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ARTICLE

# Effects of Substrate Temperature on Microstructure and Tribological Properties of Ti-Al-Si-Cu-N Films Deposited by Magnetron Sputtering

**Feng Changjie, Chen En**

*Nanchang Hangkong University, Nanchang 330063, China*

**Abstract:** Ti-Al-Si-Cu-N films were deposited on the AISI-304 stainless steel by reactive magnetron sputtering technology. The influences of the substrate temperature (deposition temperature) on the microstructure and properties of the films were researched by scanning electron microscope (SEM), energy disperse spectroscopy (EDS), X-ray diffraction (XRD), a nano-indenter, a scratch tester and a ball-on-disc rotational tribometer. The results indicate that when the deposition temperature increases from room temperature to 250 °C, the films become smoother and denser. The hardness and elastic modulus increase with the increase of the deposition temperature. The scratch tests show that when the deposition temperature is RT, 150 and 250 °C, the critical load of the films is 3.85, 3.45 and 5.10 N, respectively. The friction coefficient and wear rate of the Ti-Al-Si-Cu-N film deposited at 250 °C are the smallest, and the wear debris is mainly from the counterparts GCr15 stainless steel balls, The wear mechanism of the films deposited at lower temperatures is mainly fatigue fracture and abrasive wear, while that of the film deposited at 250 °C is abrasive wear.

**Key words:** reactive magnetron sputtering; Ti-Al-Si-Cu-N films; deposition temperature; wear mechanism

Nano-composite or nano-multilayer hard films were widely used in the area of high-speed cutting to improve the productive efficiency and reduce the cost of production[1-3]. The preparation methods of these hard films are diversified, such as chemical vapor deposition (CVD) and physical vapor deposition (PVD). PVD was used for the deposition of thin films due to its pollution-free and lower deposition temperatures[4], such as magnetron sputtering technique[5].

TiN films[6,7] are widely used in cutters, moulds and wear-resistant parts due to their high hardness and good abrasion resistance. However, TiN could be oxidized rapidly in air at temperatures above 550 ℃[8], which limited its application. Many researchers have taken great efforts to improve the properties of the TiN films. Addition of different elements[9,10] could improve the properties of the films. The hardness and oxidation resistance of the TiN films were enhanced by adding Al element[11]. In addition, TiN based nitride films, such as Ti-Al-Cr-N[12], Ti-Al-Si-N[13], Ti-Al-Y-N[14] and Ti-C-N[15], were investigated widely. Studies showed that the Ti-Al-Si-N films owned improved wear resistance[16] and higher hardness[17] compared to Ti-Al-N films.

However, the shortcomings of Ti-Al-Si-N films, such as high friction coefficient and high brittleness, are big challenges to overcome. Copper is soft metal and it is difficult to react with nitrogen. Amorphous copper might be observed in grain boundary, and many researchers considered the addition of copper might not only increase of toughness and hardness, but reduce friction coefficient owing to its lubrication[18,19]. Further, the adhesive strength of the Ti-Al-Si-N films with incorporation of Cu element could be greatly improved[20]. Therefore, the Ti-Al-Cu-Si-N films attract a lot of attention worldwide in recent years due to their good properties.

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Corresponding author: Feng Changjie, Ph. D., Professor, School of Materials Science and Engineering, Nanchang Hangkong University, Nanchang 330063, P. R. China, Tel: 0086-791-83863026, E-mail: chjfengniat@126.com

Deposition temperature is one of the important factors that affect the properties of the films. Many researchers[21-23] have studied the influence of deposition temperature on the microstructure and mechanical properties of the films. But there is not any study regarding the influence of deposition temperature on the properties of Ti-Al-Si-Cu-N films. In the present study, the influence of different substrate temperatures on the microstructure, mechanical and tribological properties of the Ti-Al-Si-Cu-N films was investigated.

## 1 Experiment

Ti-Al-Si-Cu-N films were deposited on AISI 304 stainless steel sheets (30 mm×20 mm×2 mm) by DC reactive magnetron sputtering. A $Ti_{0.5}Al_{0.4}Si_{0.1}$ (99.99%) target and a Cu (99.99%) target with a diameter of 100 mm were used as the sputtering targets. In the vacuum chamber, the substrates were hung in the holder with rotational speed 20 r/min during the deposition. The distances between the substrates and $Ti_{0.5}Al_{0.4}Si_{0.1}$ alloy target, Cu target were controlled at about 3 cm and 13 cm, respectively. Prior to deposition, the stainless steel substrates were ground by 400#, 800#, 1000# and 2000# abrasive papers in turn, polished and ultrasonically cleaned in absolute ethyl alcohol. Sputtering process parameters were as follows: base pressure $2\times10^{-2}$ Pa, partial pressure ratio($N_2$/Ar)=1:1 (gases with 99.99% purity), working pressure: 0.6 Pa, working time 200 min. The power of $Ti_{0.5}Al_{0.4}Si_{0.1}$ target was controlled at 500 W and that of Cu target was 11.25 W. The deposition temperature was set at RT, 150 ℃ and 250 ℃.

