Characterization of Sputtered Coatings with Various Nitrogen Content Deposited from High Aluminum Alloyed TiAlV Target

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In this study, a $\text{Ti}_{50}\text{Al}_{40}\text{V}_{10}$ single alloying target is used to deposit TiAlVN coatings by a direct current (dc) magnetron sputtering technique. The structural, mechanical, and frictional properties of final coatings deposited at a various N_2 content are investigated. It reveals that TiAlVN coating transforms from a single-phase (cubic phase) to a dual-phase structure (cubic and hexagonal phases) with the increase of N_2 content. The highest hardness (~ 36.5 GPa) and elastic modulus (~ 372 GPa), and a good adhesion strength (~ 24.4 N) are achieved in the sample deposited with a N_2 flow rate of 6 sccm, which are determined by the nano-indentation and scratch test measurements. In addition, TiAlVN coating deposited with a N_2 flow rate of 3 sccm has the lowest friction coefficient in the dry and oily conditions.

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1. Introduction

Coatings with low friction coefficients or self-lubrication properties in combination with high mechanical properties are highly demanded for cutting applications in the modern manufacturing industry in order to enhance performance and lifetime of tools or machine parts. In the recent years, TiAlN thin films have been developed and demonstrated excellent properties, including high hardness, good wear resistance, chemical and thermal stability compared to the conventional TiN materials.^{1–3} However, the friction coefficient still remains in a range from 0.8 to 1.1 under dry sliding motion depending on sputtered conditions,^{4,5} that is quite high values for industrial applications. By adding a third element (X) such as silicon (Si), chrome (Cr), vanadium (V), or boron (B) to the TiAlN coating to form a TiAlXN single-layer or TiAlN/XN multi-layer coatings, one can adjust the friction coefficient and enhance the hardness of the samples simultaneously.^{6–10} Among these elements, vanadium has advantages compared to its counterparts for potential uses in the tribological industry. For instance, it shows the unique friction properties due to formation of the lubricious oxide phases (Magnéli phases).^{11,12} Furthermore, vanadium acts as a substitution atom in the $\text{Ti}_{1-x}\text{Al}_x\text{N}$ solid solution, which has a stabilizing effect for the face-centered cubic (fcc) structure, resulting in its high hardness.^{13,14} Physical vapor deposition (PVD) techniques including cathodic arc evaporation, magnetron sputtering have been used to deposit the TiAlVN coatings.^{15,16} Influences of the different deposition conditions and/or V content on the structure and properties of the coatings have been investigated and reported widely so far. For example, TiAlVN coating deposited with different V content have been produced with a cathodic arc evaporation as reported by Pfeiler *et al.*¹⁷ and Chen *et al.*¹⁸ Both of them exhibited a hardness value below 30 GPa at room

temperature (RT). The friction coefficient was 0.7–0.8 at RT and increased about 1.25 times at 500°C.¹⁷ The properties of the TiAlVN coatings deposited with the different bias voltage by using a cathodic arc evaporation at 450°C, reported by Pfeiler *et al.*¹⁵ and an industry magnetron sputtering, reported by Tillmann *et al.*¹⁹ It reveals that the hardness value and friction coefficient for the samples deposited at various bias voltage of –40 to –160 V increased from 27.6 to 38 GPa and 0.85 to 1.0, respectively.¹⁵ The hardness increased from 29.18 to 43.28 GPa, and the friction coefficient increased from 0.43 to 0.57, when the bias voltage was changed from –50 to –150 V.¹⁹ Abd El-Rahman²⁰ synthesized the TiAlVN coatings by using plasma enhanced sputtering, which show the hardness of about 30 GPa and the friction coefficient of 0.36 under a load of 3 N for a sliding distance of 25 m.

