The Structural, Mechanical and Tribological Properties of Vanadium Nitride Film Deposited by Magnetron Sputtering

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Abstract

In this work, vanadium nitride (VN) thin films deposited on 52100 steel substrates with magnetron sputtering system using two vanadium targets and Ar/N₂ gas atmosphere at different substrate pulse frequencies. X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy dispersive spectrometry (EDS) were used to analyze the microstructure and elemental composition of the films. Adhesion and fatigue properties of films were analyzed a scratch tester. Pin-on-disc tribo-tester was carried out to determine tribological properties. It was observed from the test results that substrate pulse frequency has a significant effect on mechanical and tribological properties of VN films. According to XRD, all films have VN and V₂N phases. The intensity of V₂N (211) peak decreased with increasing frequency, whereas VN (111) peak intensity were increased. Also, the film thickness slightly changed depending on the pulse frequency. The best mechanical and tribological properties were found at 200kHz substrate pulse frequency.

1. Introduction

The nitrides of transition metals are hard ceramic films containing metallic bonds (Wang et al., 2015). The high hardness, toughness, good adhesion properties and low coefficient of friction of transition metal nitrides make these compounds well suited for industrial applications. Nitride films such as TiN (Efeoglu, Arnell, & Tinston, 1993), ZrN (Tung, Huang, Tsai, Ai, & Yu, 2009), VN (Qiu, Zhang, Li, Lee, & Zhao, 2012), NbN (Kim, Cha, & Yoo, 2004), AlN (J. Li, Wang, & Wang, 2014) and CrN (H. Li, Zhang, Liu, & Huang, 2019) are widely used in metal cutting- shaping, electronic and tribology applications. TiN has been generally used as a hard film to enhance the mechanical properties of cutting and dies tools but its relatively high tendency for oxidation limits its application areas. However, with the increasingly hard service environment, the TiN films cannot provide the technical requirements. In the past decades, new kind of transition metal nitrides such as VN hard film has attracted the wide attention (D'Anna et al., 2002). VN film are attractive as a hard film among transition metal nitrides. Not only mechanical properties but also the other properties such as thermodynamic stability, electrical conductivity, corrosion resistance and friction are good. Hence, VN films are used in many applications (Glaser et al., 2007; Ma, Huang, & Chen, 2000 ; Wiklund, Casas, & Stavlid, 2006). VN films have been deposited by pulsed laser ablation (PLD) (Guo et al., 2016), and reactive magnetron sputtering (Achour, Islam, Ahmad, Saeed, & Solaymani, 2019). Among the physical vapor deposition (PVD), reactive magnetron sputtering is a common and successful technology to deposit of transition metal nitride films. In this study, we investigated substrate pulse frequency effect on the structural, mechanical and tribological properties of VN films.

2. Materials And Methods

In this study, VN films were deposited on 52100 steel (to determine mechanical and tribological properties) and silicon wafer substrates (to determine structural properties). 52100 steel substrates were polished to a roughness value of $R_a \approx 0.05 \mu\text{m}$ by using SiC from 80 to 1200 mesh grit emery papers. The polished substrate surfaces were ultrasonically cleaned with ethanol and then the substrate surfaces

were etched using 5% Nital solution for 15 seconds. Deposition process was performed using an unbalanced magnetron sputtering system produced by Teer Coatings Ltd. In the system, two V target was used as a transition metal for deposition. Also, unipolar pulse frequency was applied to the substrates. For ionization and to form nitride, Ar and N₂ gases were used, respectively. Dc power supply was applied to V targets.

Before deposition of VN film, substrates were sputtered ion cleaned by Ar gas to clean the substrate surface contaminations for approximately 20 minutes (using a bias voltage of 800V). A vanadium transition layer was deposited for 10 minutes on substrates to minimize the residual stress and obtain better adhesion.

In the all processes, the working pressure of 0.33 Pa, N₂ content of 3sccm, V target current of 1.5A, substrate voltage of -100V and duty time of 2μs of substrate were kept constant. During the deposition process, the pulse frequencies were 100 kHz and 200 kHz to the substrates for R1 and R2, respectively. The deposition process continued for 60 minutes.

