A series of TiSiN coatings were deposited on the surface of Ti(C,N) based cermets by multi-arc ion plating technique with different substrate negative bias. The microstructure, composition and mechanical properties of the coatings were studied. The results showed that the TiSiN coating showed a typical columnar growth, and composed of TiN, amorphous Si$_3$N$_4$ and a few TiSi$_2$ phases. There was an element diffusion at the interface between the substrate, transition layer and coating, which resulted in a relatively smaller compressive residual stress in the coating and relatively higher adhesion of the coating on substrate. For the coating with the substrate negative bias of $-200$ V, it had a relatively higher hardness, adhesion strength and wear resistance, and the wear mechanisms were adhesive and oxidative wear.

**Key-words:** TiSiN coating, Microstructure, Residual stress, Microhardness, Adhesion strength

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1. Introduction

Over the past decades, TiN coated cutting tools have been widely used for high speed and dry machining.$^{1,2}$ However, the relative low hardness and poor oxidation resistance at temperatures above 500°C of TiN coating limits its further application. In recent years, a third element such as Al,$^3$ Si,$^4$ Cr,$^5$ and Zr$^6$ is introduced into TiN to develop a TiN-based coating with a relatively higher hardness and thermal stability. In particular, the TiSiN coatings have attracted much attention due to their extremely high indentation hardness (40–80 GPa)$^{7-9}$ In addition, the TiSiN coatings show excellent high temperature oxidation resistance, and the oxidation resistance of TiSiN is approximately 100 times higher than that of TiN for 1 h at 600°C.$^{10}$

For the coated cutting tool, the high-speed steel and cemented carbide are usually used as the substrate.$^{11-13}$ However, there are few reports for the coating with the substrate of Ti(C,N) based cermets. On the other hand, the coefficient of thermal expansion between high speed steel ($11.9-12.9 \times 10^{-6} \, \text{K}^{-1}$),$^{14}$ cemented carbide ($5.0 \times 10^{-6} \, \text{K}^{-1}$)$^{14}$ and TiSiN coating ($8.4-9.2 \times 10^{-6} \, \text{K}^{-1}$)$^{15}$ is quite different, which may result in a high thermal stress in the coating. In contrast, the coefficient of thermal expansion of the cermets ($7.8-8.0 \times 10^{-6} \, \text{K}^{-1}$)$^{10}$ is relatively close to the TiSiN coating. In particular, only TiN B1–NaCl crystallite structure occurs in the TiSiN coatings.$^8$

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2. Experimental procedures

2.1 Coating preparation

The sintered cermets sample was used as the substrate. The nominal compositions for the cermets were TiC–10TiN–6.9WC–16Mo–32Ni–1.5C (wt%). The samples were polished to mirror and cleaned applying the standard procedure of chemical cleaning using the multi-stage washing in ultrasonic cleaner, then they were ion-etched for 10 min in the chamber to remove adsorbed gas and impurity atoms with the substrate negative bias of $-200$ V.

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and the lattice mismatch inducing coherent strains between TiN and Ti(C,N) is smaller, therefore, decreasing stress.

In this study, a series of TiSiN coatings were deposited on the surface of cermets by multi-arc ion plating technique with different substrate negative bias. The microstructure, composition and mechanical properties of the coatings were studied.

2.2 Composition and structure analysis

The phases of the coating were identified by the X-ray diffraction (XRD, D8ADVANCEX) with CuKα radiation. The elemental chemical states were investigated by X-ray photoelectron spectroscopy (XPS, VG Multilab 2000) with
Mg Kα radiation. The morphology was observed by a scanning electron microscope (Philips XL30TMP) and the distribution of the elements was determined by energy dispersive X-ray analysis (Genesis 2000). In addition, a transmission electron microscopy (TEM, TECNAI G2 20) was used to study microstructures and cross-section between the substrate and coating in more details.

