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ARTICLE

Effects of Cu Content on Microstructure and High-Temperature Oxidation Behavior of Ti-Al-Si-Cu-N Nanocomposite Films

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Abstract: Ti-Al-Si-Cu-N nanocomposite films with different Cu contents were deposited on AISI-304 stainless steel by DC reactive magnetron sputtering. Both Ti-Al-Si-N and Ti-Al-Si-Cu-N nanocomposite films were oxidized at 800 ℃ to investigate the influence of Cu content on the microstructure and high temperature oxidation resistance by scanning electron microscope (SEM), energy disperse spectroscopy (EDS), X-ray diffraction (XRD), nanoindentation tester and a home-made indentation system. The results indicate that with the increasing copper content in the films, the micropores disappear on the surface of Ti-Al-Si-N nanocomposite film and compact films are obtained. A reduction of the grain size and a change of the (111) preferred orientation to (110) are observed. The microhardness of films increases from 14.76 GPa to 19.42 GPa. The elasticity modulus of Ti-Al-Si-Cu-N films with 1.72 at% Cu content is the minimum of 104.5 GPa. The incorporation of copper at high temperature influences the oxidation resistance of the Ti-Al-Si-N films in the two aspects, one is advancing the diffusion rate of Al element, and the other is inducing cracks of oxide layer and micropores. Ti-Al-Si-N films have a better oxidation resistance than that of the films added Cu element.

Key words: reactive magnetron sputtering; Ti-Al-Si-Cu-N films; microstructure; high temperature oxidation resistance

In recent decades, TiN films are widely used in cutting tools due to their high hardness, good wear-resistance and corrosion resistance [1, 2], and nanocomposite films arouse great attention because of their special structure and unique properties [3]. However, TiN films are usually oxidized into brittle TiO_2 phase layer on the top of TiN layer at temperatures beyond 550 ℃ [4-7]. This shortcoming limits the industrial application of TiN films at high-speed cutting (HSC). It is reported that metallic and non-metallic elements, such as Al, Si, Cr or B, were doped in TiN, and these ternary films had better oxidation resistance[8], higher hardness, higher friction property[9]and improved thermal stability compared with TiN. To enhance mechanical and chemical properties of TiN at high temperature, the researchers[10] paid great attention to Ti-Al-N films. The promising oxidation resistance of Ti-Al-N films was based on the formation of dense and adherent mixed oxide scales mainly composed of Al_2O_3 during exposure to the air at elevated temperatures, and Al_2O_3 layer impeded the diffusion of oxygen and metal element[11,12]. Addition of Si to Ti-Al-N films can increase their hardness, wear and oxidation resistance compared to Ti-Al-N. Ti-Al-Si-N film consists of two phases, nanocrystalline Ti-Al-N surrounded by an amorphous Si_3N_4. After the films were oxidized, the oxide layer composed of Al_2O_3 and SiO_2, acted as a barrier against oxygen diffusion into Ti-Al-Si-N films.

When nitride films combine with a soft-ductile phase, these films can become superhard while retaining exceptional mechanical properties and high chemical resistance[13,14]. Investigations[15] showed that TaN-(Cu,Ag) nanocomposite films exhibited good tribological properties due to the lubricious Ag and/or Cu layers. Our previous report[16] showed that with the addition of 1.04 at%Cu, the grain size of

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Ti-Al-Cu-N film decreased from 180 to 100 nm, but the further increase of the Cu content induced larger grains and irregularity in the Ti-Al-N film.

Although many researchers[16-18] had studied Ti-Al-Si-Cu-N films, most studies concentrated on their mechanical properties. There is almost no conclusion about anti-oxidation properties of Ti-Al-Si-Cu-N films. In the present, Ti-Al-Si-N and Ti-Al-Si-Cu-N films with different Cu contents were prepared by reactive magnetron sputtering. This work is aimed at investigating the effects of Cu content on the microstructure and high-temperature oxidation behavior of Ti-Al-Si-Cu-N films.

