Influence of $N_2$ partial pressure on structure and oxidation-resistance of (CrAlSi)N coatings by arc ion plating

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**Keywords:** Arc ion plating, (CrAl)N coating, (CrAlSi)N coating, structure, oxidation-resistance

**Abstract.** Composite (CrAl)N and (CrAlSi)N hard coatings were deposited on 1Cr11Ni2W2MoV steel sheets by arc ion plating system under different $N_2$ partial pressure (1Pa, 2Pa or 4Pa) respectively. The composition, microstructure, phase composition and oxidation resistance were characterized by SEM, EDS and XRD. With the $N_2$ partial pressure increasing from 1Pa to 4Pa, (CrAl)N kept its B1 structure and the (CrAlSi)N changed the phase structure from blends of B1 and B4 to single B4, the content of Al and Si decreased slightly, and the density of droplets decreased and the structure density improved. Oxidation experiments at 900°C show that increased of $N_2$ partial pressure and the introduction of Si into the (CrAl)N can block the phase seperationg and increase the oxidation resistance of the coatings.

**Introduction**

CrN coating prepared by physical vapor deposition (PVD) has been widely utilized as hard coatings for cutting or forming tools owing to its high hardness and good chemical stability [1, 2]. In order to further improve the hardness and the corrosion-resistance of the coating, Aluminum or Silicon can be introduced to CrN to form ternary (CrAl)N [3] or (CrSi)N [4]. solid solution strengthening plays important role to improve the young’s modulus and the hardness. And since the chromium, aluminum and silicon could form protective oxides at high temperature, (CrAl)N and (CrSi)N coatings exhibit excellent oxidation-resistance. The alloying of (CrAl)N with silicon to form quaternary (CrAlSi)N could lead to crystalline refinement, super-hardness and improved anti-oxidation properties. CrN, (CrSi)N and (CrAlSi)N can be prepare by PVD technique such as magnetron sputtering, Electron beam deposition, arc ion plating, and et al.. Among these PVD methods, arc ion plating has the outstanding advantage such as the high ionization rate, rapid deposition rate, stable process and excellent adhesion strength between coating and substrate [5]. Thus it is the most widely used in tool coating. But one of its disadvantages is the droplet deposition from the target during the coating deposition process. Reactive gas partial pressure would give rise to the change of moving path of the arc pot and the size and amount of the droplets. And the micro-structure and mechanical and chemical properties are also influenced by the active gas partial pressure. In this paper, the $\text{Cr}_{0.3}\text{Al}_{0.7}\text{N}$ and $\text{Cr}_{0.3}\text{Al}_{0.6}\text{Si}_{0.1}\text{N}$ coatings were prepared by arc ion plating method under the different $N_2$ partial pressure of 1Pa, 2Pa and 4Pa. The coating morphologies, the phase structure and the oxidation resistance at 900°C were investigated.

**Experimental methods**

1Cr11Ni2W2MoV steel sheets with the dimensions of 15mm×10mm×2 mm were used as substrates. The steel sheets were prepared by mirror polishing, followed by ultrasonic cleaning in alcohol and acetone solution, and then were sputter-cleaned using Ar ion under 1000V negative bias voltage to remove contaminant layer.
Composite metastable Cr\(_{0.3}\)Al\(_{0.7}\)N or Cr\(_{0.3}\)Al\(_{0.6}\)Si\(_{0.1}\)N hard coatings were respectively deposited in a mixed Ar/N\(_2\) atmosphere by the arc ion plating system (DH-8) using Cr\(_{0.3}\)Al\(_{0.7}\) or Cr\(_{0.3}\)Al\(_{0.6}\)Si\(_{0.1}\) alloy target. The base pressure in the chamber was less than 5×10\(^{-3}\) Pa. To clean and activate the substrates, the steel sheets were bombarded by argon ions with a pulse bias of -1000V peak voltage, 30% duty cycle and 20kHz frequency. After the substrate sheets were bombarded the (CrAl)N and (CrAlSi)N coatings were deposited. The deposition parameters were listed as following: deposition temperature 260\(^{\circ}\)C, N\(_2\) partial pressure 1Pa, 2Pa or 4Pa, the current of arc cathode target 90A, the pulsed bias -450V with duty cycle of 30% and frequency 20KHz, the distance from the target to substrates 30cm, the deposition time 105min.