In our previous study, we have investigated the TiAlVN coatings by magnetron sputtering technique using a $\text{Ti}_{60}\text{Al}_{30}\text{V}_{10}$ single alloying target.²¹ In this work, the higher aluminum alloyed target with atomic chemical composition of $\text{Ti}_{50}\text{Al}_{40}\text{V}_{10}$ has been used. The comprehensive influence of the N_2 flow rate on the structure, surface morphology, hardness, adhesion strength, and tribological properties of the TiAlVN coatings at room temperature has been investigated. Consequently, the optimal N_2 gas flow for the high performance TiAlVN coatings is determined.

2. Experimental

A $\text{Ti}_{50}\text{Al}_{40}\text{V}_{10}$ (at%) alloy target with a diameter of 75 mm and a thickness of 6 mm was fabricated by mechanical alloying and spark plasma sintering processes. Magnetron sputtering deposition was used to deposit the TiAlVN coating on the Si wafers (100) and WC-Co substrates with the diameter of 20 mm and thickness 4 mm. Before deposition, the WC-Co substrates were polished in a machine using containing discs with 1- μm diamond pastes. Before loading

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to the sputter chamber, all substrates were ultrasonically rinsed with an alcohol and acetone solution for 10 minutes and then dried at room temperature. In order to further remove impurities, the substrates were continuously cleaned by Ar^+ ion bombardment for 30 minutes. The flow rate of pure Ar sputter was kept constant at 36 sccm, while the flow rate of N_2 reactive gases was varied at 3, 6, 9, 12 sccm to investigate the influence of the N_2 content. Other parameters, including the distance between the target and substrate was kept at 50 mm. The substrate temperature was kept constant at 25°C in the during sputtering. The sputtered power, vacuum pressure, working pressure, and deposition time were fixed at 300 W, 1.5×10^{-3} Pa, 5 mtor and 30 min, respectively.

After the deposition process, the coated samples were cooled down in the chamber before venting to the atmospheric pressure. The coated samples on the WC-Co substrates are employed to investigate the hardness, friction coefficient and adhesion strength, while those on Si wafer are used to determine the phase structure and morphological structure. The deposition rates of the TiAlVN coatings were determined as 3.12, 2.67, 2.6, and 2.53 nm/s at the nitrogen flow rate of 3, 6, 9, and 12 sccm, respectively. Figure 1 shows as ketch of the magnetron sputtering system used for our deposition.

X-ray diffraction (XRD) of TiAlVN coatings was recorded using a Rigaku DMAX-2500, radiation ($\lambda = 1.5418 \text{ \AA}$) from the Cu $K\alpha$ source is scanned in the incidence angle of $20\text{--}90^\circ$ (2θ scale) with a step of 1° . Field emission scanning electron microscopy (NNSEM-450, FEI Company) in conjunction with energy dispersive X-ray spectroscopy (EDS) is employed to analyze the morphology, thickness and chemical composition of the coatings. The surface hardness investigation and elastic modulus of the TiAlVN coatings were measured by a Nano-indenter tester (Helmut Fisher HM2000) under applying a load of 10 mN for a 10 s dwell time. Five measurements were performed on each sample with the penetrative depth of $0.25 \mu\text{m}$. Surfcom 1500SD3 with a diamond tip attached to the stylus is utilized to analyze the surface roughness. A ball-on-disk (J&L Tech Tribometer)

method is used to determine the tribological properties of the TiAlVN coated WC-Co substrates under both dry and oily conditions. A SUJ2 steel ball with a diameter of 6 mm was used as a counterpart. The test load, speed and sliding distance were 5 N, 100 mm/s and 200 m, respectively. Tribological tests were performed at room temperature ($24 \pm 1^\circ\text{C}$) and an environmental humidity of 42%. The oil was used at room temperature. The scratch tests were used to determine the adhesion strength between the coating and WC-Co substrates. The tests were performed with increasing gradually load (0.1 N to 30 N), the scratch speed of 0.1 mm/s and scratch length of 10 mm.

