Oxidation Behavior of Cu Doped CrAlN Coating Deposited by Magnetron Sputtering at 800°C

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Abstract. CrAlN coating with moderate Cu content was deposited on the surface of 1Cr18Ni9Ti stainless steel by DC reactive magnetron sputtering. The oxidation behavior under 800°C of the coatings was investigated emphatically in this research. The phase construction, microstructure and chemistry contents were analyzed by X-ray diffraction (XRD), field-emission electron scanning microscope (FESEM) and energy disperse spectroscopy (EDS). And the mechanical properties of the coatings were measured by microhardness tester and multi-function scratcher. As a comparison, the properties of CrAlN coating were also analyzed in the article. The results showed that the microstructure of CrAlCuN coating became smoother and denser with a phase structure of CrN and Cu. With Cu doped in the CrAlN coating, the more excellent hardness which enhanced to 48.37 GPa was obtained. While the bonding strength of the coating was decreased because of the advanced microhardness usually released more internal stress. Both of the coatings were not complete failure and CrN diffraction peak was also tested. The oxidation rate of weight gain had significantly decreased with Cu doped, which improved the resistance of high temperature oxidation to a certain extent.

1. Introduction
The conventional binary nitride coatings have been paid extensive and close attention due to high hardness and excellent wear resistance over the past decades. TiN, as an early hard coating, has excellent mechanical properties but its moderate thermal stability limits its application areas [1]. In comparison, CrN coating exhibits enhanced performance under high temperature oxidation because of the formation of dense oxidation film. However, traditional binary coatings can’t satisfy the demand of use due to the increasingly harsh working environment [2]. Alloying transition metal elements into these binary coatings can improve the mechanical properties and thermal stability which may expand their application scope. The element Al has been studied most. CrAlN coating is developed from binary Cr-based coating, which may obtain advanced hardness and high-temperature oxidation resistance by adding Al [3-5]. The main reason for improved performance is the formation of dense and adherent (Cr, Al)2O3 mixed oxide film after high temperature annealing treatment. [6]. Previous studies indicated that the presence of Al in the coating formed a metastable phase in the cubic lattice of c-CrN coating. In addition, numerous works pointed that CrAlN coating had advanced resistance to high temperature oxidation, whereas its thermal stability is lower because of the presence of w-AlN during oxidation process [7]. And other researches pointed that the N-loss may be further aggravated with annealing process which has deteriorated the comprehensive practical properties and restricted its serviceable range. In certain studies that mixing the fourth element into CrAlN can constitute
quaternary coating and then improve the mechanical and thermodynamic properties of the coating [8]. Cu, as a transition metal element, is combined with N in terms of covalent bond in the coating, which can reduce the defect in coatings. The physical vapor deposition (PVD) to deposit coatings include high power impulse magnetron sputtering (HIPIMS), DC magnetron sputtering (DCMS), arc ion plating and so on [9].

This work is aimed to investigate the resistance of high temperature oxidation of CrAlN and CrAlCuN coatings. We deposited CrAlN and CrAlCuN coatings by closed filed unbalanced magnetron sputtering respectively. And the crystallographic phase and growth orientation of the coatings were identified by an X-ray diffractometer (XRD) with a scanning speed of 5.0 degree/min, step of 0.02° and the scanning angle was 20°-80°. The surface morphology was observed by scanning electron microscope (SEM) and the elemental composition of the films was confirmed by X-ray energy dispersive spectroscopy (EDS). Hardness of the coatings was measured by digital microhardness tester and the bonding strength was tested by multi-functional material surface performance tester that the value can be determined by the change of the sound signal. The resistance of high temperature oxidation of the coatings was investigated by the thermo gravimetric analysis where the oxidation temperature should be limited to ~800°C which is constant in 24h.

