Effect of Si Content on Structure and Friction and Wear Properties of CrSiN Coatings

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Abstract. CrN coatings with different Si contents were prepared on YG6 substrates by DC magnetron sputtering. The phase composition, morphology and element composition of the coatings were analyzed by X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy dispersive spectrometer (EDS). The hardness and adhesion of the coatings were measured by digital microhardness tester and scratch tester. The tribological properties were investigated by a friction and wear tester. The results show that all CrSiN coatings present (111), (200) oriented NaCl structure. With the increasing of Si content, the compactness of the coating increases. When Si content is low, the structure of CrSiN/YG6 coating is relatively loose and triangular granular growth. When Si content is high, the structure of CrSiN/YG6 coating is compact and circular growth. Doping Si element in CrN coating changes the crystalline structure of the coating, and four kinds of CrSiN coating are harder than CrN coating. The hardness of CrSiN/YG6 coatings increases first and then decreases with the increase of Si content. When Si atom fraction is 14.1%, the hardness of the coatings reaches the maximum value of 23.4 GPa. With the increase of Si content, the bonding force between the coatings and the matrix decreases at first. The friction coefficient of CrSiN coatings increases with the increase of Si atom fraction, but the wear rate decreases first and then it increase. When the atomic fraction of Si is 14.1%, the minimum wear rate is 0.602*10^{-8} mm^3*(N.mm)^{-1}. Adding appropriate amount of Si element can improve the hardness and wear resistance of CrSiN coating, and has a certain lubrication effect.

1. Introduction
Cemented carbide tools are widely used in the field of cutting. Their application has obviously improved the cutting speed, cutting efficiency and cutting quality. They are especially suitable for the cutting of metal materials with high hardness and good plasticity. However, cemented carbide tools have high brittleness, low impact resistance and poor vibration resistance [1]. With the development of metal cutting technology, especially high speed cutting, high efficiency cutting and dry cutting, metal cutting need higher technical requirements, such as: it should has the characteristics of high temperature resistance, oxidation resistance, self-lubrication and wear resistance [2]. As an important way to improve the comprehensive performance of cutting tools, the important significance of tool coating treatment is to combine the characteristics of tool matrix and hard coating, which not only
makes tool matrix maintain good toughness, but also possesses the characteristics of high hardness and wear resistance of hard coating [3].

The results show that the CrN coating has low density, high melting point, good wear resistance and corrosion resistance, and good high temperature oxidation resistance. It is widely used in the surface strengthening treatment of cutting tools and mould [4-5]. However, the rapid development of engineering technology has put forward higher and higher requirements for the quality of CrN thin films. Therefore, it is necessary to further improve the properties of CrN thin films through compounding and nanocrystallization. Doping other elements can improve the comprehensive properties of the coating, for example, ternary CrSiN hard coating has higher hardness and wear resistance, and high temperature oxidation resistance and corrosion resistance are better [6-10]. CrSiN is formed by Si, Cr and N. SiCrN has good wear resistance and lubrication effect. Si reacts with N to form Si₃N₄, which coats the coating surface. Comparing with single CrN coating, multi-layer and multi-layer coating has improved the comprehensive performance greatly, prolonged the service life of cutting tools and improved the processing quality [11-15]. Researches by Martinez [16] et al. showed that the hardness of CrSiN coating reached the maximum of 22Gpa, when the atomic number of Si was 3%. Benlatreche [17] et al. studied the mechanical properties of CrSiN coating. When the atomic number fraction of Si was 2.3%, the hardness of the coating was 24.4 Pa.

In this paper, CrSiN coatings were prepared by magnetron sputtering. By changing the power of Si target, CrSiN coatings with different Si content were prepared. The effects of different Si content on the properties of CrSiN coatings were analyzed. For this reason, CrSiN/YG6 coatings were prepared by DC magnetron sputtering. The effects of different Si content on the microstructure, mechanical properties and properties of the coatings were studied. The influence of tribological properties is discussed.