1 Experiment

Ti-Al-Si-Cu-N films were deposited on polished 304 stainless steel sheets with a dimension of 15 mm×10 mm×2 mm by a MS-3 DC magnetron sputtering system. 50Ti-40Al-10Si (at%) alloy and pure Cu (99.99%) with a diameter of 100 mm were used as sputtering target materials. Prior to deposition, the stainless steel substrates were ground, polished and ultrasonically cleaned in the absolute alcohol to remove surface contaminants. The stainless steel sheets were mounted on a rotational substrate holder with a revolving speed 20 r/min during sputtering. The distances between the substrate and TiAlSi, Cu target were controlled at about 3 cm and 13 cm, respectively. N_2 was introduced as the working reactive gas. The total working pressure was regulated about 0.6 Pa. The ratio of nitrogen (purity=99.99%) and argon gas (purity=99.99%) was set as 1:1. The deposition time was 4 h. Ti-Al-Si-Cu-N films with different Cu content were prepared under the conditions as follows: TiAlSi target power was kept at 537.5 W, Cu target power was adjusted to 0, 11.25 and 21.25 W.

Microhardness and elastic modulus of the films were measured by a nano-indenter (NANO G200, MTS, USA). The crack-resistance of Ti-Al-Si-Cu-N nanocomposite films was tested by a home-made indentation machine, as shown in Fig.1. In order to evaluate the ability of crack-growth resistance, the indentation morphologies were observed by the SEM (quanta 200).

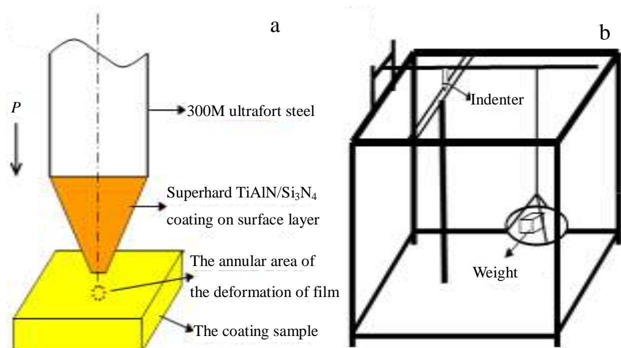

Fig.1 Schematic diagrams of indenter (a) and tester (b) for toughness measurement of films

For the high temperature oxidation experiment, the deposited Ti-Al-Si-N and Ti-Al-Si-Cu-N samples were oxidized at 800 °C for 100 h in air. The samples were removed from the muffle furnace and were weighed using an electronic balance (Germany: Saterious CP-225d, accuracy 10^{-5} g) every 20 h. The phases of the films was examined by XRD equipped with Cu Kα X-ray source (XPERT-PRO-MRD) in a scanning range of 15 °~85 °. The composition and morphologies of the oxidized films were analyzed by a field- emission scanning electron microscope (Nova Nano SEM450), an environmental scanning electron microscope (quanta 200) and an energy disperse spectroscopy (INCA 250 X-Max 50).

2 Results and Discussion

2.1 Microstructure of the films

Fig.2 shows the surface and cross-sectional morphologies of Ti-Al-Si-Cu-N nanocomposite films with different copper contents. It can be seen from Fig.2 that the roughness of the Ti-Al-Si-Cu-N films decreases with increasing of Cu content. The surfaces of Ti-Al-Si-N films have many defects, and the typical columnar structure can be observed from Fig.2d.

The improvement of compactness and the diminution of grains size are observed in the Ti-Al-Si-Cu-N nanocomposite films with the copper incorporation, Since copper plays a role of the grain growth. The Ref.[3] indicated that Ti-Al-Si-Cu-N films were composed of nanocrystalline Ti-Al-N, amorphous Cu and amorphous Si_3N. Cu and amorphous-Si_3N_4 hindered the grain growth and simulated a re-nucleation of grains. J. Shi et al[18] had prepared Ti-Al-Si-Cu-N films with different Si contents by filtered magnetic arc ion plating and found that the Ti-Al-Si-Cu-N film system showed a dense and non-columnar microstructure with Si and Cu incorporation into the film.

