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# High-Temperature Self-Lubricating Metal Nitride-Based Nanostructure Composite Films

Hongbo Ju

## Abstract

The film technology is one of the most efficient methods of modifying the surface properties of materials. The focus of recent attention in the solid lubricating materials is on the hard transition metal nitride films' excellent high-temperature tribological properties applied in powertrains and cutting tools. This chapter reviewed the formation mechanism of Magnéli phases and the influence of Magnéli phases on the high-temperature tribological properties of hard transition metal nitride films synthesized using magnetron sputtering. The self-lubricating behavior and wear mechanism of the Magnéli phases are discussed from the point of view of crystallography. Some methods to enhance the wear resistance property of the metal nitride film are also discussed.

**Keywords:** transition metal nitride films, magnetron sputtering, tribological properties, self-lubricating, Magnéli phase

## 1. Introduction

Recently, a solid lubrication known as Magnéli phases was reported in the application of oxide materials with “easy” crystallographic shear phases, and numerous related research activities have been carried out to investigate the function mechanism of Magnéli phases. Molybdenum, tungsten, and vanadium as the additional elements were initially incorporated into transition metal nitride (TMN)-based hard films, since the molybdenum oxide, tungsten oxide, and vanadium oxide are common Magnéli phases and exhibit the excellent lubricating property. The TMN matrix as the hard phase with a columnar structure could retain the strength and bearing capacity during the wear test. Both the environment heat and friction heat induce the complex tribo-chemistry reaction and the formation of Magnéli phases. The binary molybdenum nitride, the scientists have already attached importance to tungsten nitride and vanadium nitride film in solid lubricating films in recent years. In this part, the high-temperature self-lubricating property of TMN-based hard films was discussed.

## 2. Binary molybdenum nitride, tungsten nitride, and vanadium nitride films

The crystal structure of the molybdenum nitride film shows a little influence on the deposition parameters such as nitrogen partial pressure, substrate temperature,

and target power. A single fcc-Mo<sub>2</sub>N phase is usually investigated in the molybdenum nitride film deposited using magnetron sputtering system.

Hardness of the molybdenum nitride film is ~26 GPa. The film exhibits the excellent friction property at high temperature at the expense of wear resistance property. Tribo-film MoO<sub>3</sub> is considered as the main factor attributing to the relatively low friction coefficient. MoO<sub>3</sub> is composed of double layers of distorted edge-sharing MoO<sub>6</sub> octahedra parallel to (010) planes. The MoO<sub>3</sub> has low shear strength because weak van der Waals forces hold the successive layers together. The counterpart is easy to wear away the MoO<sub>3</sub> under the wear test.

The crystal structure of the tungsten nitride film depends on the deposition parameters significantly. Tungsten nitride films could present a variety of phases such as cubic W<sub>2</sub>N and hexagonal WN with large nitrogen to tungsten ratios, and the film consisting of a single phase of fcc-W<sub>2</sub>N exhibits the highest hardness and lowest friction coefficient. The tungsten or nitrogen vacancies in the binary tungsten nitride films are a common phenomenon [1, 2]. The vacancies in the films could enhance the mechanical properties. The hardness of fcc-W<sub>2</sub>N film is ~30 GPa, whose value is higher than that of molybdenum nitride and vanadium nitride films. Binary tungsten nitride film also exhibits the excellent friction property at the expense of wear resistance property. During the wear test, WO<sub>3</sub> could easily form induced by the counterpart at high temperature, and it could play an excellent lubricating role. WO<sub>3</sub> is described as crystallographic shear structure in normal as a type of typical Magnéli phases. Reeswinkel et al. [3] expounded the structure of WO<sub>3</sub> by the calculation results according to the density functional theory. The results show that there are three different types of W-O bonds co-exist in WO<sub>3</sub> owing to the distorted octahedron WO<sub>6</sub> and the shifted W cation in the WO<sub>3</sub>. It is showed that these three types of W-O bonds represent extraordinary lubrication properties.

The crystal structure of vanadium nitride film is also influenced by the deposition parameters significantly. The vanadium nitride-based film is seldom applied in the cutting tools on account of the relative low value of hardness and poor thermal stability of the vanadium nitride film. Vanadium oxide phases could lubricate the film during the wear test at high temperature, and V<sub>n</sub>O<sub>2n+1</sub> was defined as Magnéli phase because of its excellent lubricant properties. The increase in temperature was reported to induce the change of VO<sub>2</sub> to V<sub>2</sub>O<sub>5</sub> [4]. Erdemir [5] establishes the relationship between the phase lubricity of oxide and its ionization potential based on the principle of crystal chemistry. Based on this principle, oxides with high ionic potential values will show a low coefficient of friction. Because the ionic potential of V<sub>2</sub>O<sub>5</sub> (10.2) is higher than that of VO<sub>2</sub> (6.8) [6], the V<sub>2</sub>O<sub>5</sub> shows a better lubricant property than that of VO<sub>2</sub>.