2. test

JGP-450 magnetron sputtering coating equipment is used in the experiment. Its cylindrical vacuum chamber size is 450 *360mm. There are three uniformly distributed permanent magnet targets on the inner wall of the chamber. Each permanent magnet target is placed with one target. In the experiment, pure metal Cr, Si (99.99% purity, Zhongnuo new material) was used as target material. The size of target material was 60*3 mm, argon (Ar, 99.99% purity, Yao Tian instrument) was used as protective gas, nitrogen (N₂, 99.99% purity, Yao Tian instrument) was used as working gas. Argon and nitrogen mixed gas was injected into sputtering at the same time. The target-base distance is 100mm, the matrix material used is YG6 (Jinan Xinyu Cemented Carbide Company), and the size is 10*10*3 mm.

2.1. Sedimentary Process

The tool base is polished by sandpaper and cleaned by acetone for 20 minutes; when the target and base are placed in the vacuum chamber and the vacuum is 2.1*10⁻³ pa, argon is added to make the indoor working pressure reach 0.4pa, negative bias is added to 400v, and the cleaning time of the target is 25min; the target of Cr and Si is opened and nitrogen is injected at the same time. Preparation of different coatings by adjusting the power of Si target. Coatings with different Si content were prepared by target power for 180 minutes. The substrate temperature, bias, rotation speed, gas flow rate and working pressure of the coatings were kept constant. The samples were cooled and removed by vacuum. The specific sedimentary parameters are shown in Table 1.
### Table 1. Deposition parameters of CrSiN coatings

| Serial number | Si power P/W | Cr power P/W | nitrogen flow/sccm | argon flow/sccm | matrix temperature/°C | Bias U/V | working pressure P/ Pa |
|---------------|--------------|--------------|--------------------|----------------|------------------------|---------|-----------------------|
| 1             | 20           | 100          | 20                 | 30             | 200                    | -50     | 0.4                   |
| 2             | 40           | 100          | 20                 | 30             | 200                    | -50     | 0.4                   |
| 3             | 60           | 100          | 20                 | 30             | 200                    | -50     | 0.4                   |
| 4             | 80           | 100          | 20                 | 30             | 200                    | -50     | 0.4                   |

#### 2.2. Structural Characterization and Performance Testing

Phase analysis of the as coating was carried out with D8 advanced polycrystalline X-ray diffractometer (CuKa), acceleration voltage 40kV, current was 40mA and scanning range (2θ - 90 degrees). Surface morphology of the film was observed by QUANTA FEG 250 field emission scanning electron microscope (FEG 250). Bonding strength of the coating was measured by MFT-4000 scratch tester. The coating hardness was measured by HXD-1000 TMSC digital microhardness tester, and six effective values were measured from each sample to get average. The friction and wear tests were carried out by RTEC MFT-50. GCr15 bearing steel balls with diameter of 6.35mm were selected as friction couples and sliding was measured by sensors in real time. The frictional coefficient of the coatings was measured by white light interferometer to calculate the volume wear. Calculation of wear rate from classical wear equation is: \( \omega = \frac{V}{S \cdot L} \), in formula: \( V \) is wear volume, mm³; \( S \) is total sliding distance, mm; \( L \) is vertical loading force, N.

#### 3. Test results and discussion

The chemical composition of CrSiN coatings prepared at different Si target power is shown in Table 2. With the increase of target power, the content of Si atom in the coating increases.

### Table 2. Chemical Compositions of CrSiN Coatings with Different Si Contents

| Ar: N2(sccm) | Cr(at.%) | Si(at.%) | N(at.%) |
|--------------|----------|----------|---------|
| 30:20        | 47.7     | 9.6      | 42.7    |
| 30:20        | 44.3     | 14.1     | 41.6    |
| 30:20        | 42.7     | 20.1     | 37.2    |
| 30:20        | 40.8     | 24       | 35.2    |

#### 3.1. Microstructure of Coatings

![Figure 1. XRD Spectrum of CrSiN Coatings with Different Si Contents](image)
Fig. 1 shows the XRD spectra of CrSiN coatings prepared at different Si target power. It can be seen from the graphs that the four coatings mainly consist of metal phases Cr, Cr$_2$N, CrN, Si$_3$N$_4$, and CrSi$_2$. The (111) and (200) diffraction peaks of CrN appear in the coatings, which indicates that the coatings have good crystallinity and present face-centered cubic structure. With the increase of Si element, the diffraction peak broadens obviously. The diffraction peaks of Si-containing compounds such as CrSi$_2$ and Si$_3$N$_4$ do not appear, which indicates that the two substances may exist in amorphous form in the coating.

