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The Effect of N_2/Ar on the High Temperature Thermal Stability of AlCrTiN Coating

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***Abstract*—Using arc ion plating and DC magnetron sputtering composite deposition technology, five AlCrTiN coatings were prepared by changing the N2/Ar ratio. The effects of different N2/Ar ratios on the coating structure, mechanics and high temperature thermal stability were studied. The results show that the main phase structure of the five AlCrTiN coatings is NaCl-type fcc-(Al,Cr)N, which grows preferentially along the (111) crystal plane. As the N2/Ar ratio increases, the hardness and elastic modulus of the coating first increase and then decrease. When N2/Ar=4/1, the hardness and elastic modulus of the coating are the largest, 14.36GPa and 402.26GPa, respectively . After five kinds of coatings are kept at 800° C for 1 hour, the quality change of the coating first decreases and then increases. When N2/Ar=2/1, the quality change of the coating is the smallest and the thermal stability is the best.**

***Keywords*—Arc ion plating; DC magnetron sputtering; mechanical properties; high temperature thermal stability**

I. INTRODUCTION

In recent years, with the rapid development of science and technology, higher requirements have been placed on the hardness, film-base adhesion, wear resistance and high temperature oxidation resistance of the coating. In order to meet the requirements, the coating materials are constantly updated and developed. In the early days, our commonly used coating materials were TiN[1], CrN[2]and so on. As the first protective material for the surface of the tool, TiN coating has high film-base bonding force and strong oxidation resistance. However, when the temperature exceeds 550°C, the Ti in the coating will oxidize to form loose TiO_2, which accelerates the oxidation rate of the coating[3]. Similarly, CrN coating also has high hardness, good wear resistance, low internal stress, stable chemical properties, and is used in various workpiece and tool industries. Compared with TiN coating, CrN coating has better oxidation resistance, and the oxidation temperature can reach 800℃, but it still cannot meet the requirements of modern industrialization [4].

The addition of the third element often results in better performance, such as higher oxidation temperature, corrosion resistance, abrasion resistance, and higher membrane-base bonding force[5]. Common coatings are AlCrN, AlTiN and so on. AlCrN coating is widely used because of its high hardness, lower coefficient of friction and better wear resistance[6].

At present, AlCrN coatings cannot adapt to modern processing conditions. Therefore, people have begun to study multi-component coatings, multilayer coatings, gradient coatings and nanocomposite coatings. The development of these new coating technologies has improved the coating and substrate The binding force increases thermal stability. The results show that doping Ti can significantly affect the overall mechanical properties of AlCrN coatings. The addition of Ti makes the red hardness of AlCrN hard coatings significantly improved, making the cubic phase structure more stable and restraining softness. The emergence of phase hcp-AlN and hcp-Cr_2N, so the mechanical and thermal stability of such hard coatings have been well improved[7]. However, with the increase of Ti content, under high temperature, the content of TiO_2 phase with sparse porous structure increases, which leads to the decrease of compactness of the coating under high temperature, thereby improving the red hardness of the coating[8].

The AlCrTiN quaternary coating doped with Ti can inhibit the conversion of fcc-AlN to hcp-AlN at high temperatures. The high content of cubic AlN phase improves the hardness and wear resistance of the coating at high temperatures. With the increase of Ti content, TiN phase appears in the coating. The hardness of TiN is higher than that of CrN, which can increase the hardness of the coating. At the same time, adding Ti can refine the coating grains, make the coating denser, and effectively improve the coating's hardness. Hardness and oxidation resistance.

In this paper, arc ion plating and DC magnetron sputtering composite deposition technology are used to prepare different AlCrTiN coatings by changing the N_2/Ar flow ratio to study the effect of N2/Ar flow ratio on the coating properties.

