Effects of C Target Power on Microstructure, Mechanical Properties, and Tribological Properties of TiWCN Composite Films (Postprint)

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Abstract

A series of TiWCN composite films with different C target powers were deposited by magnetron sputtering. The microstructure, mechanical properties, and tribological properties of the TiWCN composite films were characterized using X-ray diffractometer, scanning electron microscope, nanoindenter, and high-temperature tribometer. The results indicate that the TiWCN composite films consist of a face-centered cubic TiWCN phase and a hexagonal Ti N phase. As the C target power increases, the hardness of the films first increases and then decreases, the friction coefficient at room temperature gradually decreases, while the wear rate first decreases and then increases. At a C target power of 90 W, the hardness reaches a maximum value of 35.97 GPa, and the wear rate reaches a minimum value of 1.26×10 $mm^3 \cdot N^{1} \cdot m^{1}$. At a C target power of 120 W, the friction coefficient reaches a minimum value of 0.322. When the temperature is below 370°C, the friction coefficient and wear rate of the TiWCN composite films are lower than those of the TiWN films; when the temperature exceeds 370°C, the friction coefficient and wear rate of the TiWCN composite films are higher than those of the TiWN films. The study demonstrates that the addition of C to TiWN films improves the mechanical properties and room-temperature tribological properties of the films, but does not improve the high-temperature tribological properties.

Full Text

Influence of C Content on Microstructure, Mechanical Properties, and Friction and Wear Properties of TiWCN Composite Films

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Abstract
A series of TiWCN composite films with varying C contents were prepared by magnetron sputtering. The microstructure, mechanical properties, and friction and wear properties of the TiWCN composite films were characterized using X-ray diffraction (XRD), scanning electron microscopy (SEM), nanoindentation, and high-temperature tribometry. The results demonstrate that the TiWCN composite films consist of an fcc-structured TiWCN phase and a hexagonal Ti N phase. With increasing C content, the film hardness initially increases and then decreases, the room-temperature friction coefficient gradually decreases, while the wear rate first decreases and then increases. At a C content of 11.25 at%, the hardness reaches a maximum value of 35.97 GPa, and the wear rate attains a minimum value of 1.26×10 $mm^3 \cdot N^{-1} \cdot m^{-1}$. At a C content of 13.68 at%, the friction coefficient reaches a minimum value of 0.32. When the temperature is below 370 °C, the friction coefficient and wear rate of the TiWCN composite films are lower than those of TiWN films; however, when the temperature exceeds 370 °C, both values become higher than those of TiWN films. The addition of C to TiWN films improves their mechanical properties and room-temperature friction and wear performance, but does not enhance their high-temperature friction and wear properties.

Keywords
magnetron sputtering, TiWCN composite films, microstructure, mechanical properties, friction and wear properties

Introduction

In recent years, the rapid development of high-performance machining has placed increasingly stringent demands on cutting tool performance under extreme service conditions involving high rotational speeds and elevated temperatures. The severe wear, high-temperature oxidation, and surface fatigue generated under these conditions significantly degrade tool performance and drastically shorten tool life. Although TiN has been widely used as a conventional coating material in the tool manufacturing industry due to its high hardness and strong chemical stability, its performance remains inadequate for the higher requirements of modern machining operations. To address this limitation, researchers have attempted to diversify conventional tool coating materials by adding metallic or non-metallic elements, thereby modifying film microstructure and enhancing comprehensive performance.

TiWN films exhibit high hardness, strong corrosion resistance, and high film-substrate adhesion, demonstrating broad application prospects in the field of tool coating materials and attracting increasing attention in recent years. Our research group has investigated the mechanical and tribological properties of TiWN films, revealing that TiWN films achieve a high hardness of 30.67 GPa. At elevated temperatures, W in the films oxidizes to form

WO with a Magnéli phase layered structure, which provides good lubrication during high-temperature friction. However, the room-temperature friction coefficient and wear rate are relatively high at 0.53 and 3.66×10 $mm^3 \cdot N^{-1} \cdot m^{-1}$, respectively. Carbon exhibits excellent solid lubrication properties and can effectively reduce the room-temperature friction coefficient and wear rate during friction processes, thereby improving room-temperature tribological performance. Zhang et al. prepared TiAlCN films using DC reactive magnetron sputtering and investigated the effect of C content on mechanical and tribological properties, finding that the room-temperature friction coefficient of TiAlCN films gradually decreased with increasing C content. Our research group studied the effect of different C target powers on the properties of TiVCN composite films using unbalanced reactive magnetron sputtering, demonstrating that room-temperature friction and wear performance improved with increasing C target power. However, few studies have reported on how C affects high-temperature friction and wear properties. Therefore, this work designed TiWCN composite films by adding C to TiWN films. A series of TiWCN composite films with different C contents were prepared using multi-target reactive magnetron sputtering to investigate the influence of C content on microstructure, mechanical properties, and friction and wear properties, and to discuss the mechanisms of C effects on tribological performance at different temperatures.