Fig.3 shows the XRD patterns of Ti-Al-Si-Cu-N films with different Cu contents (0 at%, 1.72 at% and 3.63 at%). It reveals that all the films exhibit B1-NaCl structure. Ti-Al-Si-N film have a strong TiN(111) diffraction peak and obvious preferred orientation. However, the TiN(111) peak could not be observed in the XRD pattern of Ti-Al-Si-Cu-N film with 3.63 at% Cu content, and the diffraction peak is mainly (110) peak. At the same time, the peaks of (111), (220) and (222) sharply decline or even disappear with the increase of Cu contents, which mainly result from the re-nucleation of grains induced by petty Cu grains. Due to liberal orientations of these grains, the preferred orientation decreases. As the Cu content increases from 1.72 at% to 3.63 at%, the change of the preferred orientation of films from (111) to (110) might result from lattice distortion.

Myung et al[19] found that some Cu ions replaced Ti ions within TiN lattice and in this case according to the valence band analysis, the Ti-Cu-N films formed a substitutional solid solution.

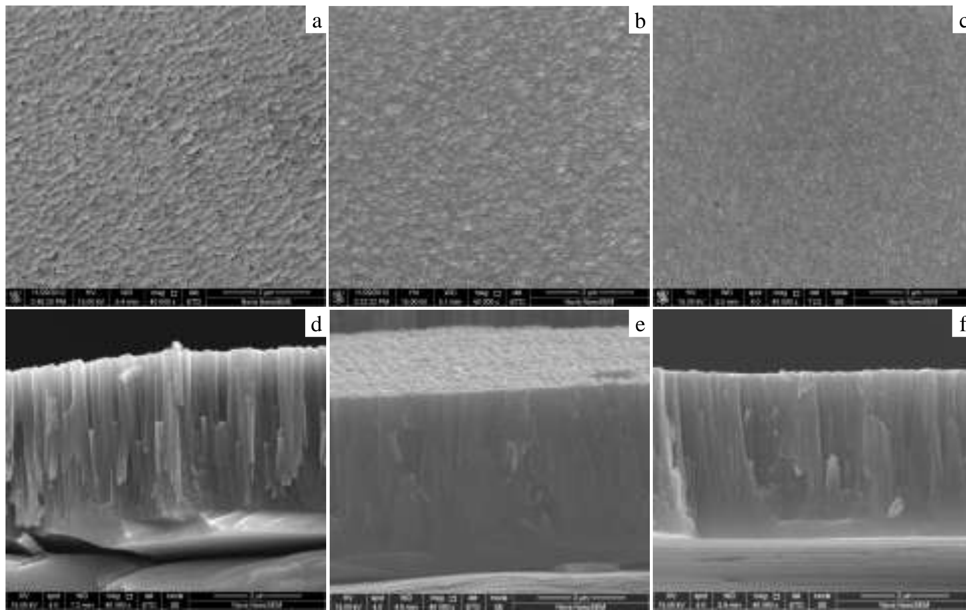

Fig.2 Surface (a~c) and cross sectional (d~f) morphologies of the Ti-Al-Si-Cu-N films with different Cu contents: (a, d) 0 at%; (b, e) 1.72 at%; (c, f) 3.63 at%

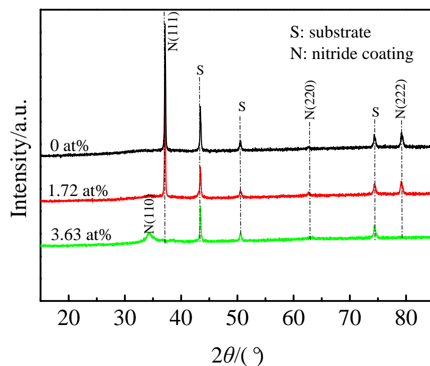

Fig.3 XRD patterns of the $TiAlN/Si_3N_4$-Cu films with different Cu contents

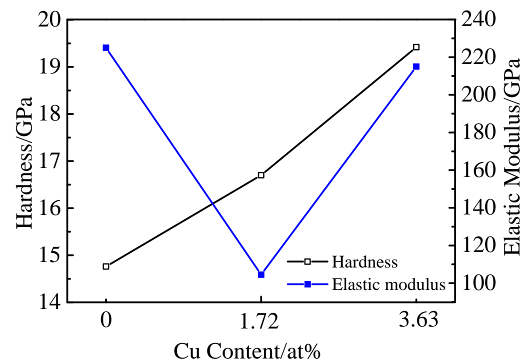

Fig.4 Hardness and elastic modulus of Ti-Al-Si-Cu-N films with different Cu contents

