The effect of Cr and Cr-Ni doping on the properties of TiAlN coatings

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Abstract: To prepare TiAlN coatings with excellent performance and obtain the influence law of doping amount on the performance of TiAlN coatings, Cr-doping and Cr-Ni co-doping were carried out under the optimal process parameters of TiAlN by multi-arc ion plating and magnetron sputtering. The paper changed the doping amount of Cr and Cr-Ni by changing doping time of magnetron sputtering, to study the influence of doping amount on phase structure, surface hardness and adhesion TiAlN coatings. The results show that, all the components in the coatings are evenly distributed and doping amount is directly proportional to the doping time, when doping time was 10min, the phase structure of the coating was consistent with of the undoped TiAlN coating. With the increase of doping time, Al-Ni alloy phase and CrN phase began to appear, and the peak strength also increased with the increase of doping amount. The surface hardness of the coating decrease with the increase of doping amount, and binding force of the coating reaches the maximum at the doping time of 30 min, which is about 40N. When doping time continues to increase, the binding force of coating decrease, which is related to the formation of composite coating.

1. Introduction

Compared with TiN coating, TiAlN coating has not only greatly improved the surface hardness, but also improved the resistance to high temperature oxidation of coating, which is of great significance for the use of coating in tool and die, especially the performance improvement under high temperature working condition [1-4].

Compounds formed by Cr and Ni have many excellent properties, such as CrN has high hardness and wear resistance, high decomposition temperature and good chemical stability and good thermal conductivity [5-6], in addition to Ni has very good corrosion resistance and roughness, and Ni and Al form Ni-Al intermetallic compounds, further improve the abrasion resistance of coating [7]. Doping Cr
and Cr-Ni further improved the performance of TiAlN in all aspects, so that it can be better applied in cutting tools, tooling and industrial production [8].

Cr and Ni doping can improve some comprehensive properties of the coating, but the level of doping will also affect the overall quality of the coating. In this paper, on the basis of the successful preparation of TiAlN coatings, Cr-doping and Cr-Ni co-doping were carried out under the optimal process parameters of TiAlN by multi-arc ion plating technology [9-10] and magnetron sputtering technology [11-12]. The influences of Cr and Cr-Ni doping amount on the microstructure, hardness and adhesion of TiAlN coatings were studied.

2. Test materials and methods

2.1 Theory basis Test materials and sample preparation

The multi-arc target used in this study was Ti-Al alloy target with an atomic ratio of 1:1, and the magnetron sputtering target used for doping was pure Cr target and Cr-Ni alloy target (20% Cr and 80% Ni). 4Cr13 martensitic stainless steel was selected as the experimental materials, with the size of 20 mm×40 mm×2 mm. Now the samples are polished and polished before furnace loading, and then the samples are respectively cleaned with acetone and alcohol, and the cleaning time is 20 min. Finally, the samples are blown dry for furnace loading and coating preparation.

2.2 Test method

Before the sample is loaded into the furnace, clean the furnace first, mainly using a vacuum cleaner to absorb the falling debris, and then using absorbent cotton dipped in alcohol to clean the door frame, to ensure the sealing degree of the chamber, after the sample is loaded into the furnace to close the cavity door. After vacuum is divided into two steps, first the intraluminal pressure pump with mechanical pump below 10 Pa again open the molecular pump start end of pumping air into vacuum state, when the indoor air pressure reaches 0.001 Pa later, open the heating system for heating, such as indoor temperature after reaching working temperature, flux into Ar gas pressure has reached around 1 Pa, open the negative bias to 600 V, bombardment cleaning time for 20 min. After cleaning, N2 and Ar were injected proportionally to reach the required pressure, the working bias was set, the bias was opened and the Ti-Al alloy target was ignited for coating, during which magnetron sputtering target was opened for doping. The total doping time of Cr-Ni was 10min, 20min, 30min and 40min respectively, and the time of Cr doping alone was 5min, 10min, 15min and 20min. The magnetic controlled target current is 1A, and the working time of the multi-arc target is set as 30min. After the coating, such as furnace temperature down to 50°C remove artifacts. Table 1 and table 2 are coating processes.