2.3 Mechanical properties testing

The micro-hardness of the coatings was measured by the nano indenter G200 system with a berkovich diamond indenter under the applied load of $5 \times 10^{-3}$ N. The coating adhesion was evaluated by using the WS-2000 scratch tester with the scratch speed of 1 mm/s and loading rate of 10 N/s. To ensure statistically results more than 5 samples were measured. The wear resistance of coatings was investigated using the ball-on-disc wear tester, and the GCr15 bearing steel (62 HRC) with a diameter of 2 mm was used as the counter wear at an applied load of 2 N, sliding speed of 300 r/min and rotating diameter of 6 mm.

The residual stress of the TiSiN coating were measured by XRD (D/Max 2500) using the sin² $\psi$ method at different tilt angles $\psi$ of 0, 10, 20 and 30°. In order to get relatively accurate results, the high-angle reflection peak is desirable for the best possible $2\theta_p$ vs. sin² $\psi$ plot. In this study, the TiN (420) with diffraction angle $2\theta = 108.67^\circ$ was chosen for the precision measurements due to the detectable intensity and no overlap with other peaks, as shown in Fig. 1. In addition, a maximum $2\theta$ step size of 0.02° and a scanning range from 106 to 109° were used to obtain sufficient peak resolution.

### Table 1. Parameters of the TiSiN coating deposition process

| Parameters                        | Value                                      |
|-----------------------------------|--------------------------------------------|
| Target material                   | Ti (purity >99.99%); Si (purity >99.9%)    |
| Reaction gas                      | Ar (purity >99.99%); N₂ (purity >99.99%)   |
| Substrate temperature (°C)        | 200                                        |
| Targets current (A)               | 60                                         |
| Working pressure (Pa)             | 0.6                                        |
| Substrate negative bias (V)       | -50; -100; -150; -200; -250               |
| Deposition time (min)             | 90                                         |

Fig. 1. Part of the XRD patterns with the TiN reflections.

Fig. 2. XRD patterns of the coatings with different negative bias.

3. Results and discussion

3.1 Phase and composition

The XRD patterns of the coatings with different negative bias are shown in Fig. 2. From Fig. 2, the TiN is mainly crystallite phase in the coating, and no crystalline Si₃N₄ phase is observed, which is consistent with the previous studies.¹⁷,¹⁸

In order to determine the element chemical states, the coatings surface with the negative bias of $-200$ V was investigated by XPS. Figure 3 shows the XPS high resolution spectra of Ti 2p, Si 2p and N 1s for the coatings. As shown in Fig. 3(a), Ti 2p spectra display three groups of peaks at 454.74 and 460.58, 456.26 and 462.06, 457.92 and 463.67 eV, respectively. The two peaks at approximately 454.74 and 460.58 eV are corresponding to TiN,⁹ while the peaks at 456.26 and 462.06 eV are assigned to N—O—Ti,¹⁷ and the peaks corresponding to 457.92 and 463.67 eV can be ascribed to TiO₂.¹⁸ The existence of N—O—Ti and TiO₂ may be attributed to the oxidation of titanium element in the ambient atmosphere. In the Si 2p spectra [Fig. 3(b)], the signal at approximately 98.69 eV is ascribed to TiSi₂. In particular, there is one peak at 102.87 eV, associating with Si₃N₄.⁹ According to XRD results, the crystalline Si₃N₄ phase cannot be found, which indicates that it exists as an amorphous phase.¹⁷ It should be noted that there is nearly 1 eV shift to higher energy for the binding energy of Si₃N₄. This may be relevant to the oxidation of silicon. Figure 3(c) shows the N 1s spectra, where the peaks at 395.71, 396.95 and 397.99 eV, which further indicates the existence of N—O—Ti, TiN and Si₃N₄ in the coatings.