2.2 Mechanical properties

With increasing Cu contents in the Ti-Al-Si-Cu-N nanocomposite films, the hardness and elastic modulus of the films show different trends in Fig.4. The hardness and elastic modulus were calculated through the nanoindentation experiments and corresponding formulas. When the Cu content of the nanocomposite films changes from 0 at% to 3.63 at%, the hardness of the films increases slightly from 14.76 to 19.42 GPa. The elastic modulus of Cu content of 1.72% is the smallest compared with those of other films. This change of elastic modulus may due to the corresponding film grain size and residual stress. Fig.5 presents the indentation morphology of the nanocomposite film with various Cu contents, and the indentation of the films was tested by a homemade indentation testing machine. Through the indentation experiment, it can be found that there are fewer cracks on the Ti-Al-Si-N film without the addition of Cu, but each crack is deep and wide and could easily develop. However, the Ti-Al-Si-Cu-N nanocomposite film with Cu content of 1.72% has shallow, flexural and more cracks, and many microcracks grow along the grain boundary. It indicates that the films release strain through a large number of microcracks. This might be attributed to the addition of Cu element and residual stress. With further adding of the Cu element, the grain size increases as shown in Fig.2, as well as the residual tensile stress.

2.3 Oxidation resistance of films

The oxidation kinetics curves of Ti-Al-Si-Cu-N films with different Cu contents at 800 °C are shown in Fig.6. From the figure, it can be seen that with the increasing Cu content in the films, the oxidation resistance declines. The oxide film formed from forming stage to the growth stage, and the oxidation process mechanism transforms from surface reaction to

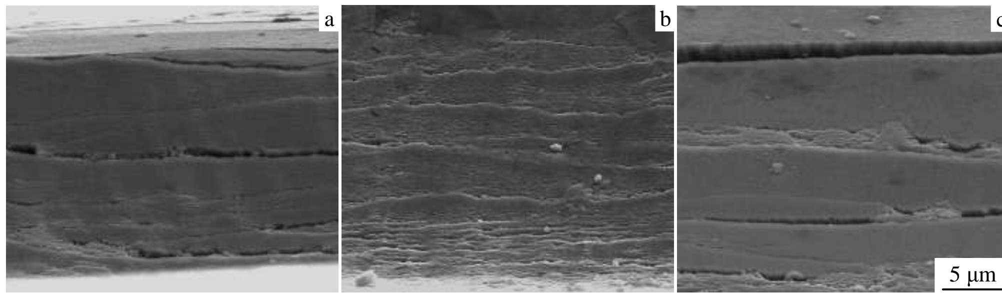

Fig.5 Indentation section morphologies of nanocomposite film with different Cu contents: (a) 0 at%, (b) 1.72 at%, and (c) 3.63 at%

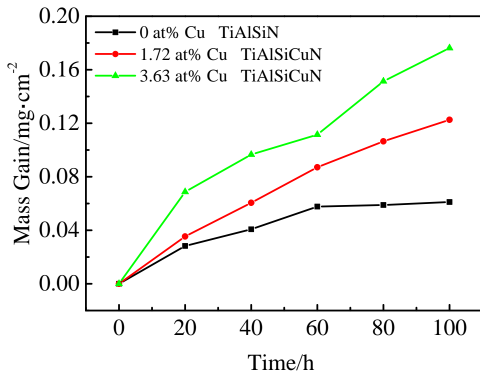

Fig.6 Oxidation kinetics curves of Ti-Al-Si-Cu-N films with different Cu contents at 800 °C for 100 h

diffusion [11,20]. It is mainly completed by the mutual diffusion of metal ions and oxygen ions. The Cu in the film surface forms Cu_2O or CuO after being oxidized, and it would have a greater change in volume, which sustains a certain amount of compressive stress local breakdown of the oxide layer occurs[21] and the unoxidized zone is exposed and oxidized again.