| Temperature (℃) | Arc current (A) | N2 Flow (sccm) | Ar Flow (sccm) | Doping Time (min) | Bias (V) |
|-----------------|----------------|---------------|---------------|------------------|--------|
| 200             | 70             | 150           | 30            | 10               | 250    |
| 200             | 70             | 150           | 30            | 20               | 250    |
| 200             | 70             | 150           | 30            | 30               | 250    |
| 200             | 70             | 150           | 30            | 40               | 250    |
Table 2 TiAlN coating process with Cr doping alone

| Temperature (℃) | Arc current (A) | N₂ Flow (sccm) | Ar Flow (sccm) | Doping Time (min) | Bias (V) |
|-----------------|----------------|----------------|----------------|------------------|----------|
| 200             | 70             | 150            | 30             | 5                | 250      |
| 200             | 70             | 150            | 30             | 10               | 250      |
| 200             | 70             | 150            | 30             | 15               | 250      |
| 200             | 70             | 150            | 30             | 20               | 250      |

3. Result and analysis

Fig.1 shows the surface morphology and cross-section morphology of TiAlN coatings undoped with other elements. The droplet size on the surface of TiAlN coatings is small, and the connection between the coatings and the matrix is dense.

![Fig.1 surface and cross-section morphology of Ti-AlN coatings](image)

3.1 Relationship between doping amount and doping time of Cr-Ni and element distribution

Fig.2 shows the distribution of each element in the coating after Cr and Ni doping. It can be seen from the figure that the distribution of each element in the TiAlN coating doped with Cr and Ni is very uniform, indicating that Cr and Ni have been uniformly doped into the coating. Fig.3 shows EDS diagram of composition of coatings prepared at different doping time. Table 3 shows the atomic percentage of coatings at different doping time. It can be seen from the data in the table that the atomic percentage of N, Al, and Ti decreases, while the percentage of Cr and Ni increases in direct proportion to time.

![Fig.2 EDS layered image of the coating](image)

![Fig.3 EDS diagram of composition of coatings](image)
Fig. 3 energy spectrum of the coating at different doping time: (a) 10 min; (b) 20 min; (c) 30 min; (d) 40 min

Table 3: Atomic percentage (at%) of the coating at different doping time

| Doping Time (min) | N  | Al  | Ti   | Cr  | Ni  |
|------------------|----|-----|------|-----|-----|
| 10               | 43.27 | 32.41 | 20.74 | 1.82 | 1.76 |
| 20               | 42.33 | 31.16 | 19.62 | 3.02 | 3.87 |
| 30               | 42.12 | 29.28 | 18.92 | 4.19 | 5.49 |
| 40               | 40.37 | 27.19 | 18.16 | 6.92 | 7.36 |

In order to better compare the effects of Cr and Ni elements on the properties of TiAlN coatings, the effects of Cr-Ni co-doping on TiAlN coatings were investigated separately. Table 4 shows the composition content of TiAlN coatings doped with Cr alone. Compared with Cr-Ni co-doping, only the doping time was changed in order to control variables, and the doping amount was similar to the Cr content in Cr-Ni co-doping. In comparison with Table 3, it can be found that the contents of Ti, Al, N and Cr in TiAlN coatings are roughly the same. The only difference is that there are more Ni elements in Table 3, so it can be used to study the role of Ni in coatings.

Table 4: Atomic percentage (at%) of the coating at different doping time

| Doping Time (min) | N  | Al  | Ti   | Cr  |
|------------------|----|-----|------|-----|
| 5                | 41.25 | 33.57 | 23.67 | 1.51 |
| 10               | 43.67 | 32.35 | 20.83 | 3.15 |
| 15               | 42.34 | 29.81 | 23.32 | 4.53 |
| 20               | 42.53 | 28.57 | 22.57 | 6.33 |

3.2 XRD analysis of TiAlN coatings with different Cr and Ni doping levels

Fig. 4 shows the XRD of TiAlN coatings at different Cr and Ni doping levels, where figure a is the XRD of the TiAlN coatings co-doped by Cr-Ni, and figure b is the TiAlN coatings separately doped by Cr. As can be seen from figure a, when the doping time is 10 min, the phase structure of the undoped TiAlN coating is basically consistent with that of the undoped TiAlN coating, and no other peaks appear after doping. This is because the doping time is too short, Cr and Ni content is too low, and X-ray
diffraction instrument cannot detect the existence of phase or element at the grain boundary of the coating. With the increase of doping time, in addition to the phase of TiN and TiAlN, Al-Ni alloy phase and CrN phase also appeared, and the peak value also became stronger with the increase of doping amount. As can be seen from figure b, the phase structure appears almost identical, except that the phase of Al-Ni alloy is missing. The doping amount and the difference of doped elements under the same process will not change the overall phase structure, but only the strength of some peaks.