2. Experimental

CrAlN and CrAlCuN coating were deposited in stainless steel 316L which were incised as lump with the size of 15mm*10mm*2mm and published with waterproof abrasive paper of 400, 800, 1200, 2000# and cloth polishing with diamond paste (Ra=0.5μm). Passed through a process of ultrasonic cleaning with alcohol and acetone orderly, the substrates need to be dried and keep them in alcohol. There is a schematic diagram of the instrument in Figure 1. The vacuum chamber has four targets and the cooling water recirculation system was behind the sheet copper on the back of the target. What’s more, the symmetrical magnetrons surround the target can release the closed magnetic field that can effectively avoid the loss of electrons thus the deposition radio of coatings and the ionization rate have been greatly improved [10-11]. The cylindrical sample stable kept a certain distance from the target that can enhance the uniformity of polymer film. The major parameters are that the based pressure was ~10⁻² Pa and the substrate temperature was kept at 270°C. The gas flow velocity of nitrogen and argon was 18 and 12 sccm, respectively. During the deposition process, the working pressure kept 0.5Pa. Prior to depositing the coatings, the stainless steel substrates should be bias cleaning 30 min. A Cr and CrN intermediate layer was prepared before depositing the CrAlN coatings, which was in order to decrease the effect of stress mutation between substrate and the CrAlN coating.

![Figure 1. The principle diagram of CFUMS system.](image-url)
Results and discussion

The phases of CrAlN and CrAlCuN coatings. Figure 2 shows the XRD patterns of the CrAlN and CrAlCuN coatings before oxidation. The diffraction patterns of CrAlN coating revealed that a crystal structure of CrN phase and a faint diffraction peak of Cu were detected in the CrAlCuN coating. Both of the coatings were presented a dramatically (200) preferred orientation with several major crystal orientation of (220), (222) and the preferential growth was not changed in the coatings [12]. However, the diffraction peaks of CrN phase were moved to the small angle that the main reason may be attributed to the adulteration of Cu. The mechanism of above reason was that Cu as a 3d transition metal element possibly changed the defect type so that cause lattice distortion [13]. What’s more, the intensity of the diffraction peak has enhanced in the CrAlCuN coating. According to the Scherrer Formula that the full width at half maximum of the preferred orientation diffraction peak decreased indicated the grain size changed larger. And the surface morphology of the CrAlN and CrAlCuN
coatings had confirmed this point, which showed in Figure 4. The patterns of the coatings after oxidation annealing were exhibited in Figure 3. In the patterns, we can find that there were some diffraction peaks of the metallic oxide (Al₂O₃, Cr₂O₃) and the diffraction peaks of CrN were also detected. Combine the EDS (Table.1) that the N-loss was extremely serious and we can draw a conclusion that the CrAlN coating was nearly complete failure. While the CrAlCuN coating still contain CrN phase with a preferred orientation of (200) after oxidation annealing that can also provide protection to the substrate.

![Figure 4](image)

**Figure 4.** The SEM image of the coatings before oxidation: (a) CrAlCuN (b) CrAlN the surface morphology of the coatings after oxidation: (c) CrAlCuN (d) CrAlN

3.1. The surface microstructure and chemical composition of the coatings

Figure 4 shows that the surface morphology about the coatings before and after oxidation. In the image (b) that the grains of the CrAlN coatings present distinct triangular pyramid shape and there were some micro cracks on the surface which can also observed little metal particles. The surface topography of CrAlCuN coating in picture (a) revealed a dense and flat structure with no obvious defection. The grain size of CrAlCuN coating was refined comparison with the CrAlN coating that attributed to the adulteration of Cu. And the images (c) and (d) exhibited that lager oxidizing materials emerged on the appearance. The metal oxide particles agglomerate into lumps with a crack on the exposed matrix that revealed the coating was severe oxidation in order that the film was not protective to the stainless steel substrate in picture (d). While the photo (c) appeared large amounts of granular oxides and the oxides were more dense compared with it in image (c), which signified the resistance of high temperature oxidation of CrAlCuN coating was more excellent contrast with the CrAlN coating.