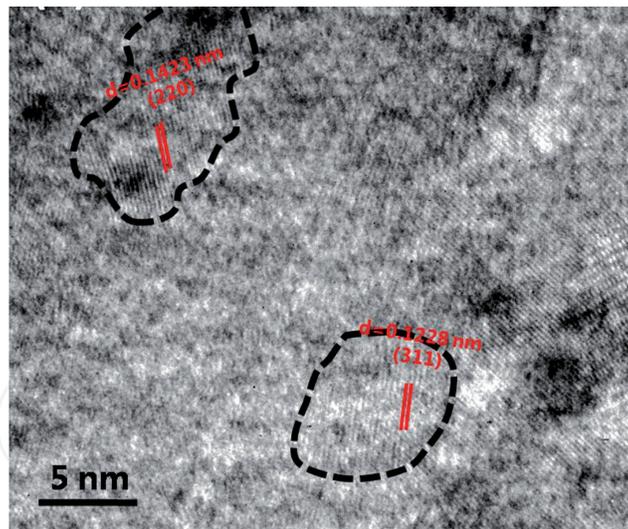
### 3. Molybdenum nitride, tungsten nitride, and vanadium nitride-based composite films

In view of the poor thermal stability and high wear rate, V-N, W-N, and Mo-N-based films are comparatively less applied in cutting tool field. As reported [7, 8], alloying metallic/nonmetallic elements into metal nitride matrix to deposit ternary, quaternary, and multicomponent hard films could combine the benefits of individual components. Therefore, the incorporation of some additional elements into the V-N, W-N, and Mo-N film could be an efficient method to improve the thermal stability and wear resistance property.

Addition of Al into transition metal nitride thin films has been regarded as an effective method to improve the hardness, crystalline orientation, wear resistance, oxidation resistance, and thermal stability of the materials [9, 10]. AlN alloys are

usually considered as a superior oxidation resistant due to the formation of  $\text{Al}_2\text{O}_3$  layers, which prevent oxygen diffusion toward the coating interior. In addition, Al and Al alloys exhibit low wear resistance although they are used in a wide range of automobile and aerospace industries [11]. Yang et al. [12] prepared  $\text{Mo}_{1-x}\text{Al}_x\text{N}$  thin films on stainless steel coins, alumina sheet, and silicon wafer substrates by using dc reactive magnetron sputtering technique and studied the effect of  $\text{N}_2$  and Al content (0.06–0.33) on the coating properties including structural, hardness, and oxidation resistance. The maximum hardness of 29 GPa was found at  $x = 0.06$ , and by further increasing of Al content, a decrease in hardness was detected owing to the weakness of fine grain strengthening. The oxidation resistance temperature increased gradually by increasing the concentration of Al. Our group [13] fabricated Mo-Al-N thin films with various Al contents (3.7–18.3 at.%) on stainless steel (06Cr19Ni10) and Si (100) wafer substrate by using reactive magnetron sputtering and studied the effect of Al content on microstructure, mechanical oxidation resistance, and tribological properties of the films. The result showed that the oxidation resistance of MoAlN thin films increased by increasing the Al content, while hardness and young modulus first increased and then started decreasing by increasing the Al content. The highest values of hardness and elastic modulus were 32.6 and 494 GPa, respectively, at 3.7 at.% Al. The film showed the lowest average friction coefficient and wear at the range between 4.1 and 9.5 at.% of Al content. Besides this, we also add the Al into the vanadium nitride film using the magnetron sputtering. The influence of Al content on the micro-structure, oxidation resistance, mechanical, and tribological properties of V-Al-N films were investigated. The crystal structure of V-Al-N film is always a single face-centered cubic structure no matter what the aluminum content is. When the content of aluminum was lower than 4.7 at.%, the hardness of the film represented an obvious increase. At the same time, the friction coefficient and wear rate showed a decrease at room temperature. The elevated Al content increases the oxidation resistance while reducing the fracture toughness. The high temperature tribological properties of the film at 4.7 at.% aluminum, which showed the highest hardness, lowest friction coefficient, and wear rate were investigated. The increase in temperature caused a change in the wear mechanism and a phase transition of the tribo-film vanadium oxides. The friction coefficient first increases to 0.7 at 300°C and decreases to 0.28 at 700°C with the wear rate gradually increases. As a result, the film at 4.7 at.% Al represented the most suitable properties in cutting tool application.