Experimental

TiWCN composite films were deposited on P-type (100) oriented single-crystal Si substrates and 304 stainless steel substrates (15 mm×15 mm×2.5 mm) using a JGP450 multi-target magnetron sputtering system. The single-crystal Si and stainless steel substrates were ultrasonically cleaned in distilled water, absolute ethanol, and acetone for 10 minutes each to remove surface oil and dust. After cleaning, the substrates were rapidly dried with hot air and loaded into the sputtering vacuum chamber. Ti (99.9%) and W (99.9%) targets were installed on two independent RF cathodes, while a graphite target (99.99%) was installed on a DC cathode. The target diameter was 75 mm, and the target-to-substrate distance was 78 mm.

When the base vacuum reached 6.0×10 Pa, Ar gas (99.999%) was introduced into the chamber to ignite the arc and clean the targets for 10 minutes to remove surface oxide layers or contaminants. A 100 nm pure Ti interlayer was then pre-sputtered to improve film-substrate adhesion. Subsequently, N (99.999%) was introduced as the reactive gas, with Ar and N flow rates of 10 sccm and 2 sccm, respectively, at a total working pressure of 0.3 Pa. The Ti target power was fixed at 250 W and the W target power at 90 W, while the graphite target power was varied at 0, 30, 60, 90, and 120 W to deposit TiWN films and TiWCN composite films approximately 2 μm thick.

Single-crystal Si substrate samples were used to investigate film microstructure and mechanical properties, while stainless steel substrate samples were used to

evaluate friction and wear performance. The elemental composition of the films was determined using an EPMA-1720 electron probe microanalyzer. Phase composition of the films and wear tracks was analyzed using an XRD-6000 X-ray diffractometer (Cu K) at a grazing angle of 1°, scanning speed of 4°/min, and scanning range of 30°–80°. The atomic bonding structure within the films was examined using a Renishaw inVia Raman spectrometer with a laser power of 50 mW and wavelength of 532 nm. High-temperature wear track morphologies were observed using a JSM-6480 scanning electron microscope (SEM). Hardness measurements were performed on a CPX+NHT2+MST nano-mechanical testing system using a load of 5 mN to ensure indentation depth remained below 10% of film thickness, with a loading rate of 10 mN/min, hold time of 10 s, and averaging nine measurements per sample. Friction tests were conducted on a UMT-2 high-temperature tribometer using a ball-on-disc configuration with an Al O ceramic ball (diameter Φd = 9.38 mm) at a rotational speed of 50 r/min, radius of 4 mm, load of 3 N, and duration of 30 min. The average wear volume of the wear tracks was measured using a 3D profilometer to calculate the average wear rate. The residual stress in the films was calculated using the Stoney formula by measuring the curvature radius of Si wafers before and after film deposition. The mass fraction of constituent phases was calculated using the adiabatic method according to the following formula:

$$X_i = \frac{I_i/R_i}{\sum_{j=1}^{n} I_j/R_j}$$

where X_i represents the mass fraction of phase i, I is the diffraction peak intensity, and the R value reflects the reflection capability.

Results and Discussion

2.1 Chemical Composition and Microstructure

Figure 1 [Figure 1: see original paper] shows the atomic fraction of each element in TiWCN composite films deposited at different C target powers. As the C target power increases, the C atomic content in the films gradually increases while the Ti, W, and N atomic contents correspondingly decrease. At C target powers of 0, 30, 60, 90, and 120 W, the corresponding C atomic fractions in the films are 0, 8.52%, 9.20%, 11.25%, and 13.68%, respectively. Thus, the C atomic content in the films increases with increasing C target power.

Figure 2 [Figure 2: see original paper] presents the XRD patterns of TiWCN composite films with different C contents. The TiWCN composite films consist of an fcc-structured TiWCN phase (TiWN phase when C content is 0) and a hexagonal Ti N phase, with preferred orientation along the (111) TiWCN plane. As the C content increases, the diffraction peaks gradually weaken and broaden, shifting toward lower angles.