3. Results and Discussion

3.1 Compositions and microstructure

Figure 2 shows the chemical composition of the target and the coating which was deposited with only Ar gas flow without N content. The composition of the TiAlV coating was determined to be $\text{Ti}_{51.22}\text{Al}_{38.15}\text{V}_{10.62}$. This changed slightly compared to the target composition of $\text{Ti}_{50}\text{Al}_{40}\text{V}_{10}$, which may be due to the effect of sputtering yields of Ti, Al and V.²²⁾ The obtained result demonstrated that the alloying target has homogenous composition with fine microstructure. It is well-known that the crystallographic structure of the TiAlVN coating can exist in a single-phase face centered cubic (fcc) structure or a dual-phase structure consisting of the fcc and hexagonal close-packed (hcp) phases.^{17,20)} Figure 3 shows the XRD patterns of the coatings deposited at various N_2 flow rates. As can be seen, only fcc-TiN or TiAlVN (220) peak is exhibited in the samples deposited at the 3 sccm N_2 flow rate. Three peaks of fcc-TiN or TiAlVN (111), (200) and (220) were also detected in the samples deposited at the 6 sccm N_2 flow rate. This result was attributed to the fact that the N_2 content was insufficient to form other phases of TiN or TiAlVN at the low N_2 flow rates. As increasing the N_2 flow rate up to 9 sccm, the presence of both hcp-AlN and fcc-TiN or fcc-TiAlVN were detected. Thus, we conclude that the structure of the coatings was transformed from the single-phase fcc structure at the low N_2 flow rates (3 and 6 sccm) into the dual-phase (fcc+hcp) structures at the higher N_2 flow rates (9 and 12 sccm). This transition zone from fcc structure to (fcc+hcp) structures is similar to the change of the Al content in the TiAlVN coating

Fig. 1 Schematic diagram of the magnetron sputtering system.

Fig. 2 Composition of the designed target and TiAlV coatings.

Fig. 3 XRD patterns of the TiAlVN coatings deposited various N_2 gas flow rates.

as reported previously.¹⁵⁾ In addition, the preferred orientation of the coatings changed from (111) plane to (200) plane with increasing N_2 flow rate.²³⁾

3.2 Morphology and roughness

Figure 4 shows the typical FESEM images of the TiAlVN coatings deposited at different N_2 flow rates. As can be clearly seen, high density and the fine grained size of around 70–90 nm were achieved at the N_2 flow rates of 3 and 6 sccm (Fig. 4(a), 4(b)). A number of voids and fractured surfaces with its morphology size around 230–260 nm were observed in the samples deposited at the N_2 flow rates of 9 and 12 sccm as shown in Fig. 4(c) and 4(d). This could be attributed to an enhancement in atomic and ion mobilities with the low N_2 flow rate because the sputtering efficiency of Ar ions is higher than N ions.²⁴⁾ The increase of N_2 flow rate led to a decrease of the Ar^+ ion intensity in plasma, causing a reduction in energy bombardment of ion. Zhou *et al.*²⁵⁾

indicated that higher energy ion bombardment combined with low ion-atom flow ratio resulted in smaller grain sizes. The grain size became coarser and separated by pores or voids with the higher N_2 flow rate, which can be attributed to the preferred growth along the (220) direction of the coatings.²⁶⁾ Wu *et al.*²⁷⁾ indicated that the grain size of the TiAlSiN coatings deposited by the modulated pulsed power magnetron sputtering (MPPMS) increases with increasing the nitrogen content.

The cross-sectional FESEM images of the samples deposited at different N_2 flow rates are indicated in Fig. 5. Dense columnar grain with the sub-dense column boundaries were observed in the samples deposited at the low N_2 flow rate (3 and 6 sccm) as in Fig. 5(a) and 5(b). When increasing the N_2 flow rate (9 and 12 sccm), the microstructure of the coatings exhibits the pores and voids, and the columnar structures became coarse as shown in Fig. 5(c) and 5(d). These results are attributed to the increased grain size with the increasing in the N_2 flow rate as discussed above. The thickness of the samples decreases linearly from 5.62 to 4.57 μm with the increase in the N_2 flow rate from 3 to 12 sccm, respectively.