Fig.7 shows the oxidation surface morphologies and cross sectional morphologies of the Ti-Al-Si-Cu-N films with various Cu contents. From Fig.7a, it can be found that the surface of the film is dense and plain, and the scale has 67.91 at% O, 13.75 at% Al, 16. 91 at%Ti and slight Si tested by EDS. It also can be seen that the outermost of the scale mainly is TiO_2, small amounts of Al_2O_3, and trace amount of SiO_2, but most nitride films have not been oxidized.

From Fig.7c, it can be observed that the oxidation surface of Ti-Al-Si-Cu-N film contains 1.72 at% Cu had a small round ball type oxide, and the oxide particles are small. The main ingredients of the oxide are Al_2O_3, which was analyzed by the surface energy spectrum, containing 21.13at%Al, 10.96at% Ti, 3.11at%O, Cu and Si. It can be found that the outermost layers of the main oxidation section are rich in Al as shown in Fig.7d, and Al is reduced gradually from the surface to the inner;

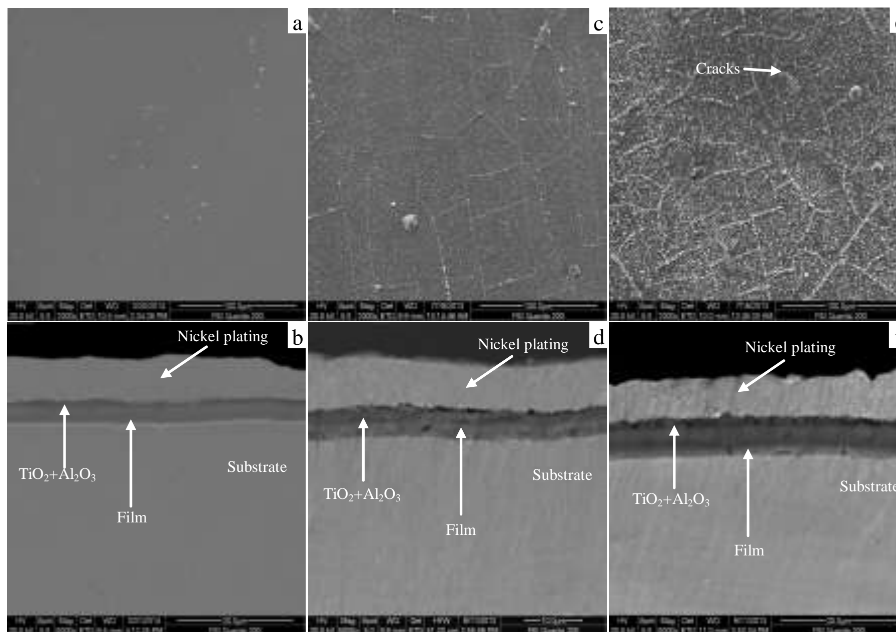

Fig.7 Surface (a, c, e) and cross sectional (b, d, f) morphologies of the Ti-Al-Si-Cu-N films with different Cu contents after being oxidized for 100 h at 800 ℃: (a, b) 0 at%, (c, d) 1.72 at%, and (e, f) 3.63 at%

conversely, the Ti content of the film increases gradually from the surface to the inner. The surface of the Ti-Al-Si-Cu-N film containing 3.63 at% Cu has much spherical oxide and rod oxide after being oxidized as shown in Fig.7e.

A large number of mesh structures from Fig.7e are formed and this can be explained from two aspects: (1)The different thermal expansion coefficients of the stainless steel substrate and the film. When the sample is cooled to room temperature after high temperature oxidation treatment of 800 °C, the uneven heat shrinkable leads to stress, and produces film surface cracks[22], and the cracks are more easy to be oxidized to form a mesh structure. (2)The volume change resulting from copper oxides it causes the surface sustain certain stress, producing surface microcracks, holes and defects (Fig.8).