Based on above investigation, the addition of Al into the  $\text{Mo}_2\text{N}$ , VN matrix to the formation of the substitutional solid solution could enhance the mechanical properties. Besides this, the addition of Al also could improve the oxidation resistance temperature. The oxidation behavior of the films containing Al is mainly controlled by the Al content in the films.  $\text{Al}^{3+}$  diffuses outward to the surface of the films with the inward diffusion of oxygen will form  $\text{Al}_2\text{O}_3$  layer during the oxidation process.  $\text{Al}_2\text{O}_3$  phase is stable over a wide temperature range and easy to be formed. At low temperature ranging from 400 to 600°C, amorphous  $\text{Al}_2\text{O}_3$  is formed [9]. The amorphous  $\text{Al}_2\text{O}_3$  layer on the surface of the films is more effective to prevent the diffusion of oxygen into the films. However, the further increase in temperature induces the  $\text{Al}_2\text{O}_3$  from amorphous to crystalline. Compared with the amorphous  $\text{Al}_2\text{O}_3$ , oxygen is easily diffused internally due to the grain boundary [10, 13, 14] of the crystalline oxide layer, while  $\text{Al}_2\text{O}_3$  and  $\text{MoO}_3$  grow rapidly. The oxidation diffusion mechanism is transferred from atomic diffuse to mass transfer. At the same time, the exchange of Al caused an increase in Al-N covalent bonds in the films, which represents excellent thermal stability property. The addition of Al could improve the wear resistance property of the films due to the enhancement of thermal stability and the decrease in the Magnéli elements in the films.



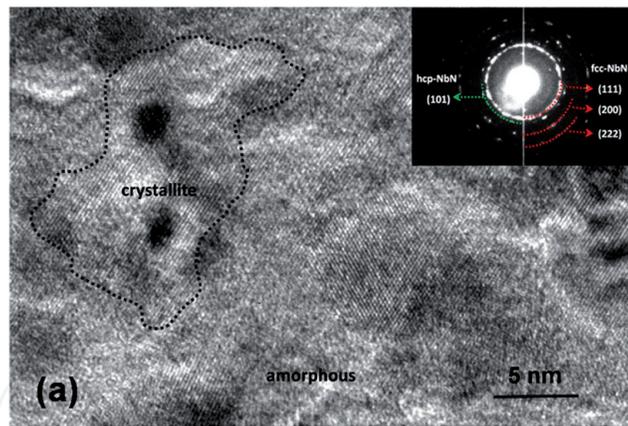
**Figure 1.**  
HRTEM image of W-Si-N film with a Si content of 23.5 at. %.

Silicon is another additional element to improve the mechanical, thermal stability, and wear resistance properties of the films. Limited solid solubility of Si in the TMN matrix induces the formation of amorphous  $\text{Si}_3\text{N}_4$  phase. **Figure 1** shows the TEM image of the W-Si-N composite film with a Si content of 23.5 at.%. As shown in the figure, the nanograins of fcc- $\text{W}_2\text{N}$  are embedded into the amorphous phases. The amorphous  $\text{Si}_3\text{N}_4$  exhibits an excellent thermal stability property, and its oxidation resistance temperature is above  $1200^\circ\text{C}$ . Therefore, the addition of Si into the TMN matrix could increase the oxidation resistance temperature. The nanograins of tungsten nitride are wrapped up by the amorphous phase. This microstructure could provide better protection for tungsten nitride against oxidation and prolong the service life during the wear test.