The surface morphologies and composition of the films were analyzed by SEM (quanta 200) equipped with energy disperse spectroscopy and FESEM (Nova Nano SEM 450). The phase of the films was studied by X-ray diffraction (XPERT-PRO-MRD). The scanning angle was ranged from 15° to 85° using CuKα radiation.

The microhardness of the films was determined by nanoindentation under the maximum load of 150 mN. The adhesion properties of the films were measured by a WS-2005 automatic scratching tester equipped with diamond scriber, and the top of diamond scriber was a half ball with a radius of 200 um. The parameters of scratching test were as follows: scratch speed 0.06 mm/s, final load 40 N, the total scratch length 4 mm. The tribological performance of the films was tested by a ball-on-disc rotational tribometer at room temperature and a relative humidity of 50%~60% under dry sliding conditions. Stainless steel balls (GCr15) with a diameter of 6 mm were used as the counterparts. All the sliding tests were conducted for 20 min at a load of 2.6 N and at the rotation speed of 336 r/min with sliding radius 3 mm. The wear volume was calculated using the equation: $V=S\times L$, where $S$ is the cross-section area of the wear track, which was determined by profilometry using optical microscopy (KH-7700), and $L$ is the rotation circumference.

## 2 Results and Discussion

### 2.1 Microstructure and composition of the films

The surface and cross-sectional morphologies of the Ti-Al-Si-Cu-N films deposited at various substrate temperatures are shown in Fig.1. The films deposited at temperatures of RT and 150 ℃ (shown in Fig.1a, 1d and Fig.1b, 1e) exhibit a rough surface with many micropores and obvious columnar grains. The microstructure becomes more compact and the columnar grains size become smaller when the deposition temperature increases to 250 ℃, as shown in Fig.1c, 1f. The results show that the microstructure of the films becomes more homogeneous as the deposition

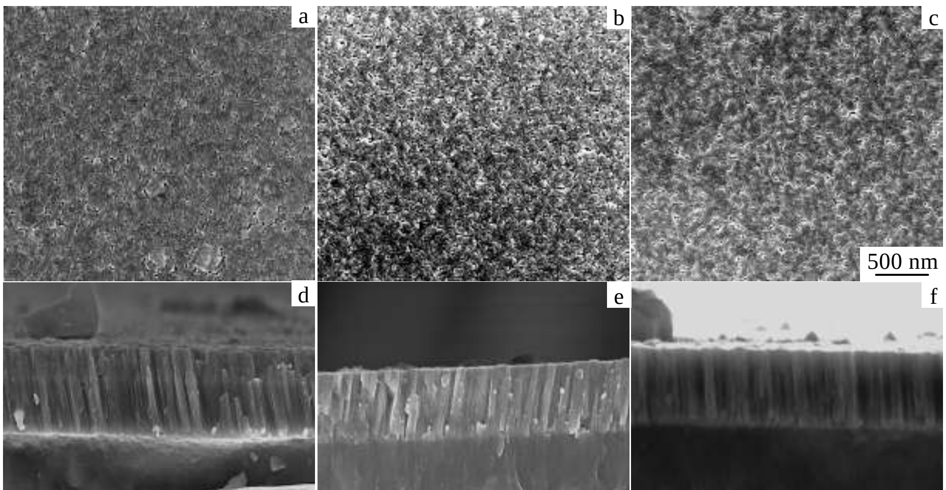


Fig.1 SEM micrographs of surface (a~c) and cross-section (d~f) of the Ti-Al-Si-Cu-N films at different deposition temperatures: (a, d) RT; (b, e) 150 °C; (c, f) 250 °C

temperature increases, which is the same with the result of Hasegawa et al.[23] The microstructures of the films are similar to Zone One of temperature ratio $T_a/T_m$ ($T_a$: substrate temperature, $T_m$: melting point of films) structure model put forward by Thornton[24]. The reason may be that the activation energy and surface diffusion of the sputtered atoms increase with the increasing of substrate temperatures. The insufficient nucleation, coarse microstructure and micropores could be due to short preliminary bombardment and lower atomic diffusion energy at lower temperatures[25]. However, the mobility rate of adsorbed atoms on the substrate surface is enhanced with the increasing of deposition temperatures. Therefore, the higher temperature is beneficial to the formation of films with dense and uniform columnar structure.