The section morphology and line scanning energy spectrum analysis of the Ti-Al-Si-Cu-N films with 1.72at% and 3.63at% Cu after oxidized for 100 h at 800 °C are shown in Fig.9 and Fig.10, respectively. It shows that the oxide layer of Ti-Al-Si-Cu-N films with 3.63 at% Cu, compared that with 1.72% Cu, is thicker and the oxidation resistance is worse through the analysis of O and N elements distribution.

It also can be seen from Fig.9 and Fig.10, Al element content is higher in the outermost layer of the oxidation layer, and decreases in the internal layer of the oxidation layer. This phenomenon can be attributed to that Al element diffuses outwards during the process of high temperature oxidation, which is also the reason why the oxide film of the film has good oxidation resistance, as shown in Fig.4. Mcintyre, etc.[23] studied the oxidation mechanism of $Ti_{0.5}Al_{0.5}$ N film at the temperature of 750 to 900 °C in the pure oxygen, and they found that Al diffused outward during the initial stage of oxidation. The Gibbs free energy of Al_2O_3 is much lower than that of TiO_2. Al element in the film is prone to diffusion and oxidation at high temperature; however, according to the analysis of EDS, the Al content in the Ti-Al-Si-Cu-N film contained 3.63 at% Cu is significantly higher only at the outermost layer. J. H. Xiang [24] found that the diffusion rate of Al increased and Al tended to diffuse faster to the interface of alloy/oxide by adding Cu element in the Ni-Al alloys. According to the above analysis, it shows that, during the high temperature oxidation process of Ti-Al-Si-Cu-N film, adding Cu element in the films has two effects at least: on the one hand, it plays a positive role in the process of oxidation, which accelerates the diffusion rate of Al; on the other hand, the oxide layer is destroyed due to Cu addition, which is

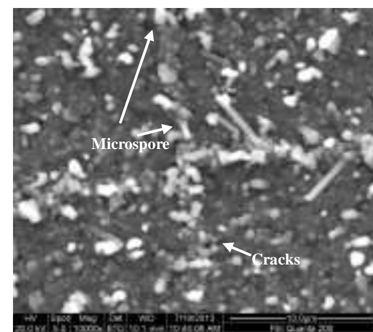

Fig.8 Surface morphology of the Ti-Al-Si-Cu-N films with 3.63 at% Cu after oxidation for 100 h at 800 °C