The microstructure and film thickness were evaluated with a SEM (FEI-Quanta) system. The chemical composition of the films was analyzed by energy dispersive spectrometry (EDS). To determine crystal phases, XRD analyses were performed using Rigaku 2200 Dmax diffractometer with Cu-Kα ($\lambda = 1.5404 \text{ \AA}$) radiation source.

To determine adhesion of films, critical load (L_c) values was measured by scratch tester using a Rockwell-C diamond indenter with a 200 μm radius hemispherical tip under a loading rate of 100 N/min and a sliding speed of 10 mm/min. Also, multi pass scratch tests can be used to define the fatigue behavior of thin films. The multi-pass scratch tests were carried out at a subcritical load of the L_c values obtained from the scratch tests. The multi-pass scratch tests were made over the same track at loads of 15 and 30 N with WC (5 mm diameter) balls on 3 mm scratch tracks over 100 cycles. Failure mechanisms have been discussed according to optic microscope images of the scratch tracks. The chemical compositions of scratch tracks obtained from multi-pass scratch tests were determined by EDS.

The wear behaviors of VN films were tested with TEER POD-2 pin-on-disk tester. All experiments were conducted with 5 mm diameter alumina (Al₂O₃) balls. Wear tests with sliding time of 600 second were carried out at room temperature ($\approx 20 \pm 3 \text{ }^\circ\text{C}$) with a relative humidity of about $45 \pm 5\%$, a sliding speed of 191 rev/min, wear track diameter of 5 mm and normal load of 5 N. Furthermore; the wear rates of the films were determined by a Mahr surface profilometer. The wear tracks were characterized by SEM. After all tests, the chemical compositions of wear tracks were analyzed with EDS.

3. Result And Discussion

VN films have showed dense and columnar structure called Zone T in Structure Zone Modes (P. J. Kelly et al., 2003; P.J. Kelly, Braucke, Liu, Amell, & Doyle, 2007). SEM images of the films are given in Fig. 1. It is obtained from the SEM images, the column density of the VN films increased with the increasing

substrate pulse frequency (Gangopadhyay, Acharya, Chattopadhyay, & Paul, 2010). Essentially, higher frequencies have higher plasma discharge per second than lower frequencies. This situation increases the rate of coating. This helps to increase the coating thickness (Abuali Galedari & Mousavi Khoei, 2013). Thickness values of the VN films deposited by magnetron sputtering are given in Table 1. With substrate pulse frequency increasing from 100 kHz to 200 kHz the thickness of the VN films increasing from 1 μm to 1.2 μm .

Table 1. The chemical compositions, hardness and thickness of the VN films

	V rate (at.)	N rate (at.)	Thickness (μm)	Microhardness (GPa)
R1	74	26	1	11.8
R2	64	36	1.2	15

Fig. 2 shows the XRD graphs of VN films deposited at different substrate pulse frequencies. The effect of pulse frequency clearly observed from the XRD patterns. R2 film (at 200 kHz frequency) have a mixture of VN (111), V_2N (211), V (110) and VN (200) orientations and R1 film (at 100 kHz frequency) contain predominantly a mixture of VN (111) and VN (200) orientations with small volume fraction of V_2N (211) and V (110) orientations. While the VN (111) and VN (200) peaks are available in both films, VN (111) peaks are denser in R2. The VN films showed a preferential orientation of (111) plane with increasing substrate pulse frequency.

The chemical composition values (EDS), hardness and thickness of the VN films are summed up Table 1.

According to the EDS results, nitrogen atom ratios (at.) are 26% and 36% for R1 and R2, respectively. It is clearly observed that the increase in pulse frequency increased nitrogen ratio. The reason of this, the degree of ionization at the plasma increases with increasing the pulse frequencies during process (P.J. Kelly & Arnell, 2000). Furthermore, according to EDS analysis, the changing of V and N ratios are supported by XRD analysis as increasing all peak intensities in R2.

