MICROSTRUCTURE, MECHANICAL AND TRIBOLOGICAL BEHAVIOR OF THE TiAlVN COATINGS

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Received: 18.10.2018
Accepted: 26.10.2018

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Abstract
In this present work, the TiAlVN coatings were deposited by magnetron sputtering using a single alloy target of $Ti_{60}Al_{30}V_{10}$. The effect of the argon (Ar) to nitrogen (N_2) gas flow ratio on the structure, morphological characteristics and mechanical properties of the TiAlVN coating were investigated. The results of X-ray diffraction show the coatings have only face-centred cubic (fcc) structures at different gas ratio of Ar:N_2. FE-SEM observation analysis each of the TiAlVN coatings indicated that the change of the gas ratio affects the surface morphology. The nano-indentation results demonstrated that coatings deposited with the gas ratio of Ar:N_2 being 9:1 exhibited the highest hardness and elastic modulus. Moreover, with the various gas ratio of Ar:N_2, ball-on-disc against SUJ2 ball in air at room temperature indicated friction coefficient from 0.43 to 0.58 in dry condition and 0.073 to 0.12 in oil condition, respectively, which is related to the surface roughness and grain sizes of the coatings.

Keywords: TiAlVN coatings, magnetron sputtering, gas ratio, tribological

1 Introduction
In industrial metal cutting applications the protection of the various tools by hard coatings became standard due to the achievable superior properties [1]. In the last decades, $Ti_{1-x}Al_xN$ coatings have been developed and demonstrated excellent properties such as high hardness, good wear resistance, chemical and thermal stability compared with TiN coatings [2-4]. However, the friction coefficient of TiAlN coating is approximately 0.9-1.1 under dry sliding motion, depending on the deposition conditions [5-8]. Therefore, the addion of valadium (V) to the TiAlN coating by forming TiAlN/VN multilayer or as solid solution TiAlVN coating provides a possible way to adjust the friction coefficient and enhance the hardness of the coatings by varying the content of crystalline and amorphous phases [9-12]. Furthermore, vanadium as a substitutional atom in the $Ti_{1-x}Al_xN$ solid solution has a stabilizing effect for the face-centered cubic (fcc) structure, which is characterized by high hardness and Young's

DOI 10.12776/ams.v24i4.1187 p-ISSN 1335-1532
e-ISSN 1338-1156

modulus [13]. The TiAlVN coatings could be depostited by using various physical vapor deposition (PVD) techniques. M. Pfleiler et al. [14] synthesized TiAlVN coating by cathodic arc evaporation. The result indicated that the hardness of the coatings increased from 21 GPa to 27.5 GPa with increasing V content from 0 to 16.5 at%, respectively. Tillmann et al. [15] deposited TiAlVN coating by an industry magnetron sputtering using binary targets of TiAl and V at a substrate temperature of 650°C. It is reported that the hardness increased from 29.18 GPa at negative bias voltage of -50V to 43.28 GPa at negative bias voltage of -150V. A.M. Abd El-Rahman [16] synthesized the TiAlVN coating by using plasma enhanced sputtering with obtained hardness of about 30 GPa. These deposition processes are, however, comples, difficult to control, and costly compared to magnetron sputtering using a single alloy target. Therefore, a technique using an inexpensive, straightforward, and efficient method to improve the properies of coatings is in great demand from the viewpoint of industrial application, and finding such a technique remains an important task for materials scientists.

The purpose of the present work was to deposit TiAlVN coatings by magnetron sputtering using a single alloy target of $Ti_{60}Al_{30}V_{10}$. The influence of Ar : N_2 gas ratio on the phase structure, surface morphology, hardness and elastic modulus, roughness, and tribological properties were investigated and evaluated.

2 Experimental

2.1 Coating deposition

TiAlVN coatings were deposited on Si wafers (100) and polished WC-Co substrates by direction current (dc) magnetron sputtering system. A target with a diameter of 75 mm and thickness of 6 mm used in a gun, it was $Ti_{60}Al_{30}V_{10}$ (at. %) alloy that was fabricated by powder metallurgy processes. The distance between the target and substrate was kept at 50 mm. Before deposition, the samples were ultrasonically pre-cleaned in methanol and acetone solution for 10 min. Samples were subsequently fixed in the substrate holder and continuously cleaned by Ar^+ ion bombardment for 30 min using dc pulse discharge (Us=600 V, P_{Ar}=1.2 Pa, Is=0.02 A) to further remove the adsorbents and residual oxides on the substrate surfaces. During sputtering, the substrate temperature was kept constant at 25°C. The pure Ar gas (99,99 % purity) and N_2 gas (99,99% purity) were used as sputter and reactive gases, respectively. The Ar to N_2 gas flow ratio was varied at (12:1), (9:1), (7:1), (5:1). Other conditions such as power density, base pressure, working pressure and deposition time were fixed at 6.5 W/cm^2, 1.5x10^{-3} Pa, 0.66 Pa, 30 min, respectively. Namely, the deposition parameters are indicated in **Table 1**. After the deposition process has ended, the coated samples were cooled down in the chamber before venting to atmosphere pressure. The deposition rates of the TiAlVN coatings were 3.24 nm/s, 2.81 nm/s, 2.72 nm/s, 2,6 nm/s for the gas ratio of (12:1), (9:1), (7:1), (5:1), respectively.