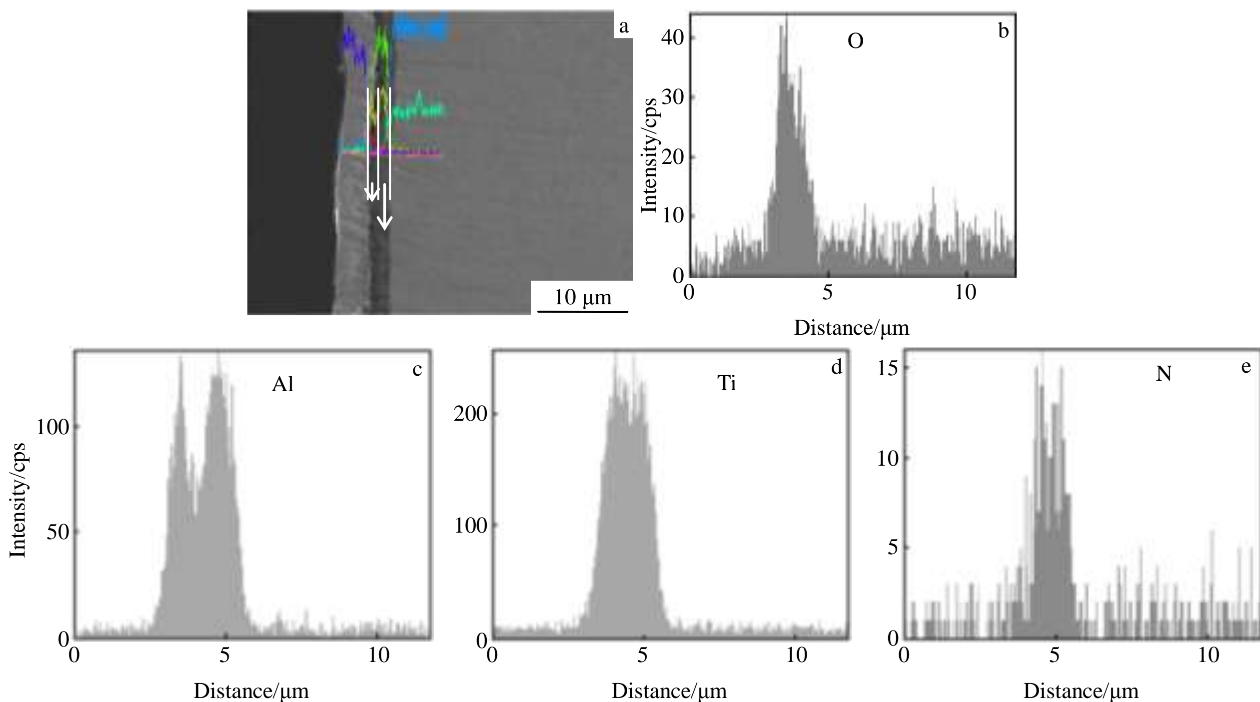

Fig.9 Cross-section morphology (a) and EDX line scanning (b, c, d, e) of Ti-Al-Si-Cu-N films with 1.72 at% Cu after oxidation at 800 °C for 100 h: (b) O, (c) Al, (d) Ti, and (e) N

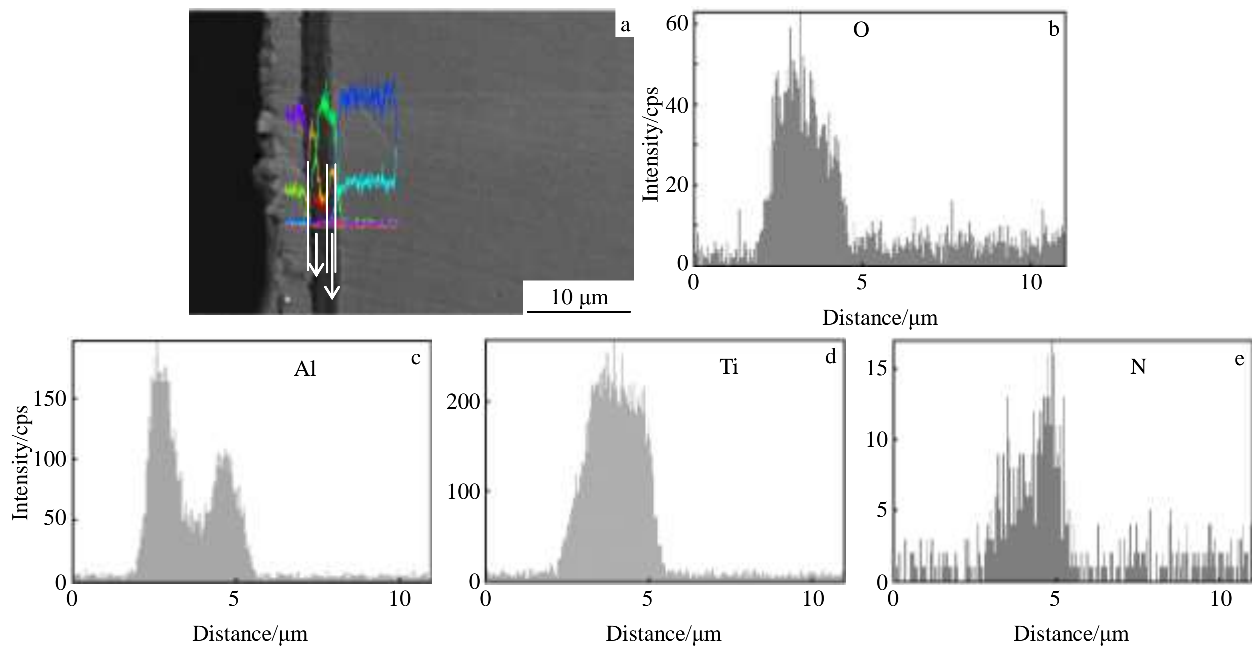

Fig.10 Cross-section morphology (a) and EDX line scanning (b, c, d, e) of Ti-Al-Si-Cu-N films with 3.63 at% Cu after oxidation at 800 ℃ for 100 h: (b) O, (c) Al, (d) Ti, and (e) N