![Figure 5](image)

**Figure 5.** The hardness and bonding strength of the coatings.

3.2. The mechanical properties of the coatings

The hardness and bonding strength of the coatings were showed in Figure 5. The hardness presented enhanced tendency and the bonding strength was reduced with Cu doped. The soft metal Cu
adulterated in the coating may cause the hardness decreased. While the surface microstructure of the CrAlCuN coating showed in Figure 4 indicated that the grain had refined, and became more smoother. Some research pointed that the Cu content in the coating had a limitation about 1%-5%. The Cu as soft phase played a leading role when it exceeded the limitation. In this work, the Cu content was 1.41at% and the result brought into correspondence with Pan’s research [14-17]. And compared with the increasing trend of hardness, the bonding strength usually presented a reverse tendency.

Table 1 enumerated the chemical composition of the coatings after oxidation annealing with surface scanning. From the Table 1, a variety of elements have been detected including several matrix elements such as Fe, Mn, Ni and O, whereas no N was discovered that the result was in agreement with the phase analysis in Figure 3. It can observe that the outer diffusion of the matrix elements appear, which may produce the crisp oxide and further cause the film to crack or fall off. And in the Table 2 the same situation was happened except that the N still preserved in the coating which account for that although the coating was oxidation, still kept excellent thermal stability and played a protective role to a certain degree.

### Table 1. The chemical composition of CrAlN coating after oxidation annealing by EDS.

| Elements | Weight [%] | Atom [%] |
|----------|------------|----------|
| O        | 22.21      | 46.07    |
| Al       | 7.58       | 9.33     |
| Si       | 0.33       | 0.39     |
| Cr       | 60.90      | 38.88    |
| Mn       | 1.06       | 0.64     |
| Fe       | 7.29       | 4.33     |
| Ni       | 0.63       | 0.35     |
| Summation| 100.00     | 100.00   |

### Table 2. The chemical composition of CrAlCuN coating after oxidation annealing by EDS.

| Elements | Weight [%] | Atom [%] |
|----------|------------|----------|
| N        | 7.16       | 15.27    |
| O        | 21.14      | 39.47    |
| Al       | 8.57       | 9.48     |
| Cr       | 56.22      | 32.29    |
| Mn       | 1.64       | 0.89     |
| Fe       | 1.84       | 0.99     |
| Cu       | 3.43       | 1.61     |
| Summation| 100.00     | 100.00   |

3.3. The analysis of the oxidation weight curve of thin films

Figure 6 shows the kinetic curve about the coatings. From the image that the general trend of the coatings after oxidation annealing is that as the oxidation time changes its oxidation rate increases first and then decreases and the main reason was that the initial phase of oxidation is dominated by the diffusion of oxygen so that it did not produce enough dense metal oxide protective film. As the oxidation time lengthened, the coatings surface were cladding with (Cr, Al)2O3 oxide film which could postpone the process of oxidation [18]. However, the diffusion of oxygen aggravated that caused the bonding force of the coatings became weaken, what’s more, crack of drop occurred followed. The matrix element such as Fe, Ni presented external diffusion in this process, which is consistent with the EDS analysis results. The oxidative weight curve of CrAlN coating is much lower than the CrAlCuN coating. The main reason is that the primary channel of the oxygen atoms diffuse depended on the grain boundary and defect [19], the Cu can refine the size of grains and reduce the boundary,
what’s more, it can change the type of the deflection in the coatings to a certain extent, which reduced the diffusion rate of oxygen in the coatings and slow the oxidation process [20-21].

![Figure 6. The oxidizing dynamics curve of coatings.](image)

4. Conclusion
The phase structure of CrAlN and CrAlCuN coatings deposited by DC reactive magnetron sputtering was basically CrN and Cu with a preferred orientation of CrN (200) before oxidation. And after oxidation annealing, both of the coatings were appeared the diffraction peaks of metal oxide.

The size of grains in CrAlCuN coating was smaller than CrAlN coating. And the CrAlN coating oxidized seriously than CrAlCuN coating.

The hardness of the coatings was increasingly from 30.17 GPa to 4837 GPa with the adulteration of Cu. While the bonding force of the CrAlCuN coating was 8N that lower than the CrAlN coating with a value of 16N.

The oxidation process of the CrAlCuN coating was slower than CrAlN coating and trend of coatings after oxidation annealing is that as the oxidation time changes its oxidation rate increases first and then decreases.

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