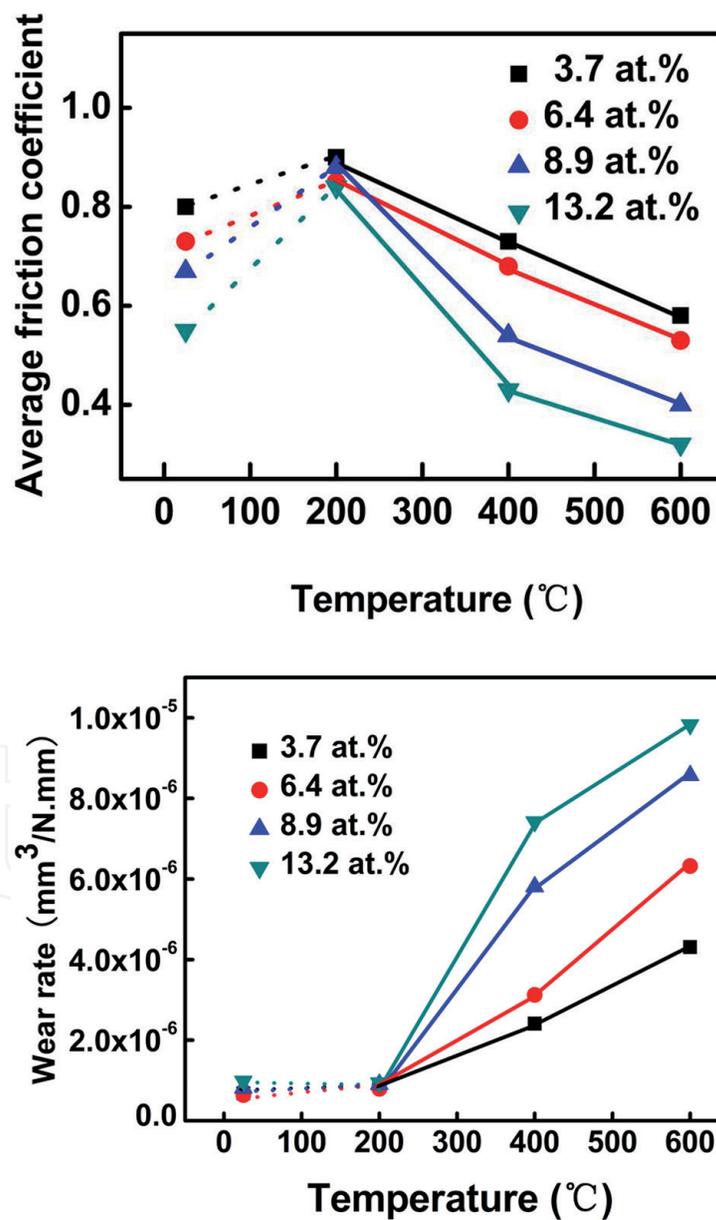
Some other additional elements such as titanium and niobium also could improve the wear resistance properties of molybdenum nitride, tungsten nitride, and vanadium nitride-based films [15–17]. For instance, the incorporation of titanium into the tungsten nitride matrix could form a solid solution of  $(\text{W}_{1-x}\text{Ti}_x)_{2-y}\text{N}_y$  and exhibited a single face-centered cubic (fcc)  $\text{W}_2\text{N}$  structure. Both the sub-stoichiometric nitrogen content and solid solution strengthening could enhance the mechanical properties. The incorporation of titanium also drops the wear rate at room temperature significantly. This could be attributed to the increase of hardness to elastic modulus ratio, elastic recovery, and hardness. Besides this, the addition of titanium into the tungsten nitride matrix decreases the tungsten content in the film, and this finally induces the decrease in the content of Magnéli phase on the wear track surface. The decrease in the poor wear resistance Magnéli phase also attributes to the decline of wear rate. Tungsten titanium nitride film exhibits the higher working temperature than the binary  $\text{W}_2\text{N}$  film.

#### 4. TMN-based composite films containing Magnéli elements

The molybdenum, tungsten, and vanadium Magnéli elements have been widely incorporated into some traditional TMN-based films to improve the high-temperature self-lubricating property. For instance, V was incorporated into the Nb-Si-N matrix, and the Nb-V-Si-N composite films were synthesized using the magnetron sputtering to improve the high-temperature tribological properties. The results show that the incorporation of V into the matrix could form the substitutional solid solution of  $(\text{Nb}, \text{V})\text{N}$ . **Figure 2** shows the HRTEM image of the Nb-V-Si-N