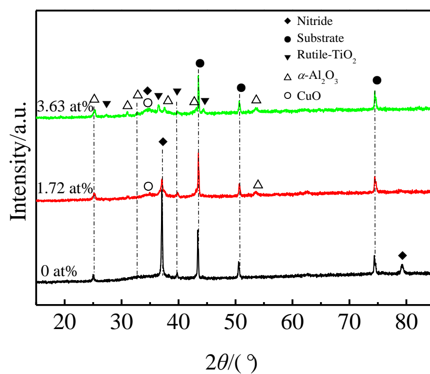

Fig.11 XRD patterns of Ti-Al-Si-N and Ti-Al-Si-Cu-N films after oxidation at 800 °C for 100 h in air

oxidized to CuO, breaks the dense Al_2O_3 layer and promotes the oxygen into the interior of the film.

Fig.11 demonstrates the XRD patterns of Ti-Al-Si-N films and Ti-Al-Si-Cu-N films after oxidation at 800 °C for 100 h. It can be found from the figure that the diffraction peak intensity of nitride is weakened obviously. The corresponding peaks of Al_2O_3, TiO_2, CuO and the substrate are detected in the XRD patterns. The corresponding diffraction peaks of SiO_2 are not detected, which might be attributed to that the content of SiO_2 is too less to be detected or SiO_2 exists in oxide film in the form of amorphous [25]. Compared to the XRD pattern of Ti-Al-Si-N film, the Ti-Al-Si-Cu-N film has more diffraction peaks of TiO_2 and Al_2O_3, and its antioxygenic property becomes worse.

3 Conclusions

1) The increasing Cu content in the Ti-Al-Si-Cu-N films decreases the surface roughness and the grain size, and makes the column structure less obvious. The preferred orientation changes gradually from (111) to (110) with the Cu addition increase for the Ti-Al-Si-N films.

2) The oxidation kinetic curves of the films after oxidation at 800 °C for 100 h match up with the parabolic rule, and their oxide scales have good oxidation resistance, mainly composed of Al_2O_3, TiO_2, CuO and a small amount of SiO_2.

3) With the addition of Cu element in the Ti-Al-Si-Cu-N films, on the one hand, the diffusion rate of Al element is improved; on the other hand, it breaks the surface oxidation film, the holes and defects form, and the film oxidation performance degrades.

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Cu 含量对 Ti-Al-Si-Cu-N 纳米复合涂层微观结构和高温氧化行为的影响

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摘　要：通过磁控溅射技术，在 AISI-304 不锈钢表面制备了不同 Cu 含量的 Ti-Al-Si-Cu-N 纳米复合涂层。通过扫描电镜 (SEM)、 能谱 (EDS) 仪、X 射线衍射 (XRD) 仪、纳米压痕仪和自制压痕仪等设备研究 Ti-Al-Si-N 和 Ti-Al-Si-Cu-N 纳米复合涂层的结构和在 800 ℃氧化的行为。结果表明：随着涂层中 Cu 含量的增加，涂层表面的微孔数量减少，涂层更加致密，涂层晶粒尺寸减小，择优取向由（111）向（110）逐渐转变。涂层的硬度由 14.76 GPa 增加至 19.42 GPa。Cu 含量为 1.72%（原子分数）的 Ti-Al-Si-Cu-N 弹性模量最小，为 104.5 GPa。Cu 元素对 Ti-Al-Si-Cu-N 纳米复合涂层抗氧化性能有两方面的影响：一是促进 Al 元素的扩散，二是在氧化膜表面形成裂纹和微孔缺陷。Ti-Al-Si-N 涂层比 Ti-Al-Si-Cu-N 涂层具有更好的抗氧化性能。

关键词：反应磁控溅射；Ti-Al-Si-Cu-N 涂层；微观结构；抗高温氧化性能

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