The average surface roughness (R_a) was measured at the five positions near the center of the tested specimens with a track length of 4 mm. Figure 6 indicates the surface roughness values of the polished WC-Co substrates before and after deposition of the TiAlVN coatings at the different N_2 flow rates. The surface roughness of the polished substrates is relatively uniform at $\sim 0.015 \mu\text{m}$. The samples with the TiAlVN coatings show the decreased surface roughness when deposited at the low N_2 flow rates (3 and 6 sccm), but the roughness gradually increases when the N_2 flow rate is higher, reaching a value of $\sim 0.0174 \mu\text{m}$ in the case of the 12 sccm flow rate. This can be attributed to the formation of a thick nitride layer on the target surface at the high N_2 flow rates. Thus, the atom clusters are easily

Fig. 4 FESEM images of the TiAlVN coatings at the different N_2 flow rates including (a) 3, (b) 6, (c) 9, and (d) 12 sccm.

Fig. 5 Cross-sectional FESEM images of the TiAlVN coatings at various rates. The insets thicknesses of the coatings deposited at the different N_2 flow rates including (a) 3, (b) 6, (c) 9, and (d) 12 sccm.

Fig. 6 Average surface roughness (R_a) values of the TiAlVN coatings deposited at different N_2 flow rates.

Fig. 7 Hardness and elastic modulus of the TiAlVN coatings produced at various N_2 gas flow rates.

dislodged on the target surface when the ions are accelerated and bombarded the target's surface. Raaif⁽²⁸⁾ showed that the surface roughness of TiAlN coatings deposited by dc pulsed magnetron sputtering increases with increasing the N_2 content.

3.3 Mechanical properties

Figure 7 illustrates the hardness (H) and elastic modulus (E) of the TiAlVN coatings deposited at various N_2 flow rates. The hardness of the coatings increased with the rise of the N_2 flow rate up to 6 sccm then decreased with the higher N_2 flow rate. The maximum hardness value of 36.5 GPa was achieved with the optimal N_2 flow rate of 6 sccm. The results can be explained via some parameters including phase structures, crystallographic orientation, grain size, dense, and so on.⁽⁸⁾ In this case, the increase in the hardness of the samples can be ascribed to the formation of uniform fine particles or the changes of microstructure to the increased area fracture of grain boundaries, which may hinder

dislocation movements. On the contrary, the decrease in the hardness for the samples deposited at the higher N_2 flow rate is attributed to the appearing of the dual-phase (fcc + hcp) structures and/or the increased grain size.^(20,24) In addition, the previous studies also indicated that the decrease/increase in the hardness is related to the appearance/vanishing of the hcp phase.^(15,17,18) The elastic modulus (Young's modulus) of the TiAlVN coatings exhibited similar trends with the hardness. When increasing the N_2 flow rate from 3 to 6 sccm, the elastic modulus of the samples increased from 338 to 372 GPa. This value then significantly decreased from 323.5 to 298 GPa, with the rising of the N_2 flow rate from 9 to 12 sccm, respectively. The calculated H/E values of the TiAlVN coatings were found to be 0.09, 0.098, 0.093 and 0.092 with the N_2 flow rates of 3, 6, 9 and 12 sccm, respectively. It can be clearly seen that highest H/E value of the coating produced with the N_2 flow rate of 6 sccm, which indicated high fracture toughness in the coating.⁽²⁷⁾ On the other hand, this coating presented a high resistance to

Fig. 8 Friction coefficient of the TiAlVN coatings at different N_2 flow rates in the dry condition. (a) 3 sccm; (b) 6 sccm; (c) 9 sccm; and (d) 12 sccm.

plastic deformation, which related to wear resistance of the coating.