For the high temperature oxidation experiment, the deposited samples were annealed at 900\(^{\circ}\)C for 50h in a chamber-type electric furnace. Prior to producing cross samples, chemical plating Ni protective films were deposited on the surface of oxidized samples.

The surface and cross-sectional morphologies of the as-deposited and oxidized coatings were investigated using a field emission scanning electron microscope (FESEM). The chemical composition was identified by EDS. The phase structures were characterized by XRD with Cu K\(\alpha\) radiation.

### Results and Discussion

Elemental compositions of the (CrAl)N and (CrAlSi)N, which was analyzed by EDS, were listed as Table 1. For (CrAl)N, the ratio of Al/(Cr+Al) was lower than that in the Cr\(_{0.3}\)Al\(_{0.7}\) target. In the same way, the ratio of Al/(Cr+Al+Si) or Si/(Cr+Al+Si) was lower than that in the Cr\(_{0.3}\)Al\(_{0.6}\)Si\(_{0.1}\). During the deposition process of arc ion plating, the high ionization and the application of bias lead to the “resputtering” of the as-deposited coating. The atom Al or Si is lighter and is bonded to the coating less firmly than Cr and is easier resputtered off from the coating. For both (CrAl)N and (CrAlSi)N coatings, the nitrogen content was higher than 50% and almost kept unchanged with the increase of N\(_2\) pressure.

<table>
<thead>
<tr>
<th>Nitrogen partial Pressure(Pa)</th>
<th>Composition[at.%]</th>
<th>Al/(Cr+Al)</th>
<th>Al/(Cr+Al+Si)</th>
<th>Si/(Cr+Al+Si)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(CrAl)N-1Pa</td>
<td>55.89</td>
<td>29.24</td>
<td>14.87</td>
<td>66.42</td>
</tr>
<tr>
<td>(CrAl)N-2Pa</td>
<td>55.68</td>
<td>29.89</td>
<td>14.43</td>
<td>67.44</td>
</tr>
<tr>
<td>(CrAl)N-4Pa</td>
<td>55.33</td>
<td>29.65</td>
<td>15.02</td>
<td>66.38</td>
</tr>
<tr>
<td>(CrAlSi)N-1Pa</td>
<td>53.59</td>
<td>29.04</td>
<td>4.31</td>
<td>13.06</td>
</tr>
<tr>
<td>(CrAlSi)N-2Pa</td>
<td>55.61</td>
<td>26.28</td>
<td>3.83</td>
<td>14.29</td>
</tr>
<tr>
<td>(CrAlSi)N-4Pa</td>
<td>56.12</td>
<td>24.37</td>
<td>3.69</td>
<td>15.82</td>
</tr>
</tbody>
</table>

The surface morphologies and cross-section morphologies were shown in Fig. 1 and Fig. 2. For all the coatings there existed big amount of droplets of different size from several hundred nanometers to several micrometer. The increased active reactive N\(_2\) pressure led to the obvious decrease of the quantity and number of the droplets. As shown in Fig.2, (CrAl)N coatings deposited under 1Pa and
2Pa form exhibited typical columnar structure. For the (CrAl)N of 4 Pa, the columnar structure disappeared. The introduction of Si into the coatings caused the featureless dense structure instead of the columnar one. There were few droplets embedded inside the coating, indicating most of the droplets were respattered away from the coating surface under -450V pulse bias voltage.