**Figure 2.**  
 HRTEM image and its corresponding SAED pattern of Nb-V-Si-N film at 3.7 at.% vanadium.

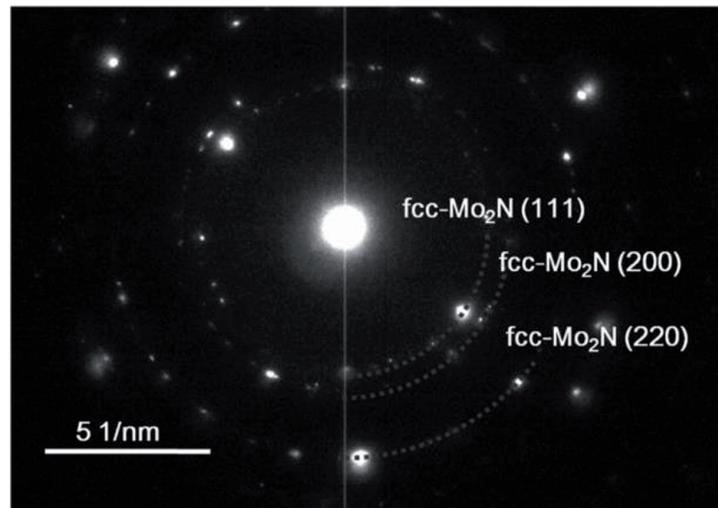


**Figure 3.**  
 Friction coefficient and wear rate of Nb-V-Si-N films as a function of vanadium content.

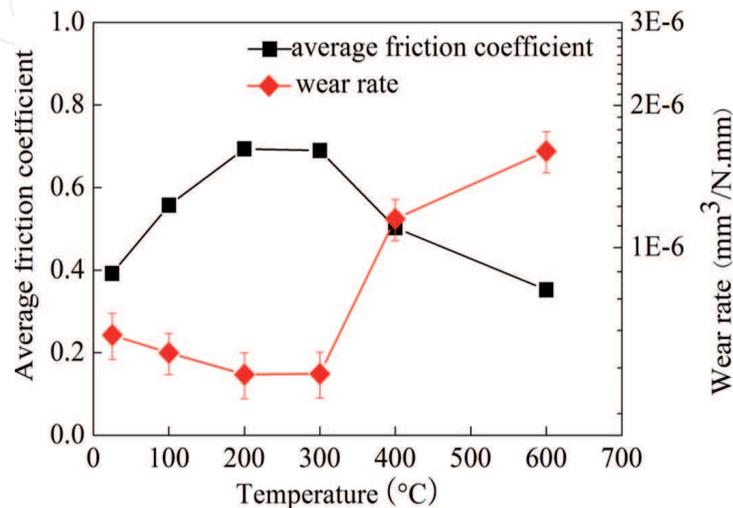
film with a vanadium content of 3.7 at.%. The amorphous Si<sub>3</sub>N<sub>4</sub> phases enclose the substitutional solid solution. This microstructure could provide better protection for Nb-V-N against oxidation at the high temperature environment. The solution

of V could improve the mechanical properties such as the hardness and toughness. **Figure 3** illustrates the friction coefficient and wear rate of the films at different testing temperatures. The incorporation of V into the film could improve the friction property at elevated temperatures at the expense of wear resistance property due to the Magnéli phase with weakly bonded lattice planes.

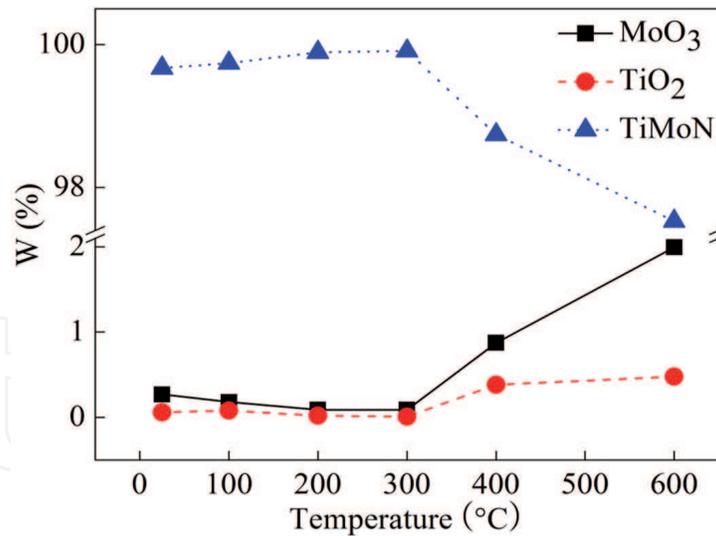
Molybdenum can also bring positive influence to high-temperature friction performance of the film. We add molybdenum into the classic titanium nitride film in order to improve its tribological properties. The result shows that the Ti-Mo-N film exhibits a single face-centered cubic structure, as same as binary TiN film. With the increase of molybdenum content, the Mo<sub>2</sub>N phase appears in the film because of the precipitated molybdenum. **Figure 4** illustrates the SAED pattern of the Ti-Mo-N film at 46.0 at.% Mo. Calculated the data given in **Figure 4**, it can be seen that the selected electron diffraction pattern matches fcc-Mo<sub>2</sub>N. The composite film represents the highest hardness and the lowest friction coefficient in room temperature at 46.0 at.% Mo. **Figure 5** shows the average friction coefficient and wear rate of Ti-Mo-N films at 46.0 at.% Mo under different testing temperatures. **Figure 6** shows the relative mass fraction of Ti-Mo-N, MoO<sub>3</sub>, and TiO<sub>2</sub> on the wear tracks of Ti-Mo-N films at testing temperatures. When the testing temperature is higher than