The chemical composition of the Ti-Al-Si-Cu-N films deposited at different temperatures is shown in Table 1. The atomic percent of N element in films deposited at RT is less than that of the films deposited at 150 ℃ and 250 ℃. The content of sputtered atoms, such as Ti, has remained little changing at different deposition temperatures. The detected oxygen element could be due to the $O_2$ release from the vacuum chamber walls during deposition at RT. However, the adsorbed air in the vacuum chamber's walls could be released in the process of heating prior sputtering and is pumped outside the chamber at higher deposition temperatures.

Fig.2 shows XRD patterns of the Ti-Al-Si-Cu-N films deposited at different temperatures. It can be seen that films deposited at RT exhibit the TiN(111) and TiN(220) weak peaks. With deposition temperature increasing, the TiN(111), TiN(220) peaks disappear, and the film deposited at 250 ℃ exhibits obvious nitrides(110) preferred orientation, which confirms the good crystallinity due to the higher atomic diffusion energy at higher substrate temperature. The nitrides(110) peaks maybe result from the formation of the Ti-Al-Si-N solid solution. T. Vasco Boutos[25] had studied the effects of deposition temperature and bilayer thickness on the mechanical properties of AlN/TiN multilayer films and found that the intensity of TiN(111) peak increased when the deposition temperature rised from room temperature to 800 ℃.

## 2.2 Mechanical and tribological properties of the films

**Table 1 Composition of the Ti-Al-Si-Cu-N films analyzed by EDS (at%)**

| Temperature/ °C | Ti | Al | Si | Cu | N | O |
|---|---|---|---|---|---|---|
| RT | 28.59 | 21.76 | 2.93 | 2.73 | 30.09 | 13.89 |
| 150 | 29.85 | 22.03 | 3.43 | 3.69 | 41.00 | 0 |
| 250 | 28.96 | 22.78 | 3.48 | 3.66 | 41.12 | 0 |

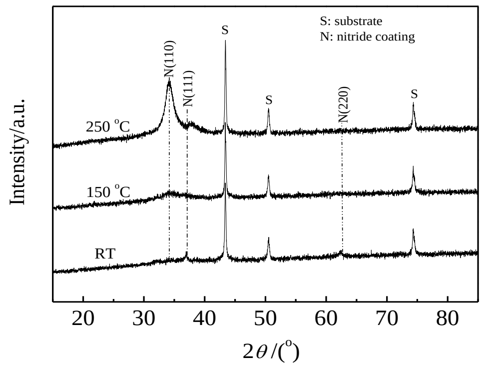


Fig.2 XRD patterns of Ti-Al-Si-Cu-N films

The values of microhardness and elastic modulus of Ti-Al-Si-Cu-N films deposited at different temperatures are shown in Fig.3. It can be seen that there is only minor increase in coating hardness from 14.4 GPa to 15.3 GPa and more significant increase in the elastic modulus from 180.7 GPa to 293.4 GPa. Compared with the films deposited at 150 ℃ and 250 ℃, the microhardness of films deposited at room temperature is lower due to its porous structure and bad density, as shown in Fig.1a. The more compact Ti-Al-Si-Cu-N films at higher deposition temperature lead to the improvement of elastic modulus. Combadiere et al.[22] had studied the influence of substrate temperature on the mechanical properties of the TiN films and found two types of evolution of the microhardness of films with the increasing of substrate temperature. Firstly, the microhardness increased with the increasing of temperatures, and then it seemed to stabilize around a value. Secondly, the hardness increased when the temperature increased in a certain temperature range. However, when the temperature exceeded 270 ℃, the hardness of films decreased quickly. The diffusion rate of adatoms, the integrating probabilities of Ti and N atoms and integrity of lattice increased with increasing substrate temperature.

The adhesion properties between the substrate and Ti-Al-Si-Cu-N films were evaluated by scratch tester. The critical loads of coatings deposited at RT, 150 ℃ and 250 ℃ was 3.85 , 3.45 and 5.10 N, respectively. Fig.4 shows the corresponding scratch morphologies of the Ti-Al-Si-Cu-N films. It can be seen that the scratch morphology of the film deposited at substrate temperature 250 ℃ has inconspicuous peelings, which may be due to that the higher substrate temperature accelerates the diffusion effect between thin films and substrate. On the other hand, the less peelings may be attributed to the highest elastic modulus of the film deposited at 250 ℃. However, the peeled films deposited at 150 ℃ are severer than that of RT in the scratch morphologies. The reason might be that the increasing temperature