The XRD spectra of the as-deposited (CrAl)N and (CrAlSi)N coatings were shown in Fig.3 and Fig.4. (CrAl)N coatings have B1 NaCl phase with the diffraction peaks of (111), (200), (220), (311) and (222). There is no obvious preferred orientation for all (CrAl)N coatings. The difference of the N\textsubscript{2} pressure hardly
had effects on the phased structure and the diffraction peak intensity. (CrAlSi)N Coating of 1Pa exhibited a dual-phase structure with B1 NaCl and B4 ZnS. While the (CrAlSi)N Coatings prepared under 2Pa or 4Pa still kept the B1 structure. The critical content of AlN for phase transition in the Cr1-xAlxN pseudobinary system was 77.2%, which predicted by using the structural map based on the band parameters [6]. Clearly the incorporation of Si into the coating decreased the critical content of AlN for transition from B1 to B4. All B1 peaks are considerably shifted to higher angles while B4 peaks shifted to lower angles compared with the standard peak positions of AlN or CrN, and which was ascribed to intersubstitution of Cr and Al in the lattice. For (CrAlSi)N, the decrease of N\textsubscript{2} pressure gave rise to significant decrease of grain size which was indicated by the increase of the FWHM.

![Fig.3 XRD patterns of as-deposited of (CrAl)N coatings of different N\textsubscript{2} partial pressure](image)

![Fig.4 XRD patterns of as-deposited of (CrAlSi)N coatings of different N\textsubscript{2} partial pressure](image)

Fig. 5 showed the surface morphologies of (CrAl)N and (CrAlSi)N after oxidation at 900°C for 50h. The crystals of oxide were clearly identified on the surface of (CrAlN). The oxide film became denser and the crystals became finer as the (CrAl)N was prepare under the higher N\textsubscript{2} pressure. For the oxidized (CrAlSi)N of 1Pa, a dense and uniform oxide was formed. But there was no obvious change on the surface of (CrAlSi)N coatings deposited under 2Pa or 4Pa. The cross-section morphologies shown in Fig.6 indicated the a continuous and compact thin oxide film was formed on the (CrAl)N surface and the increased N\textsubscript{2} pressure during the preparation of the coatings caused the thinner oxide films. The incorporating of element silicon into the coatings made the oxide films thinner. Moreover the increased N\textsubscript{2} pressure led to the decrease of the thickness of oxide. For (CrAlSi)N deposited under pressure of 2Pa or 4Pa, the oxide layer was too thin to identified in SEM magnification. For all (CrAl)N of different N\textsubscript{2} pressure and (CrAlSi)N of 1Pa N\textsubscript{2} pressure the nitride layer became thicker compared with the as-deposited coating, which indicating some change took place in the nitride layer. While the (CrAlSi)N prepare under N\textsubscript{2} pressure of 2Pa or 4Pa show no change of thickness. For (CrAl)N and (CrAlSi)N of 1Pa N\textsubscript{2} pressure, the interface of nitride and steel became irregular, which show the interdiffusion between the nitride coating and steel. The EDS revealed the element Cr was accumulated in the interface. The application of higher N\textsubscript{2} pressure inhibited the interdiffusion and eliminated the accumulation of element Cr in the interface.
The XRD patterns of oxidized (CrAl)N and (CrAlSi)N for 50h at 900°C were respectively shown in Fig. 7 and Fig.8. For all (CrAl)N coatings, the blend oxide of Al₂O₃ and Cr₂O₃ formed. The patterns of B1 and B4 were detected, illustrating the metastable (CrAl)N separated into CrN and AlN. The annealed (CrAlSi)N of 1Pa N₂ pressure occurred decomposition and oxidation. But when the deposition pressure got to up 2Pa and 4Pa, the (CrAlSi)N did not occurred separation and only was oxidized slightly. From above mentioned, it was concluded that the doping of Si and increasing N₂ pressure was conductive to the stability and oxidation-resistance for the coatings.
The incorporation of element silicon into (CrAl)N and the increase of N2 pressure during the deposition process gave rise to the improvement of coating density and increase of phase stability and anti-oxidation for (CrAl)N coatings.

Acknowledgement
This research was financially supported by the Provincial Scientific and Technological Support Plan of Jiangxi (No. 20122BBE500030), the National Natural Science Foundation (No. 51461016) and the Province Natural Science Foundation of Jiangxi (No. 20122BAB206019).

References