Table 1 Deposition parameters for TiAlVN coating

Deposition parameters	
Base pressure (Pa)	1.5x10^{-3}
Working pressure (Pa)	0.66
Target power (W)	300
Power density (W/m^2)	6.5
Target to substrate distance (mm)	50
Temperature (°C)	25
(Ar : N_2) gas ratio	(12:1); (9:1); (7:1); (5:1)
Target material	$Ti_{60}Al_{30}V_{10}$

DOI 10.12776/ams.v24i4.1187 p-ISSN 1335-1532
e-ISSN 1338-1156

2.2 Coating characterization

The phase structure of TiAlVN coatings was identified by X-Ray Diffraction (RD, DMAX-2500, Rigaku, 2001, 40 kV and 40 mA). The source used was Cu Kα radiation (λ=1.5418 Å) in the range of 20° to 90° (2θ scale) with the incidence angle of 1°. The surface hardness and elastic modulus of coatings were measured by nano-indenter (Helmut Fisher HM2000). The surface morphologies of the coatings were observed by using FE-SEM (Nova NanoSEM 450, FEI Co.). The surface roughness was measured were examined using a Surfcom 1500SD3 with a diamond tip is attached to the stylus. The average surface roughness (Ra) was measured at five positions near the center of the test specimen with a track length of 4mm.The tribological properties of the coatings were determined by a ball-on-disk method with SUJ2 steel ball diameter of 6 mm under dry and oily conditions. The test load, speed, and moving distance were 5N, 100 mm/s, and 500 m, respectively.

3 Results and discusion

Fig. 1 shows X-ray diffraction patterns of the coatings deposited with various gas ratio of Ar:N_2. All coatings resulted in a single-phase fcc structure at different gas ratio of Ar:N_2. Nother hexagonal close packed (hcp) phases were detected in the patterns. This indicated the phase stability of fcc TiAlN in the lattice. In addition, the highest intensity of coating obtained at at Ar:N_2 gas ratio of (9:1). With decreasing gas ratio of Ar:N_2 down to (7:1) to (5:1), the peak intensities of the coatings decreased and disappeared at the gas ratio of (5:1). Only fcc VN peak obtained at gas ratio of (12:1). According to previous investigation, this due to change of Al or V content [10, 14, 17].

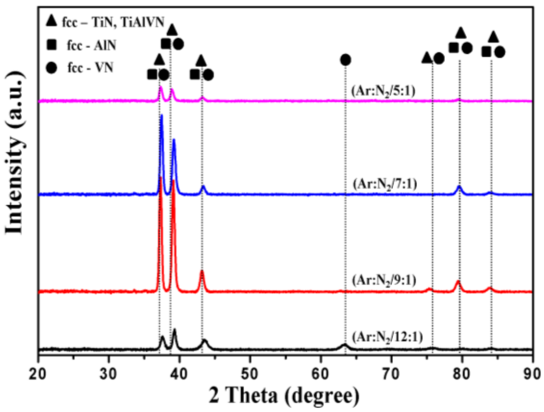

Fig. 1 XRD patterns of the TiAlVN coatings at different gas ration of Ar:N_2

Typical FE-SEM micrographs illustrating the surface and cross section of TiAlVN coating deposited at various gas ration of Ar:N_2 are shown in **Fig. 2** and **Fig. 3**. A denser, isotropic, fine grained microstructure was obtained at Ar:N_2 gas ratio of (12:1) and (9:1) in **Fig. 2a**,**b**. Rough and fractured surfaces were observed in samples reacted at Ar:N_2 gas ratio of (7:1) and (5:1) as shown in **Fig. 2 c,d**. This suggested that the surface of the coatings consisted of densified and fine grain structure at higher gas ratio. The results can be explained as enhancement in atomic mobility with higher the gas ratio. The grain size became coarser grains separated by pores or

DOI 10.12776/ams.v24i4.1187 p-ISSN 1335-1532
e-ISSN 1338-1156

voids, which can be related to the crystal orientation of the coatings [18]. The cross-sectional images indicated non-columnar structures in all the coatings. Moreover, the columnar structures of the coatings became coarser with decreasing the gas ratio of Ar:N_2 in **Fig. 3**.