The highest microhardness value for the VN films grown on 52100 steels was measured as 15 GPa (Table 1). The substrate hardness (52100 steel) is 5 GPa. The film hardness increased with increasing pulse frequency and the results were consistent with the literature (Hsiao, Lee, Yang, & Lou, 2013). Also, VN film hardness values vary depending on the amount of V and N atoms. According to EDS results, the nitrogen content increases and vanadium decreases with increasing substrate pulse frequency. Increase nitrogen content causes decrease in grain size (Qiu, et al., 2012). (111) preferred orientation increased with the increase pulse frequency, and therefore the film deposited at higher frequency (R2) exhibit higher hardness.

The normal load and friction graphs obtained from scratch tests are shown in Fig. 3. The critical load values of VN films deposited at 100 kHz and 200 kHz were determined as approximately 58N and 68N, respectively. Critical loads of the films were affected by the variation of the pulse frequency applied to the

substrate. The critical load values of the VN films increased with increasing pulse frequency (Hsiao, et al., 2013). Also, the increase in critical load with the increase in the hardness is in accordance with the results in the literature (Ichimura & Rodrigo, 2000). When the optical microscope images were evaluated (Fig. 4), adhesive spallation occurred with an increased load on the R1 film (100 kHz frequency). It was observed that only micro cracks occurred with increasing load in the harder R2 film (frequency of 200 kHz).

Fig. 5 shows the friction coefficient-number of cycles graphs for each load obtained from multipass scratch. The coefficient of friction for R1 and R2 decreased with the increasing number of the cycle. R2 exhibited lower friction coefficient than R1 under 15N and 30N loads. The increase pulse frequency has caused a decrease low friction.

The optic microscope images of scratch tracks obtained from multipass scratch tests for R1 and R2 are given in Fig. 6 and Fig. 7, respectively. As can be seen at Fig. 6 that adhesive failure and chevron cracks occurred under 15 N load in R1. It was observed that the amount of adhesive failure significantly increases with increasing load (30N) and flaking and chipping also occurred. But, for the VN film deposited at R2, no film failure was observed under 15N (Fig. 7). However, it was observed that the film got thinner due to plastic deformation under 30 N load.

The EDS results of scratch tracks obtained from multi-pass scratch tests were given in Table 2. As a result of the multi pass scratch tests, oxide was available on both film surfaces. However, it has seen that the oxide amount on VN film surface deposited with high frequency (R2) is more than the film surface deposited with low frequency (R1). Fallqvist and Olsson (Fallqvist & Olsson, 2013) reported that V_2N phase have a high oxidation tendency. A higher amount of oxide was formed in the R2 film with a higher V_2N phase density. The amount of oxide on the surface decreases the friction coefficient and increases the life of the film, thereby causing an abrasive effect on the counter face (Arslan, Bülbül, Alsaran, Celik, & Efeoglu, 2005). In the VN film coated under R2 film conditions, during the multi-pass scratch test, lower friction coefficient and lower film damage occurred due to high oxide formation.

Table 2. EDS analyses performed on scratch tracks obtained from multi-pass scratch tests

	under 15N load					under 30N load				
	Fe	V	N	O	Others	Fe	V	N	O	Others
R1	15.8	40.31	15.07	26.54	2.28	18.35	32.24	15.47	31.21	2.73
R2	0.9	44.3	20.02	33.65	1.13	3.6	37.93	20.55	35.68	2.24

