiometric sputtered vanadium nitrides films. *Catalysis Today*, 2006; 113: 270-274.
- [6] X. Chu, S. A. Barnett, M. S. Wong, W. D. Sproul. Reactive magnetron sputter deposition of polycrystalline vanadium nitride films. *Journal of Vacuum Science and Technology A*, 1996; 14(6): 3124-3129.
- [7] G. Farges, E. Beauprez, D. Degout. Preparation and characterization of V-N films deposited by reactive triode magnetron sputtering. *Surface and Coating Technology*, 1992; 54/55: 115-120.

- [8] V. Chawla, R. Jayaganthan, Ramesh Chandra. A study of structural and mechanical properties of sputter deposited nanocomposite Ti–Si–N thin films. *Surface and Coatings Technology*, 2010; 204:1582-1589.
- [9] H. Wang, S. Zhang, Y. Li, D. Sun. Bias effect on microstructure and mechanical properties of magnetron sputtered nanocrystalline titanium carbide thin films. *Thin Solid Films*, 2008; 516: 5419-5423.
- [10] S. Zhang, X. L. Bui, Y. Fu, H. Du. Development of Carbon-Based Coating of Extremely High Toughness. *International Journal of Nanoscience*, 2004; 3(4-5): 571–578.
- [11] Tian minbo. *Thin coating technologies and materials*. Beijing, Tsinghua university press; 2006.
- [12] T. Elangovan, P. Kuppasami, R. Thirumurugesan, V. Ganesan, E. Mohandas, D. Mangalaraj. Nanostructured CrN thin films prepared by reactive pulsed DC magnetron sputtering. *Materials Science and Engineering B*, 2010; 167: 17-25.
- [13] T. Zhou, P. Nie, X. Cai, P. K. Chu. Influence of N₂ partial pressure on mechanical properties of (Ti,Al)N films deposited by reactive magnetron sputtering. *Vacuum*, 2009; 83: 1057-1059.
- [14] D.M. Devia, E. Restrepo-Parra, P.J. Arango, A.P. Tschiptschin, J.M. Velez. TiAlN coatings deposited by triode magnetron sputtering varying the bias voltage. *Applied Surface Science*, 2011; 257: 6181-6185.
- [15] Q. Kong, L. Ji, H. Li, X. Liu, Y. Wang, J. Chen, H. Zhou. Influence of substrate bias voltage on the microstructure and residual stress of CrN films deposited by medium frequency magnetron sputtering. *Materials Science and Engineering B*, 2011; 176: 850-854.
- [16] J. K. Park, Y. J. Baik. Increase of hardness and oxidation resistance of VN coating by nanoscale multilayered structurization with AlN. *Materials Letters*, 2008; 62: 2528-2530.
- [17] J. W. Lee, S. K. Tien, Y. C. Kuo. The effects of pulse frequency and substrate bias to the mechanical properties of CrN coatings deposited by pulsed DC magnetron sputtering. *Thin Solid Films*, 2006; 494: 161-167.