3.2 Residual stress

The residual stress in thin hard coatings has great influence on its microhardness, adhesive strength and wear-resistance. In this study, the residual stress of the coating was measured by XRD using the sin² $\psi$ method, which can be calculated by the following:

$$\sigma = K \cdot M$$  \hspace{1cm} (1)
\[ K = -\frac{5E}{1 + \nu} \cdot \text{ctg} \theta_0 \cdot \frac{\pi}{180} \text{ (N/mm}^2\text{)} \]  \hspace{1cm} (2) \\
\[ M = \frac{\partial^2 \theta_\psi}{\partial \sin^2 \psi} \text{ (}) \hspace{1cm} (3) \\

Where \( E \) and \( \nu \) is the Young’s modulus and Poisson ratio of the coating; \( \theta_0 \) is the diffraction angle without stress; \( \psi \) is tilt angle (the angle between the lattice plane and the free surface); \( \theta_\psi \) is the measured diffraction angle corresponding to the tilt angles \( \psi \); \( K \) is the stress constant; \( M \) is the slope of the straight line obtained by plotting \( 2\theta_\psi \) vs. \( \sin^2 \psi \).

Figure 4 shows the value of residual stress (\( \sigma \)) for the coating with different negative bias. It can be seen that all the coatings exhibit compressive residual stress, and the residual stress varied from \(-189 \) to \(-533 \) MPa, which is one order of magnitude lower than available experimental results reported in the references\(^{7),8),20}\). In general, the stresses can generally be classified into two types in the coating prepared by physical vapor deposition: thermal stress \((\sigma_T)\) and intrinsic stress \((\sigma_I)\), and the residual stress \((\sigma)\) of the coating can be expressed as: \( \sigma = \sigma_T + \sigma_I \).\(^{21}\) The thermal stress \((\sigma_T)\) is an extrinsic stress resulted from the difference in coefficient of thermal expansion between the coating and the substrate. For the TiSiN coating on the cermets substrate, the effect of thermal stress on the residual stress is relatively small, assuming that the coefficient of thermal expansion of the coating and substrate is equal to \(8.4-9.2 \times 10^{-6} \) and \(7.8-8.0 \times 10^{-6} \text{ K}^{-1} \), respectively. So, the value of residual stress is mainly decided by intrinsic stress. On the other hand, the intrinsic stress is caused when the lattice spacing of the coating is distorted by the energetic ionic bombardment during deposition.\(^{22}\)

In this study, a TiN transition layer is deposited firstly on the substrate before the coating deposition process, and the differences in lattice parameters TiN and Ti(C,N) is relatively smaller. Due to the partially similar nature of coating, transition layer and substrate, the lattice mismatch inducing strains is smaller, therefore, decreasing stress.

### 3.3 Microhardness and adhesion strength

The microhardness of the coating with different negative bias is shown in Fig. 5. The microhardness firstly increases and reaches a relatively higher value of about \(32.5 \) GPa with the negative bias of \(-200 \) V. At a higher negative bias, the microhardness slightly decreases. It
should be noted that the measured microhardness is basically consistent with the previous studies. However, the microhardness is obtained in the coating with a much smaller compressive residual stress in the present study. As reported in the literature, the residual stress appears to strongly affect coating hardness, and the compressive stress tends to increase the hardness.

Figure 6 shows the adhesion strength of the coating on substrate with different negative bias. It can be seen that a relatively higher adhesion strength of about 54 N is obtained with the negative bias of $-200 \text{ V}$, which is much higher than the value in the literature. The significantly better adhesion of the coating on substrate may be partially attributed to the smaller residual stress.

In order to further elucidate mechanical properties of the coating with the negative bias of $-200 \text{ V}$, the microstructure observations were carried out. Figure 7 shows cross-section images of the coatings. It can be seen that the coating is relatively dense and no crack and spalling occur at the interface between the coating and substrate. During deposition, an increase of negative bias enhances the sputtering effect of the deposited coating, which is beneficial to obtain a relatively dense coating and increase the adhesion of the coating on substrate. However, the further increase of negative bias will lead to the occurrence of resputtering.