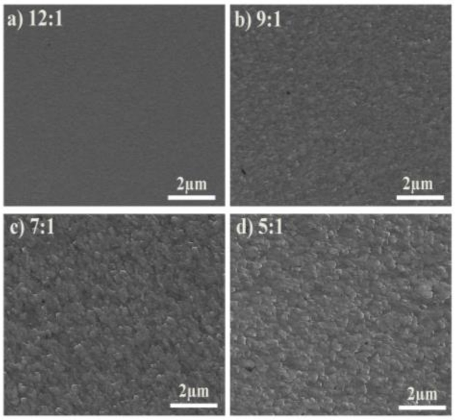

Fig. 2 Surface images of the TiAlVN coatings produced at different gas ratio

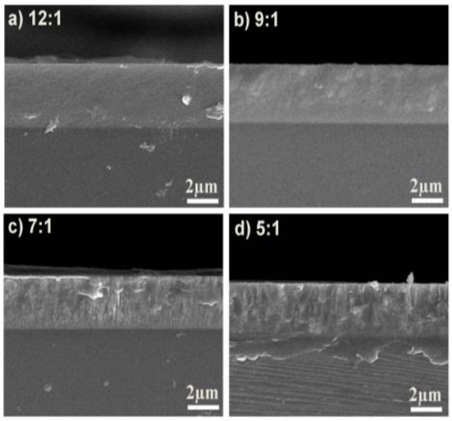

Fig. 3 Cross-section images of the TiAlVN coatings produced at different gas ratio

The surface roughness depends meanly on the type of growth and the grain size of the coatings. The average surface roughness (Ra) values for the substrates and coated substrates at different gas ratio is illustrated in **Fig. 4**. As can be seen that the average roughness value of substrates exhibited about 0.015 - 0.0155 μm for all samples under the same condition. After deposition, the lower roughness values are observed at the gas ratio of (12:1) and (9:1). With decreasing gas ratio of Ar:N_2, the roughness value of the coatings increases gradually to 0.0158 μm for the gas ratio of (7:1) and 0.0162 μm for the gas ratio of (5:1). The results can be attributed to increase grain size with the decrease gas ratio, this led to an increase of the surface roughness.

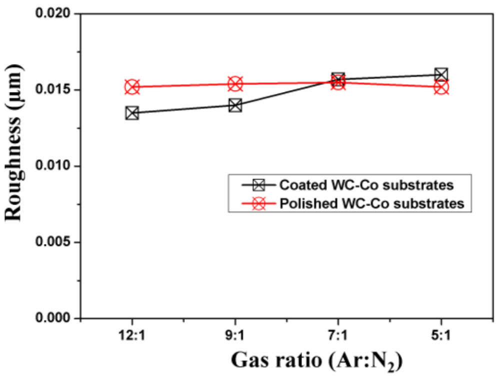

Fig. 4 Average surface roughness (Ra) values of the TiAlVN coatings at different gas ratio.

The nano-indenter test was performed on the coating to investigate their mechanical properties. Ten measurements were carried out on each sample with applied load 10 mN for 10 s dwell time, penetrative depth of 0.25 μm. **Fig. 5** illustrates the effects of the gas ratio on the hardness

DOI 10.12776/ams.v24i4.1187
p-ISSN 1335-1532
e-ISSN 1338-1156

and elastic modulus of the TiAlVN coating. As can be seen that for sample produced with gas ratio of (9:1) was obtained the highest value of the hardness which corresponds to 32.5 GPa. The lower values of the hardness are observed with the gas ratio of (12:1), (7:1) and (5:1). The results can be explained in terms of replacement the metallic bond with ion binding during the deposition process. Furthermore, small grain sizes consisting in the crystallographic lattice of the compound, leading to densification of the crystallographic arrangement and hence to obtain this high hardness values. In addition, the hardness of coatings can be affected by crystal lographic orientation, and stoichiometry [19]. Thus, the atainment of the best crystallization quality can be attributed to the highest level of hardness. The evolution of the elastic modulus (Young's modulus) of the TiAlVN coating present a very similar behaviour as that observed for hardness. Thus, for the gas ratio of Ar:N_2 between (12:1) and (9:1), elastic modulus present the increasing from 320 GPa up to 370 GPa, then the significant decrease of its value from 335.5 GPa down to 290 GPa with the gas ratio of (7:1) and (5:1), respectively.