II. EXPERIMENT

A. *Coating preparation*

Using arc ion plating and DC magnetron sputtering co-deposition technology to deposit AlCrTiN coating on the surface of single crystal Si wafers and cemented carbide wafers. The AlTi target is connected to the arc power source, and the AlCr target is connected to the DC magnetron sputtering power source. Put the cleaned substrate into the furnace, vacuumize to 6.7×10^{-3}Pa, and heat the furnace to 300°C. Set the substrate forward rotation frequency to 30Hz, and when the vacuum in the furnace reaches below 6.7×10^{-3}Pa again, let in 250sccm of argon gas and adjust the throttle to keep the pressure in the furnace at 1.5Pa, and then apply a bias of -800V Perform glow cleaning. The glow cleaning time is 15 minutes to remove contaminants on the surface of the substrate. Switch on the AlTi target arc power supply, adjust the current to 60A, keep the voltage constant, adjust the throttle valve to keep the pressure in the furnace at 1Pa, and bombard and clean the substrate for 10 minutes. After the bombardment was completed, the argon gas flow was reduced to 200 sccm, the bias voltage was reduced to -90V, the

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working pressure in the furnace was adjusted to 0.8 Pa, and the AlTi transition layer was deposited. This process was maintained for 2 minutes. Subsequently, the flow of argon was reduced to 40 sccm, and 160 sccm of nitrogen was introduced to deposit an AlTiN transition layer, and this process was maintained for 10 minutes. Finally, switch on the AlCr target DC magnetron sputtering power supply, set the target power to 2.2kw, adjust the AlTi target current to 70A, and set N_2/Ar to 1/1, 2/1, 3/1, 4/1, 5/1 The AlCrTiN coating was deposited, and the deposition time was 4h. The specific parameters of the coating are shown in *TABLE 1*:

TABLE1 The deposition parameters of five AlCrTiN coatings

Parameters	Value
Base pressure (Pa)	6.7×10^{-3}
Working pressure (Pa)	0.8
Bias voltage (V)	-90V
N_2/Ar(sccm)	1/1（75/75） 2/1（50/100） 3/1（114/38） 4/1（120/30） 5/1（125/25）
Deposition temperature (ºC)	300
Deposition time (min)	240
AlCr target power (kW)	2.2
AlTi target current (A)	70
Rotation speed of the sample (r/min)	30
Distance between the substrate and target (mm)	100

B. Performance characterization

Use an X-ray diffractometer to determine the phase composition of the coating; use an ultra-depth-of-field microscope to observe the surface morphology of the coating, use a stress meter to measure the residual stress in the coating through the radius of curvature method, and use a G300 nanoindenter to test the coating The hardness, elastic modulus and We value of the coating were tested with a scratch tester to test the film-base bonding force of the coating.

Put five kinds of AlCrTiN coatings into Al_2O_3 crucibles, put them in a vacuum annealing furnace and heat them to 800°C, keep them for 1 hour, and then cool them down with the furnace. In this experiment, before the heat treatment, the initial total amount of the sample should be weighed with a balance. After the heat treatment, the sample was taken out and re-weighed and the data was recorded. In order to reduce the error, the average value was taken for 3 times of weighing.

III. RESULTS AND DISCUSSION

A. Organizational structure

Fig. 1. shows the XRD diffraction patterns of five AlCrTiN coatings. It can be seen from the figure that the main phase structure of the five coatings is NaCl-type fcc-(Al,Cr)N, and they grow preferentially along the (111) crystal plane. The growth process of the coating will produce thermal stress and growth stress. Al is dissolved in CrN and the strain energy increases. In order to suppress the growth of strain energy, the coating grows preferentially along the (111) crystal plane. In addition, there are a small amount of Ti_2N, CrN and hcp-AlN phases in the coating. As the ratio of nitrogen to argon increases, the fcc-(Al,Cr)N phase of the coating gradually increases, while the CrN phase shows a decreasing trend. At the same time, we can see that the ratio of nitrogen to argon increases from 1/1 to 4/1, and the hcp-AlN phase gradually weakens, indicating that an appropriate increase in the ratio of nitrogen to argon is beneficial to inhibit the formation of hexagonal structure, and then increase the ratio of nitrogen to argon. The diffraction peak of hcp-AlN is weakly enhanced, indicating that the ratio of nitrogen to argon is too high, which promotes the formation of hcp-AlN.