Figure 2 shows the SEM morphology of CrSiN coatings prepared at different Si contents. As can be seen from the figure, when the content of Si is relatively low, the coating particles are uniform in size, dispersed and triangular in growth; with the increase of the content of Si, the coating particles become larger, the voids become smaller, and the growth is circular. Film-forming particles have poor diffusion ability on YG6 matrix surface. Film-forming particles are easier to combine with their own particles, which reduces their own energy and does not have enough energy to diffuse to the matrix surface. With the increase of Si content, the number of Si particles bombarding the matrix increases, and the diffusion ability of film-forming particles increases.

![Figure 2. Surface Morphology of CrSiN Coatings under Different Si Conditions](image)

3.2. Mechanical Properties of Coatings

The scratch test instrument was used to measure the bonding force of the coating. The scratch test parameters as follow scratch length 7mm, termination load 100N, loading speed 100N/min and indenter diamond. The bonding force and hardness of the CrSiN coating with different Si content were measured as shown in Figure 3. It can be seen from the figure that the bonding force of the coating decreases with the increase of Si content. With the increase of Si content, the main phase of the coating is CrN, Si$_3$N$_4$, CrSi$_2$, Cr$_2$N. The lattice distortion caused by the introduction of Si generates internal stress. Therefore, the binding force of the coating decreases, and increases with the increase of Si content. The main phase of the coating is Si$_3$N$_4$ and CrSi$_2$, and the adhesion of the coating is poor.
Fig. 3 shows the microhardness of CrSiN coatings prepared at different Si content ratios. It can be seen from Fig. 3 that there is a corresponding relationship between the micro-hardness and Si content of the coating: with the increase of Si content, the micro-hardness of the coating increases first and then decreases. When the content of Si is relatively low, the thickness of amorphous layer at this time can effectively prevent the internal dislocation of nanocrystalline grains and avoid crystal slip, thus enhancing the hardness of nanocrystalline grains. With the increase of Si content, the hardness of the coating decreases, which is due to the increase of amorphous phase.

![Figure 3. Hardness and Binding Force of CrSiN Coatings with Different Si Contents](image)

**Figure 3.** Hardness and Binding Force of CrSiN Coatings with Different Si Contents

### 3.3. Mechanical Properties of Coatings

Fig. 4 shows the curve of friction coefficient changing with time under constant loading force 5N, sliding distance 4.5mm and sliding frequency 2Hz. It can be seen from the figure that the trend of friction coefficient of four coatings with different Si content is not very different, and the friction coefficient increases with the increase of Si content. The four coatings all reach stable friction state in a very short time (about 50s).

![Figure 4. The variation curve of friction coefficient under different Si content](image)

**Figure 4.** The variation curve of friction coefficient under different Si content

Fig. 5 shows the wear rate of CrSiN with different Si content. The wear volume was calculated according to the two-dimensional morphology, and the wear rate was calculated from the wear volume,
sliding distance and loading force. It can be seen from the figure that with the increase of Si content, the wear rate decreases first and then increases. When the Si atom fraction is 14.1%, the wear rate is the lowest, because the falling off and wearing of the coatings were less at this time. The wear rates of the four coatings are $1.838 \times 10^{-8}$ mm³*(N.mm)⁻¹, $0.602 \times 10^{-8}$ mm³*(N.mm)⁻¹, $1.701 \times 10^{-8}$ mm³*(N.mm)⁻¹ and $2.914 \times 10^{-8}$ mm³*(N.mm)⁻¹.

**Figure 5.** The wear rate of CrSiN coatings with different Si content

4. **Conclusion**

(1) With the increase of Si content, the particles in the coating structure change from triangle to circle, and the distribution tends to be uniform, and the density of the coating increases.

(2) With the increase of Si content, the bonding strength of the coatings decreases, while the hardness of the coatings increases first and then decreases (the maximum value is 23.4GPa when the Si atom fraction is 14.1%).

(3) With the increase of Si content, the friction coefficient of the coating does not change much, but with the increase of Si content, the wear rate first decreases and then increases (when the Si atomic fraction is 14.1%, the minimum is $0.602 \times 10^{-8}$ mm³*(N.mm)⁻¹).