![Figure 4: XRD of TiAlN coatings with different doping amounts](image)

### 3.3 Effects of Cr and Ni doping on the surface hardness and adhesion of coatings

Fig.5(a) in fig.5(b) is Cr-Ni doping amount of coating surface hardness. We can see coating that the surface hardness as the doping time decreases with the increase of the doping amount, this is due to the Cr, Ni elements were added to formed Al-Ni alloy phase CrN, the hardness of the material is relatively lower TiAlN itself, especially for Ni-Al alloy, hardness value is much lower, directly reduce the coating surface hardness of the whole. With the increase of doping amount, the higher the content of these substances, coating overall hardness value will drop more. Figure (b) as separate doping Cr surface hardness, the overall trend is also increased with the increase of doping amount of coating surface hardness gradually reduce, compared with Cr-Ni doping, surface hardness of the coating increased, this is because Ni is a ductile material, have played an important role in increasing coating toughness in the coating, so the doping Cr than Cr-Ni doped total hardness is higher.

Fig.5(A) and fig.5(B) in figure for Cr-Ni doping and the combination of doping Cr TiAlN coating to alone, compared with and without doping of TiAlN coating can be found that doping only within a certain range, the adhesion strength of the coating is increased with the increase of doping time increase, this is because the TiAlN coating with coating toughness increased after Cr, Ni, reduce the coating surface brittleness, so the adhesion strength of the coating increased. The adhesion of coating is related to the surface quality and microhardness of coating, and also to the composition and residual stress of coating. For TiAlN coatings co-doped with Cr-Ni, the binding force is higher than that of TiAlN coatings doped with Cr alone. This is because Ni in the former further increases the toughness of the coating and reduces the brittleness of the coating surface, so the binding force is improved. However, when the time of Cr-Ni co-doping and single doping Cr was 40min and 20min, the binding force of the coating was reduced, which may be because the doping time was too long, the coating was stratified and formed TiAlN composite coating, and the binding force between the coatings was reduced.
Fig. 5 surface hardness and adhesion of TiAlN coatings doped with Cr and Ni: (a) Surface hardness of Cr-Ni co-doped TiAlN; (B) Bonding force of Cr-Ni co-doped TiAlN coating; (b) Surface hardness of Cr-doped TiAlN coating; (B) Bonding force of Cr-doped TiAlN coating.

4. Conclusions
On the basis of the successful preparation of TiAlN coatings, Cr-doping and Cr-Ni co-doping were carried out under the optimal process parameters of TiAlN by multi-arc ion plating technology and magnetron sputtering technology. The doping amount of Cr and Cr-Ni was changed by changing the doping time of the magnetron controlled target, so as to study the influence of doping amount on the phase structure, surface hardness and adhesion of the coating. The research results are as follows:

1) According to EDS stratification diagram, it can be seen that the distribution of various components in the coatings is uniform, and the doping amount is directly proportional to the doping time.

2) According to the XRD diagram, the phase structure of the coating was consistent with that of the undoped TiAlN coating at the doping time of 10min. With the increase of doping time, Al-Ni alloy phase and CrN phase began to appear, and the peak strength also increased with the increase of doping amount.

3) The surface hardness value of the coating decreases with the increase of doping amount, and the binding force of the coating reaches the maximum at the doping time of 30 min, which is about 40 N. On this basis, if the doping time continues to increase, the binding force of the coating decreases, which is related to the formation of composite coating.

Acknowledgments
The authors wish to thank the Natural Science Foundation of Guangxi Province (2018GXNSFAA281244 and 2020GXNSFAA297060), China Postdoctoral Science Foundation Fund-
ed Project (2020M681092), the Projects of MOE Key Lab of Disaster Forecast and Control in Engineering in Jinan University (20200904006), and Guangdong Basic and Applied Basic Research Foundation (2020B15150004), Scientific Research and Technology Development Program of Guilin (2020010903), Engineering Research Center of Electronic Information Materials and Devices, Ministry of Education (EIMD-AB202009), Guangxi Key Laboratory of Information Materials (171019-Z, 191006-Z, and 201016-Z), and Innovation Project of GUET Graduate Education (2020YCX5118) for the financial support given to this work.

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