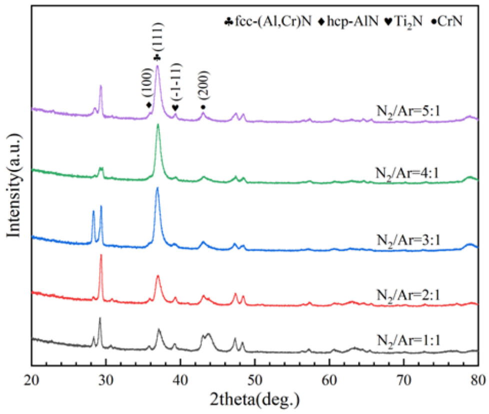

Fig. 1. XRD diffraction patterns of five AlCrTiN coatings

Fig.2. shows the surface topography of five AlCrTiN coatings. As shown in the figure, the five coatings have irregularly arranged black dots, and the topography after magnification is found to be tiny holes, which are typical features of arc ion plating coatings. As the ratio of nitrogen to argon increases, the reaction becomes more complete, the internal defects of the coating are reduced, the holes are reduced, and the coating is denser.

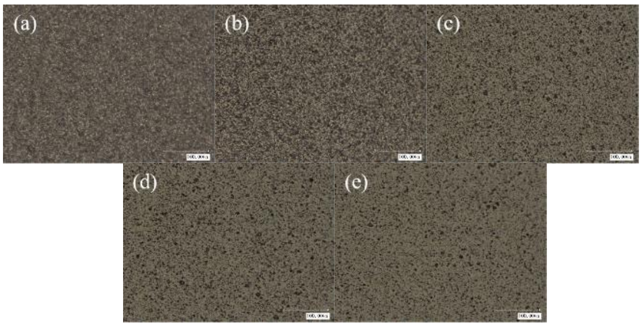

Fig. 2. Surface topography of five AlCrTiN coatings(a)N_2/Ar=1/1(b) N_2/Ar=2/1(c) N_2/Ar=3/1(d) N_2/Ar=4/1(e) N_2/Ar=5/1

B. Mechanical properties

TABLE 2 shows the H, E*, H/E*, H^3/E^{*2}, We, σ, and L_{C2} values of the five AlCrTiN coatings. From the table, we can see that as the ratio of nitrogen to argon increases, the H, E*, We, and σ of the coating show a trend of first increasing and then decreasing. When the ratio of nitrogen to argon is 4/1, the coating has the largest hardness and elastic modulus, respectively 14.36GPa and 402.26GPa; when the ratio of nitrogen to argon is 1/1, the coating has the largest H/E*, H^3/E^{*2} are 0.048 and 0.0246 respectively. It is generally believed that H/E* reflects the ability of the coating to resist elastic deformation. The larger the H/E* value, the stronger the ability of the coating to resist elastic deformation.

H^3/E^{*2} reflects the plastic deformation resistance of the coating. The larger the H^3/E^{*2} value, the better the plastic deformation resistance and toughness of the coating[9, 10]. It can be seen that the coating has better resistance to plastic deformation and crack propagation when the ratio of nitrogen to argon is 1/1.

TABLE 2 H, E*, H/E*, H^3/E^{*2}, We, σ and L_{C2} values of five AlCrTiN coatings

N_2/Ar	H(GPa)	E*(GPa)	H/E*	H^3/E^{*2}	We(%)	σ(GPa)	L_{C2}(N)
1/1	7.53	218.92	0.048	0.0246	32.35	-1.201	42.78
2/1	11.87	346.55	0.037	0.0192	32.54	-1.143	29.01
3/1	12.05	353.00	0.036	0.0209	35.18	-2.019	32.31
4/1	14.36	402.26	0.035	0.0197	38.31	-2.67	40.93
5/1	10.58	401.80	0.027	0.0079	29.24	-2.042	39.16