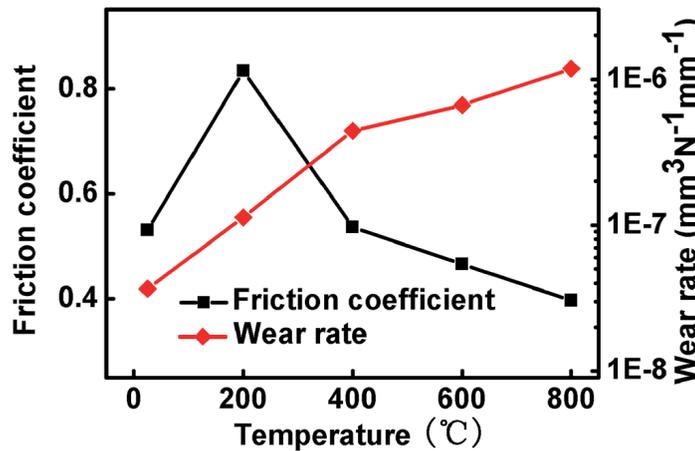
**Figure 4.**  
The SAED patterns of Ti-Mo-N films with 46.0 at.% Mo content.



**Figure 5.**  
The average friction coefficient and wear rate of Ti-Mo-N films at different temperatures.



**Figure 6.**  
 The relative mass fraction of Ti-Mo-N, MoO<sub>3</sub>, and TiO<sub>2</sub> on the wear tracks of Ti-Mo-N films at testing temperatures.



**Figure 7.**  
 The friction coefficient and wear rate of Ti-W-N composite films at different temperatures.

400°C, the Magnéli phase MoO<sub>3</sub> and oxidized phase TiO<sub>2</sub> appeared contributes to the decrease of average friction coefficient, and the relative mass fraction of the friction phase in the film wear marks increases gradually with the increase of ambient temperature, which can lubricate the wear marks and friction pairs and make the interaction between them tend to ease, so the average friction coefficient of the film decreases gradually with the increase of ambient temperature. However, the MoO<sub>3</sub> layers are only combined by van der Waals force. MoO<sub>3</sub> is very diffusive and easy to be worn by counterpart during the wear test, so MoO<sub>3</sub> is not wear-resistant although it can decrease the friction coefficient.

In addition, there are similar conclusions in Ti-W-N composite film. TiN incorporating tungsten can form the substitutional solid solution of (Ti, W) N as well and precipitate W<sub>2</sub>N when the content of tungsten reaches a specific value. **Figure 7** illustrates the friction coefficient and wear rate of Ti-W-N composite films at 35.29 at.% W under different temperatures. When the temperature rises to 400°C, the friction coefficient decreases sharply because the TiWN composite film is oxidized, and the oxidation phases of Ti and W are formed on the surface of the film, which means TiO<sub>2</sub> and WO<sub>3</sub>. WO<sub>3</sub> with layered structure plays a role in the lubricant under the high-temperature friction. When the content of WO<sub>3</sub> increases, the coefficient of friction decreases. WO<sub>3</sub>

has a melting point of about 730°C, and when the temperature continues to rise to 800°C, the melted WO<sub>3</sub> has better lubricating properties than the dry friction, which leads to the further decrease of friction coefficient. Beside this, the friction coefficient will keep a low value due to the constant formation of liquid WO<sub>3</sub> during the friction process.

## 5. Conclusion

1. The Magnéli phase exhibits the excellent lubricating properties at high temperatures; however, it could be worn away easily by the counterpart during the wear test due to its weakly bonded lattice planes.
2. Addition of aluminum and silicon into the TMN-based films containing Magnéli elements could improve the thermal stability and decrease in the content of Magnéli phase on the wear track surface. It could enhance the wear resistance property to some extent.

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