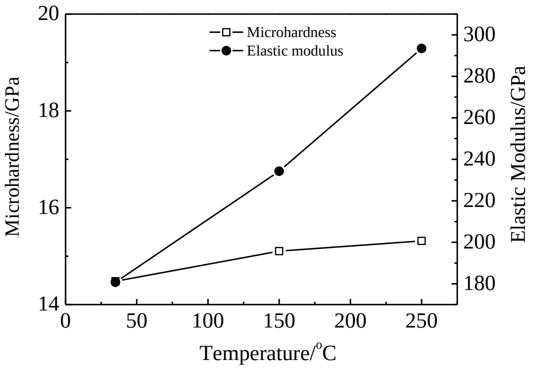


Fig.3 Microhardness and elastic modulus of Ti-Al-Si-Cu-N films deposited at different temperatures

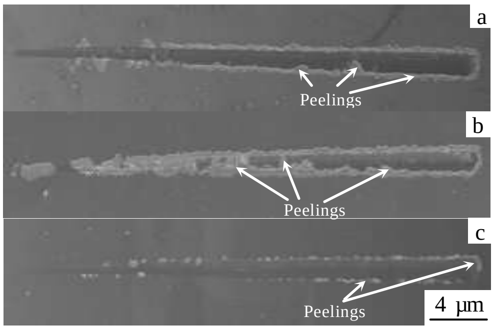


Fig.4 Scratch tracks of Ti-Al-Si-Cu-N films deposited at different temperatures: (a) RT, (b) 150 °C, and (c) 250 °C

increases the residual stress. Adhesion of the coating to the substrate increases with the residual stress decreasing[26].

Fig.5 shows the variation of the friction coefficient with sliding time of the Ti-Al-Si-Cu-N films deposited at different temperatures. The average value of friction coefficient of the films deposited at RT, 150 ℃ and 250 ℃ is 0.90, 0.92 and 0.74, respectively. The friction coefficient values of films deposited at RT and 150 ℃ is bigger, which is mostly due to the more micropores and larger size of columnar grains, as shown in Fig.1a and Fig.1b. The film deposited at substrate temperature 250 ℃ exhibits the lowest friction coefficient, possibly due to the improvement of coating microstructure.

Fig.6 shows SEM images of wear tracks of Ti-Al-Si-Cu-N films. It is observed in Fig 6a that the Ti-Al-Si-Cu-N film deposited at RT is subjected to a severe wear condition characterized by material transfer and abrasion. The slight grooves and dentation borders are obviously observed on the wear track of the film deposited at RT, which indicates the mechanisms including abrasion wear and fatigue fracture.

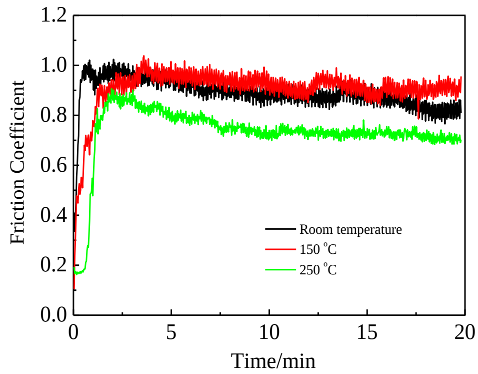


Fig.5 Friction coefficient of Ti-Al-Si-Cu-N films deposited at different temperatures

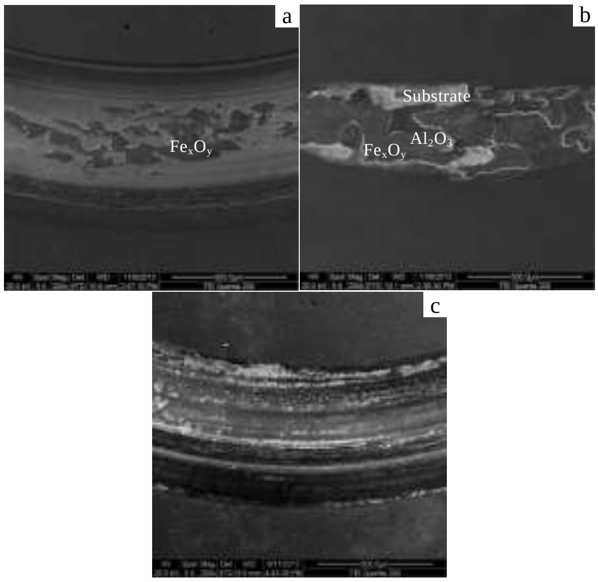


Fig.6 SEM images of the worn surfaces of Ti-Al-Si-Cu-N films deposited at different temperatures: (a) RT, (b) 150 °C, and (c) 250 °C

In the contact area of the film deposited at 150 ℃, the film flakes off partly and aluminum oxides are detected by EDS. It is mostly due to that the poor adhesion properties has promoted the peeling of films, as Fig.4b. With the disk sliding, cracks initiate in the contact area, then the coating flakes off, and the generated wear debris react with $H_2O$ or $O_2$[27]. On one hand, the peelings contribute to the wear. On the other hand, the products of reactions have good lubricity, which could improve the wear resistance of the film[28], indicating the wear mechanisms is mainly fatigue fracture.