Figure 3 [Figure 3: see original paper] shows the Raman spectra of TiWCN composite films with different C contents. According to literature [17,18], the G and D peaks correspond to characteristic peaks of sp^2 and sp^3 hybridized C–C bonds in Raman spectra, respectively, and their appearance indicates the presence of an amorphous graphite phase in the films. When the C content is 11.25%, a weak D peak appears at 1390 cm ^{1} while a more pronounced G peak appears at 1580 cm ^{1}, because as the C target power increases, the C atoms added to the film reach saturation and excess C forms an amorphous graphite phase. When the C content increases to 13.68%, the intensities of both D and G peaks significantly increase, indicating a substantial increase in the amorphous graphite phase.

Figure 4 [Figure 4: see original paper] shows the grain sizes of TiWCN composite films calculated using the Debye–Scherrer formula [19]. The grain size gradually decreases with increasing C content, because C atoms promote film nucleation while the formed amorphous graphite phase inhibits grain growth, leading to progressively smaller grain sizes [14,20].

2.2 Hardness and Residual Stress

Figure 5 [Figure 5: see original paper] presents the hardness and residual stress of TiWCN composite films with different C contents. The TiWN film exhibits a hardness of 30.7 GPa. With increasing C content, the hardness of TiWCN composite films first increases and then decreases, while the residual stress within the films is compressive and follows the same trend. When the C content reaches 11.25%, the film hardness achieves a maximum value of 35.97 GPa, because partial substitution of N atoms by C atoms forms a substitutional solid solution, producing solid solution strengthening [21]. Additionally, grain refinement strengthening [22,23] and the presence of compressive stress in the films [15,24] also contribute to hardness enhancement. Meanwhile, the small amount of amorphous graphite phase formed has minimal impact on film hardness. When the C content increases to 13.68%, the film hardness drops sharply to a value lower than that of the TiWN film, because the significantly increased graphite phase content, with its low hardness, causes a dramatic decrease in film hardness [21,25].

2.3 Room Temperature Friction and Wear Properties

Figure 6 [Figure 6: see original paper] shows the room-temperature friction curves, friction coefficients, and wear rates of TiWCN composite films. As seen in Figure 6a, the friction curves exhibit a slight increase during the initial 200 s, followed by a gradual decrease and stabilization. This occurs because macroscopic and/or microscopic geometric defects on the film surface increase the contact pressure between the ball and film, resulting in a slightly higher friction coefficient. As friction proceeds, wear and plastic deformation at the ball contact points alter the contact surface morphology and pressure state, leading to a decrease in friction coefficient and entry into a stable friction regime [26].

Figure 6b reveals that the friction coefficient gradually decreases with increasing C content, while the wear rate first decreases and then increases. At a C content of 11.25%, the wear rate reaches a minimum value of 1.26×10 $mm^3 \cdot N^{-1} \cdot m^{-1}$; at a C content of 13.68%, the friction coefficient reaches a minimum value of 0.32. Analysis combined with Figure 3 indicates that when the C content is below 11.25%, C atoms exist in the film as a substitutional solid solution, and the dissolved C in the lattice provides lubrication, reducing the friction coefficient. At a C content of 11.25%, a small amount of amorphous graphite phase forms in the film, and due to the good lubricating properties of graphite, the friction coefficient decreases significantly. When the C content increases to 13.68%, the amorphous graphite phase increases substantially and accumulates on the friction pair surface to form a transfer film, reducing interfacial shear stress and friction force, which further decreases the friction coefficient [12]. The wear rate is related to factors such as hardness and phase structure [9,27], where high-hardness materials exhibit strong wear resistance, while the layered structure of the graphite phase is highly diffusive and easily worn. When the C content is below 11.25%, increasing C content raises film hardness and enhances wear resistance. Since the amorphous graphite phase content is low in this range, hardness becomes the dominant factor affecting wear rate, causing the wear rate to gradually decrease. When the C content increases to 13.68%, the increased amorphous graphite phase reduces film wear resistance, resulting in an increased wear rate.

2.4 High Temperature Friction and Wear Properties

Figure 7 [Figure 7: see original paper] shows the friction coefficients and wear rates of TiWN films and TiWCN composite films (C content = 13.68 at%) at different temperatures. As the temperature increases from room temperature (25 °C) to 700 °C, the friction coefficients of both TiWN and TiWCN films first increase and then decrease, while the wear rates continuously increase. Furthermore, when the temperature is below approximately 370 °C, the friction coefficient and wear rate of TiWCN composite films are lower than those of TiWN films; however, when the temperature exceeds approximately 370 °C, both values become higher than those of TiWN films.