Figure 8 shows TEM and high-resolution TEM images of the coatings. From the Fig. 8(a), the coating exhibits columnar grain structure with the columnar width 30–50 nm. From the Fig. 8(b), the nanosized grains embed in an amorphous matrix. According to the results of XRD and XPS, the nanosized grains and amorphous matrix are TiN and Si$_3$N$_4$, respectively. That the fine TiN grains dispersed in amorphous Si$_3$N$_4$ provides a higher resistance to plastic deformation and results in an increase of hardness. The cross-section between the substrate and coating is shown in Fig. 9. There is an obvious TiN transition layer between the coating and the substrate, and the thickness of TiN transition layer is about 200 nm. The interface between 1, 2 and 3 is not obvious, indicating that element diffusion occurs at the interface. In the case of depositing the coatings on the cermets, the nitrogen and titanium of interface between the substrate and coating may not only come from the working gas and target, but also from the substrate due to bombardment of energetic ions. The simultaneous mutual diffusion of elements between the substrate and coating decreases the residual stress and increases adhesion of the coating on substrate.

3.4 Wear behavior

Figure 10 shows two typical wear surface morphology of the coating for the negative bias of $-50$ and $-200 \text{ V}$ with a sliding wear test time of 120 min. A continuous/discontinuous debris layer smearing onto wear tracks is the basic wear feature for the coatings. The energy dispersive X-ray spectrometry analysis for the wear debris reveals the presence of Ti, Si, Fe and O. The results indicate that the mass transfer occurs from the soft counter steel, and the debris are further oxidized during the wear test. On the other hand, a great difference in damage degree for the coating is observed. In the case of the coating with the negative bias of $-50 \text{ V}$, there is an obvious coating spalling [marked by the arrows in Fig. 10(a)], which may be
attributed to a small adhesion of the coating on substrate. In contrast, no visible damage is observed for the coating with the negative bias of $-200 \text{ V}$, and it appears in a slight wear with a continuous thin debris layer.

Figure 11 shows the corresponding curves of coefficient of friction for the coating. Two curves exhibit a similar pattern, which is characterized by the initial transient state and follows by a relatively steady state. However, the coefficient of friction for the coating with negative bias of $-200 \text{ V}$ is relatively smaller than that of the coating with the negative bias of $-50 \text{ V}$. In particular, the coating with negative bias of $-200 \text{ V}$ presents a slightly descended tendency with an increase of sliding time, which may be attributed to the self-lubricating layer on the worn surface. In general, Si$_3$N$_4$ reacts with H$_2$O to produce SiO$_2$ or...

Fig. 8. TEM and high-resolution TEM images of the coatings: (a) the coating; (b) TiN particles and amorphous matrix.

Fig. 9. TEM image of cross-section between the substrate and coating: 1 substrate; 2 transition layers; 3 coating.

Fig. 10. Wear surface morphology of the coating with different negative bias: (a) $-50 \text{ V}$; (b) $-200 \text{ V}$. 
Si(OH)$_2$ tribo-layers as self-lubricating layer. More fluctuations and slight increase of the coefficient of friction of the coating with negative bias of $-50$ V are observed after the sliding time is over 100 min.

4. Conclusion

1) TiSiN coating was composed of TiN, amorphous Si$_3$N$_4$ and a few TiSi$_2$ phases. The coating showed a typical columnar growth, and the fine TiN grains were dispersed in amorphous Si$_3$N$_4$.

2) The TiSiN coating deposited on the cermets showed a much smaller compressive residual stress. In addition, no obvious decrease of microhardness occurred in the coating with a small compressive residual stress.

3) The relatively smaller lattice mismatch and simultaneous mutual diffusion of elements between the substrate and coating resulted in a relatively higher adhesion of the coating on substrate.

4) The wear mechanisms were adhesive and oxidative wear when the GCr15 bearing steel was used as the counter wear.

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