C. High temperature thermal stability

Fig.3. shows the surface morphology of five AlCrTiN coatings after heat preservation at 800° C for 1 hour. As shown in the figure, the five kinds of coatings peeled off to varying degrees after being kept at 800° C for 1 hour. When the ratio of nitrogen to argon is 2/1, the coating surface peels off relatively seriously. We can see that the surface is divided into three colors, white is the substrate, dark gray is the coating, and light gray is the transition layer. Because of the low bonding force, the bonding strength between the transition layer and the substrate is low, and the peeling after heat treatment is more serious. None of the other four coatings exposed the substrate. When the ratio of nitrogen to argon is 4/1, peeling coating is attached to the surface of the coating, which is relatively lighter.

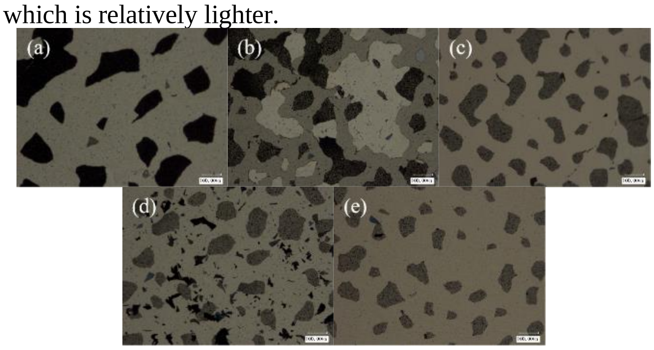

Fig. 3. The surface morphology of five AlCrTiN coatings after heat preservation at 800°C for 1 hour (a) N_2/Ar=1/1(b) N_2/Ar=2/1(c) N_2/Ar=3/1(d) N_2/Ar=4/1(e) N_2/Ar=5/1

Fig.4. shows the quality changes of five AlCrTiN coatings after being kept at 800°C under vacuum for 1 hour. It can be seen from the figure that the quality of the coating is reduced after vacuum annealing. It can be seen from the surface map that part of the reason for the reduction in quality is that the five coatings have fallen off to varying degrees; on the other hand, the nitrogen atoms in the coating volatilize, and CrN reacts with heating to generate Cr_2N and N_2, and N_2 volatilizes. Cr_2N will transform Cr and N_2 under high temperature conditions. As the ratio of nitrogen to argon increases, the mass change first decreases, then increases and then decreases. When the ratio of nitrogen to argon is 2/1, the spalling is serious, but the minimum mass change is $-2.57\times10^{-6}g/mm^2$, indicating that it may be oxidized to form a dense oxide film, and the mass is relatively increased, so the mass change is small.

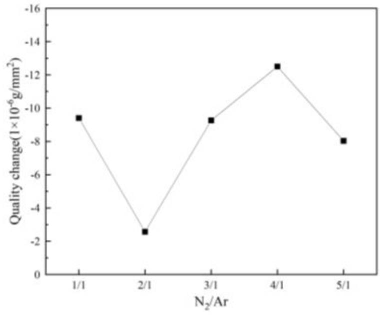

Fig. 4. The oxidation quality change diagram of five AlCrTiN coatings after being kept at 800°C for 1 hour in vacuum

IV. CONCLUSION

a) The main phase structure of AlCrTiN coatings prepared under different nitrogen-argon ratios is NaCl type fcc-(Al,Cr)N, and it grows preferentially along the (111) crystal plane.

b) As the ratio of nitrogen to argon increases, the hardness and elastic modulus of the coating first increases and then decreases. When the nitrogen-argon ratio is 4/1, it has the highest hardness and elastic modulus, which are 14.36GPa and 402.26GPa, respectively. It shows that a proper ratio of nitrogen to argon is beneficial to improve the mechanical properties of the coating.

c) After the five AlCrTiN coatings are kept at 800°C for 1 hour, when the ratio of nitrogen to argon is 2/1, the quality of the coating changes the least, indicating that its thermal temperature is better.

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