The friction coefficient graphs for substrate and VN films are given in Fig. 8. Friction coefficient value for 52100 steel substrates is about $\mu \sim 0.58$. The average friction coefficient values of VN films are obtained as 0.42 for R1 and 0.35 for R2. It was observed that the friction coefficient values of the VN films have decreased with increasing substrate pulse frequency. Wear rate of substrate has been calculated as $7.70 \times 10^{-5} \text{ mm}^3/\text{Nm}$. The wear rate of VN films for R1 and R2 have been calculated as $4.30 \times 10^{-6} \text{ mm}^3/\text{Nm}$ and $2.20 \times 10^{-7} \text{ mm}^3/\text{Nm}$, respectively. VN films have improved the wear resistance of substrate surface. Also, the wear rate values for VN films have generally showed a parallel characteristic with the friction

coefficient values. The lower friction coefficient has showed the lower wear rate. Also, the results were obtained from many studies (Fouvry, Kapsa, & Vincent, 1994; Holmberg, Ronkainen, & Matthews, 2000). VN film grown with high frequency (200 kHz) (R2) showed lower wear rate and the other hand, VN film grown with low frequency (100 kHz) (R1) showed higher wear rate. Nakazawa et.al. (Nakazawa, Kamata, Miura, & Okuno, 2015) reported that the wear rate of the films decreases with increasing frequency. With increasing frequency, vanadium oxide can occur instead of iron oxide, which can reduce the friction coefficient.

SEM images for wear tracks and pins (WC) are given in Fig. 9. VN films showed a smooth wear track. Adhesive wear has been observed on film surfaces. Also, no break-up on the films is observed. Adhesive wear rate decreased with increasing hardness (R2) (Konyashin et al., 2015). During the wear tests on VN films deposited with higher frequency (R2), a dense transfer layer was formed on the surface of the WC pin during sliding (Fig. 9). This transfer layer acts as a solid lubricant and significantly reduces wear and friction at the contact surfaces. Also, the tribological contact is not only controlled by material transfer but is also affected by tribo- induced oxidation resulting in the formation of different oxide products at the sliding interface.

The EDS results on wear tracks are given Table 3. According to the EDS results, the Fe amount for R1 and R2 were determined as 11.92 at. % and 2.63 at. %, respectively. Also, O amount for R1 and R2 were determined as 35.33 at. % and 39.02 at. %, respectively.

Table 3. The EDS results on wear tracks

	Fe	V	N	O	Cr	C	Mn
	(at.%)						
R1	11.92	26.8	23.05	35.33	1.52	1.03	0.35
R2	2.63	30.12	26.03	39.02	0.96	0.99	0.25

The oxide formed on films caused low friction coefficient, due to lubricant behavior of oxide (Velkavrh et al., 2016). The oxide formed on the VN grown with high substrate pulse frequency caused a decrease in the wear rate of the film. In addition, as a result of EDS, less elements from the substrate was exposed on R2 film surface, so the friction coefficient was reduced. The increased amount of V and N creates a solid lubrication effect on the contact surfaces, thus the wear rate reduces and the life of the films increase.

4. Conclusion

VN films grown by magnetron sputtering have showed dense and smooth structure. The increasing substrate pulse frequency increased the film thickness and hardness. The higher hardness concluded the higher critical load. Only micro cracks are determined with the higher critical load value. Oxide was formed both films. Therefore, the oxide amount increased with increasing substrate pulse frequency. The higher oxide formed on VN films (R2) showed lower coefficient of friction throughout the multi-pass scratch and wear tests. Also, less film damages were occurred. VN films grown with high frequency (200

kHz) showed lower wear rate. VN film deposited at substrate pulse frequency of 200 kHz showed optimum mechanical and tribological properties.

Declarations

Availability of data and materials: Not applicable

Competing interests: Not applicable

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Figures

Figure 1

SEM images of the VN films

Figure 2

XRD patterns of VN films deposited with R1 and R2 deposition parameters

Figure 3

The critical load values obtained from scratch tests under increasing normal load for VN films

Figure 4

Optic microscopic images of scratch tracks

Figure 5

Friction coefficients obtained from multipass scratch tests for VN films

Figure 6

Optic microscopic images obtained from multipass scratch tests for VN films deposited with R1 deposition parameters

Figure 7

Optic microscopic images obtained from multipass scratch tests for VN films deposited with R2 deposition parameters

Figure 8

Friction coefficient graphs for substrate and VN films

Figure 9

SEM images of wear tracks and pins obtained from pin on disc wear tests for R1 and R2 VN films