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**References**

[1] T.V.Sreerama Reddy et al. Machining performance of low temperature treated P-30 tungstencarbide cutting-tool inserts [J], Cryogenics, 2008, (48) 458-461.

[2] Anil Mital, Arunkumar Pennathur. Advanced technologies and humans in manufacturing workplaces: an interdependent relationship [J]. International Journal of Industrial Ergonomics, 2004, 4 (33): 295-313.

[3] Bouzakis K D, Michailidiss N, Skordaris G, et al. Cutting with coated tools: coating technologies, characterisation methods and performance optimization [J]. CIRP Annals-Manufacturing Technology, 2012, 61 (2): 703-723.

[4] Zhang U A, Yan P X, Wang P, et al. Influence of nitrogen content on the structural, electrical and mechanical properties of CrN, thin films [J]. Materials Science and Engineering: A, 2007, 4
60-461: 301-30.

[5] Thobor-Keck A, Lapostolle F, Dehlinger A S, et al. Influence of silicon addition on the oxidation resistance of CrN coatings [J]. Surface & Coatings Technology, 2005, 200 (1/2/3/4): 264-268.

[6] WO P C, MUNROE P R, LI Z, et al. Factors Governing the Mechanical Behaviour of CrSiN Coatings: Combined Nanoindentation Testing and Transmission Electron Microscopy [J]. Materials Science and Engineering A-Structural Materials Properties Microstructure and Processing, 2012, 534: 297-308.

[7] ZHANG G G, WANG L P, WANG S C et al. Structure and Mechanical Properties of Reactive Sputtering CrSiN Films [J]. Applied Surface Science, 2009, 255 (8): 4425-4429.

[8] BARSILIA H C, DEEPTHI B, RAJAM K S. Deposition and Characterization of CrN/Si3N4 and CrAlN/Si3N4 Nanocomposite Coatings Prepared using Reactive DC Unbalanced Magnetron Sputtering [J]. Surface & Coatings Technology, 2007, 201 (24): 9468-9475.

[9] WANG Q M, PARK I W, KIM K. Influence of N2 Gas Pressure and Negative Bias Voltage on the Microstructure and Properties of Cr-Si-N Films by a Hybrid Coating System [J]. Journal of Vacuum Science & Technology A, 2008, 26 (5): 1188-1194.

[10] WANG Q M and KIM K H. Microstructural Control of Cr-Si-N Films by a Hybrid Arc Ion Plating and Magnetron Sputtering Process [J]. Acta Materialica, 2009, 57 (17): 4974-4987.

[11] Azzi M, Benkahoul M, Szpunar J A, et al. Tribological properties of CrSiN coated 301 stainless steel under wet and dry conditions, Wear, 2009, 267 (5/6/7/8): 882-889.

[12] Park J H, Chung W S, Cho Y R, et al. Synthesis and mechanical properties of Cr-Si-N coatings deposited by a hybrid system of arc ion plating and sputtering techniques [J]. Surface Coatings Technology, 2004, 188-189: 425-430.

[13] Lee H Y, Jung W S, Han J U, et al. The synthesis of CrSiN film deposited using magnetron sputtering system [J]. Surface & Coatings Technology, 2005, 200 (1/2/3/4): 1026-30.

[14] Veprek S, Mannling H D, Jilek M, et al. Avoiding the hightemperature decomposition and softening of (Al1-xTi)xN coatings by the formation of stable superhard (Al1-xTi)xN/a-Si3N4 nanocomposite [J]. Materials Science and Engineering A, 2004, 366: 202-205.

[15] Veprek S, Argon A S. Mechanical properties of superhard nanocomposites [J]. Surface and Coatings Technology, 2001, 146-147: 175-182.

[16] MARTINEZ E, SANJINES R, BANAKH O, et al. Electrical, Optical and Mechanical Properties of Sputtered CrNy and Cr1-xSi0.5N1.02 Thin Films [J]. Thin Solid Films, 2004, 447: 332-336.

[17] MUSIL J, JIROUT M. Toughness of Hard Nanostructured Ceramic Thin Films [J]. Surface & Coatings Technology, 2007, 201 (9-11): 5148-5152.