Figure 8 [Figure 8: see original paper] presents the XRD patterns of TiWN films and TiWCN composite films (C content = 13.68 at%) after high-temperature friction at 300, 500, and 700 °C. At 300 °C, a small amount of WO forms in the TiWN film, while no oxides appear in the TiWCN composite film. At 500 °C, both TiWN and TiWCN films undergo oxidation, with Ti and W atoms oxidizing to form corresponding oxides (TiO and WO) [28,29]. When the temperature rises to 700 °C, the TiO and WO diffraction peaks in both films significantly intensify and multiply, indicating further oxidation. Based on Figure 8a, the adiabatic method [30] was used to calculate the WO content in the wear tracks of TiWN films and TiWCN composite films (C content = 13.68 at%) after friction at 300, 500, and 700 °C, as shown in Figure 8b. The WO

content in the wear tracks of both films gradually increases with temperature. Moreover, at the same temperature, the WO content in TiWN film wear tracks is higher than that in TiWCN composite films, primarily because the addition of C atoms reduces the W atomic content in the film, resulting in less WO formation in TiWCN composite films at high temperatures.

As temperature increases from room temperature (25 °C) to 300 °C, the friction coefficients of both TiWN and TiWCN films gradually increase, mainly because evaporating moisture in the air reduces water content, leading to increased friction coefficients under high-speed dry friction conditions [14]. With further temperature increase, the WO content formed during intense friction gradually increases, and WO acts as a lubricant, enhancing film lubrication performance [10]. Consequently, the friction coefficients of both TiWN and TiWCN films significantly decrease at 500 °C. When the temperature reaches 700 °C, the friction coefficients of both films decrease and stabilize because the elevated ambient temperature combined with localized frictional heating causes the local temperature to approach the melting point of WO (approximately 730 °C [31]), resulting in partial melting of WO . The molten WO acts as a liquid lubricant during friction, providing better lubrication than dry friction and causing the friction coefficient to continue decreasing and stabilize [29].

The friction coefficients of both TiWN and TiWCN films increase first and then decrease with temperature (Figure 7a). However, compared to TiWN films, the presence of amorphous graphite phase and dissolved C in the lattice provides lubrication in TiWCN composite films, resulting in lower friction coefficients below 300 °C. When the temperature exceeds 300 °C, the graphite phase structure in TiWCN films is destroyed and the dissolved C in the lattice begins to oxidize. Combined with Figure 8b, the lower WO content in TiWCN composite films compared to TiWN films, along with the excellent lubricating properties of WO , results in higher friction coefficients for TiWCN composite films.

The wear rates of both TiWN and TiWCN films increase with temperature (Figure 7b). When the temperature is below approximately 370 °C, the wear rate of TiWN films is higher than that of TiWCN films because more WO forms in TiWN films, and the layered structure of WO is easily worn. When the temperature exceeds approximately 370 °C, the wear rate of TiWCN films becomes higher than that of TiWN films due to severe oxidation of C in TiWCN films, which accelerates wear.

Figure 9 [Figure 9: see original paper] shows the wear track morphologies of TiWN and TiWCN films at 500 and 700 °C. At 500 °C, the TiWN film wear track surface is smooth with shallow wear tracks and minor spalling, while the TiWCN film wear track is significantly widened with numerous wear particles on the surface. At 700 °C, both TiWN and TiWCN film wear tracks become noticeably deeper with severe spalling, and the stainless steel substrate becomes visible, confirming that the wear rate reaches a maximum at 700 °C (Figure 7b).

Conclusions

1. TiWCN composite films consist of an fcc-structured TiWCN phase and a hexagonal Ti N phase. With increasing C content, the hardness of TiWCN composite films first increases and then decreases, reaching a maximum value of 35.97 GPa at a C content of 11.25 at%.

2. With increasing C content, the room-temperature friction coefficient of TiWCN composite films gradually decreases, while the wear rate first decreases and then increases. At a C content of 11.25 at%, the wear rate reaches a minimum value of 1.26×10 $mm^3 \cdot N^{1} \cdot m^{1}$; at a C content of 13.68 at%, the friction coefficient reaches a minimum value of 0.32. In high-temperature friction and wear tests, when the temperature is below approximately 370 °C, the friction coefficient and wear rate of TiWCN composite films are lower than those of TiWN films; when the temperature exceeds approximately 370 °C, both values become higher than those of TiWN films. Therefore, the addition of C to TiWN films improves their room-temperature friction and wear performance, but does not enhance their high-temperature friction and wear properties.

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Note: Figure translations are in progress. See original paper for figures.