The parallel grooves and scratches are observed in wear tracks of the film deposited at 250 ℃, which indicates the abrasive wear. There is no obvious peeling in the wear track, which is ascribed to its higher elastic modulus and better adhesion property. The EDS analysis shows that the iron oxides appear in wear tracks of all the films, and the Fe element may be transferred from GCr15 stainless steel ball. The phenomenon may be ascribed to the higher hardness of Ti-Al-Si-Cu-N films compared with GCr15 stainless steel ball.

Wear rate of these films is shown in Fig.7. The wear rate of films deposited at 250 ℃ is smaller than that of the films deposited at RT and 150 ℃, and the wear track of film deposited at substrate temperature 250 ℃ keeps a better condition. One can conclude that the wear resistance of films deposited at 250 ℃ is better than that of other films deposited at RT and 150 ℃.

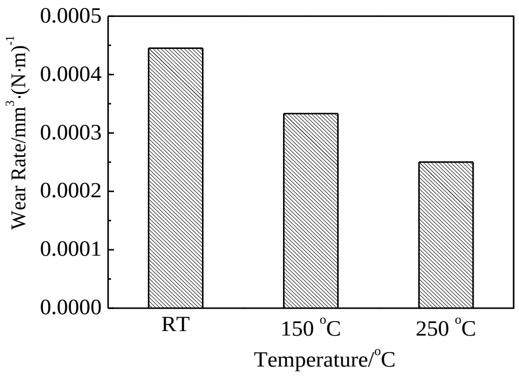


Fig.7 Wear rate of Ti-Al-Si-Cu-N films deposited at different temperatures

## 3 Conclusions

1) When the deposition temperature increases from RT to 250 ℃, the microstructure of Ti-Al-Si-Cu-N films becomes more compact. Compared with other films, the films deposited at 250 ℃ has smaller grain size and greater density.

2) With the increase of deposition temperature, the hardness and elastic modulus of the films increases from 14.482 GPa to 15.315 GPa, 180.775 GPa to 293.418 GPa, respectively. Compared with the films deposited at RT and 150 ℃, the films deposited at 250 ℃ has better adhesion property.

3) At deposition temperature 250 ℃, the friction coefficient and the wear rate of the films are the smallest due to the high elastic modulus and good adhesion property. Fatigue fracture occurs in the wear tracks of the films deposited at lower deposition temperatures. The primary wear mechanism of the films deposited at 250 ℃ is abrasive wear.

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# 基材温度对磁控溅射制备的 Ti-Al-Si-Cu-N 涂层的微观结构及摩擦学性能的影响

冯长杰，陈　恩

（南昌航空大学，江西　南昌　330063）

**摘　要：**采用反应磁控溅射技术在 304 不锈钢基片上沉积 Ti-Al-Si-Cu-N 涂层。通过扫描电镜（SEM）、能谱仪（EDS）、X 射线衍射仪（XRD）、纳米压痕仪、划痕仪和球盘式摩擦磨损试验机研究了不同基材温度(沉积温度)对涂层结构和摩擦学性能的影响。结果表明：随着沉积温度从室温升至 250 ℃，涂层表面变得平滑，结构致密。硬度和弹性模量随沉积温度的升高而升高。划痕试验表明：当沉积温度分别为室温，150 和 250 ℃时，临界载荷为 3.85, 3.45 和 5.10 N。当沉积温度为 250 ℃时，涂层的摩擦系数和磨损速率最小，摩擦过程中产生的磨屑主要来自 GCr15 不锈钢珠。在较低的沉积温度下，涂层的磨损机理主要为疲劳断裂和磨粒磨损，而 250 ℃沉积的涂层的磨损机制主要为磨粒磨损。

**关键词：**反应磁控溅射；Ti-Al-Si-Cu-N 涂层；沉积温度；磨损机理

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作者简介：冯长杰，男，1977 年生，博士，教授，南昌航空大学材料科学与工程学院，江西　南昌　330063，电话：0791-83863026, E-mail: chjfengniat@126.com