3.4 Tribological properties

The friction behavior is affected by the surface morphology and hardness of the coatings.²⁹⁾ Figure 8 indicates the change of the friction coefficients of the samples produced at the various N_2 flow rates in a dry condition. The first stage of the friction coefficient of the TiAlVN coatings displayed the same trend. After that, it tends to decrease gradually for all the coatings, except for the sample deposited at 12 sccm N_2 flow rate. The minimum coefficient value of friction was observed in the sample produced at the N_2 flow rate of 3 sccm (~ 0.52). It then slightly increases to 0.53 for the sample deposited at the N_2 flow rate of 6 sccm (Fig. 8(a)). As a rising the N_2 flow rate above 9 sccm, the friction coefficients of the samples increased significantly, reaching at 0.89 for the sample deposited at the N_2 flow rate of 12 sccm (Fig. 8(d)). These results were attributed to the rise of the grain size and average surface roughness value of the TiAlVN coatings as increasing the N_2 flow rate. In addition, the decrease of the hardness values also affects the friction behavior of the coatings.²⁰⁾ TiAlVN coatings produced in this work possess a lower friction coefficient at room temperature compared to TiAlVN coating deposited in Refs. 15, 17) and a higher friction coefficient of TiAlVN coatings deposited in Refs. 19, 20). Figure 9 displays the coefficient values of friction for the samples determined under dry and oily conditions. In the dry condition the coefficient of friction increases from 0.094 to 0.143 with the variation of the N_2 flow rate from 3 to 12 sccm. This value decreases about 5~6 times in the oily condition.

3.5 Adhesion strength

The critical load is the load at which the first cracks appear in the coating. The critical loads depend on several factors including the adhesion of the coating to the substrate, stylus radius, loading rate, mechanical properties of the coating and substrate, coating thickness, residual stresses in the coating, and friction between coating and stylus.³⁰⁾ Figure 10 shows

Fig. 9 Friction coefficient of the TiAlVN coatings in dry condition compared with oily conditions.

the morphology of the tracks after the scratch test for the samples deposited at the different N_2 flow rates. It found that a superior adhesion of the TiAlVN coating to the substrate was achieved in the case of the sample deposited at the N_2 flow from 3 to 6 sccm (Fig. 10(a), (b)). The sample coated at the N_2 flow from 9 to 12 sccm shows the lower adhesion strength (Fig. 10(c), (d)). This can be distributed that these interactions between atoms and substrate are strong at low N_2 flow rates, the nucleation density is high, which causes a larger contact area between coatings and substrate, simultaneously lesser cavities in the interface. On the contrary, the interactions are weak at higher N_2 flow rates, the nucleation density will appear more cavities in the interface and thus lower adhesion strength is observed.

4. Conclusions

We have investigated and clarified the relation of the N_2 flow rate with the microstructure, mechanical and tribological properties of the TiAlVN coatings deposited by the dc magnetron sputtering technique. The TiAlVN coatings displayed the single-phase fcc structure at the deposition condition with the low N_2 flow rate (3 and 6 sccm) and transforms into the dual phase (fcc+hcp) structure with higher N_2 flow rate (9 and 12 sccm). The grained size in the range around 70–90 nm was obtained at the N_2 flow rate of 3 and 6 sccm. The coatings deposited at the 6 sccm N_2 flow rate indicated the maximum hardness (~ 36.5 GPa), elastic modulus being 372 GPa, and adhesion strength of 24.4 N. The friction coefficient of the TiAlVN coatings also depends on the N_2 flow rate, and the lowest value of 0.52 and 0.094 in the dry and oily conditions, respectively, were achieved in the sample deposited at the 3 sccm N_2 flow rate.

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Fig. 10 Optical microscopy images of the scratch track of the TiAlVN coatings on WC-Co substrates with the different nitrogen gas flow rates including (a) 3, (b) 6, (c) 9, and (d) 12 sccm.

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