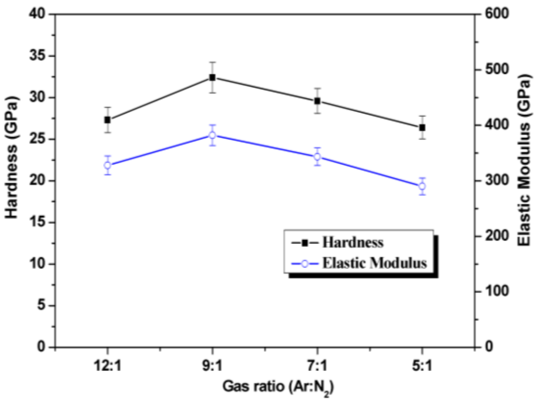

Fig. 5 Effects of the gas ratio on the hardness and the elastic modulus of TiAlVN coatings

The coating properties including microstructure, surface morphology, and hardness play essential roles in controlling the friction behaviours [20-22]. **Fig. 6** shows the variation of the friction coefficients for the TiAlVN coatings deposited at different gas ratio of Ar:N_2. The friction coefficient of the coatings exhibited the same tendency in the initial stage. After that, the friction coefficient decreased gradually with the increased of sliding distance. The lowest and stable friction coefficient were observed for the coating deposited at the gas ratio of (12:1). With decreasing gas ratio, the friction coefficients of coatings increased. The highest friction coefficient was obtained for the coating at the gas ratio of (5:1). All these results are due to the increase in the grain size with the decrease gas ratio of Ar:N_2. On the other hand, the surface roughness and hardness values affect the tribology properties of the coatings.

Fig. 7 shows the friction coefficient values of the coatings measured in dry and oily conditions. GF4 engine oil was used in the oily condition. The results of ball-on-dick test in dry condition indicated that the friction coefficient value of the coatings increased from 0.43 at the gas ratio of (12:1) to 0.58 at the gas ratio of (5:1). In oily condition, the friction coefficient values of the coatings were almost the same, ranging from 0.073 to 0.12 with different gas ratio. The results showed that the friction coefficient values in oily conditions decreased from about 5 to 6 times, compared to the friction coefficient value in dry condition.

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e-ISSN 1338-1156

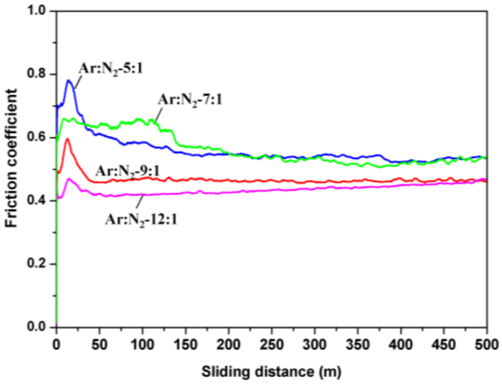

Fig. 6 Friction coefficient of TiAlVN coatings deposited at different gas ratio

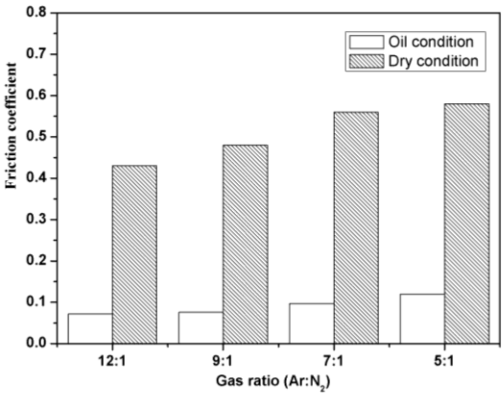

Fig. 7 Comparation of the friction coefficient of TiAlVN coating between dry and oily conditions

Conclusion

TiAlVN coatings were deposited at different gas ratio of ($Ar:N_2$). The influence of the gas ratio on the structure, surface morphology, hardness and tribological properties were investigated. The results showed that the TiAlVN coatings have only single phase fcc structure at all the gas ratio. Fine grained microstructure with its morphology size was obtained at higher gas ratio of $Ar:N_2$. In addition, the nano-indenter results exhibited the highest hardness of 32.5 GPa, elastic modulus of 370 GPa at the gas ratio of $Ar:N_2$ being (9:1). Moreover, ball-on-dics test showed friction coefficient of TiAlVN coating depend on the gas ratio of $Ar:N_2$. It was correlated to the surface roughness and grain sizes.

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DOI 10.12776/ams.v24i4.1187 p-ISSN 1335-1532
e-ISSN 1338-1156