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

Ren-Dong WANG[1,a], Zhao-An LIU[2,b], Shu-Juan ZHANG[1,c] and Ming-Sheng LI[1,d*]

[1] Jiangxi Normal University of Science and Technology, Nanchang, 330038, China

[2]Rizhao Technicians college, Rizhao 276800, China

[a]rdwang_jx@163.com, [b]liuzhaoan_rz@163.com, [c]shujuan866@163.com, [d]mshli@163.com

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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 stuctrue 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 depostion from the target during the coating depostion process. Reactive gas partial pressure would give rise to the change of moving path od 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 gase partial pressure. In this paper, the $Cr_{0.3}Al_{0.7}N$ and $Cr_{0.3}Al_{0.6}Si_{0.1}N$ 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 bombed by argon ions with a pulse bias of -1000V peak voltage, 30% duty cycle and 20kHz frequency. After the substrate sheets were bombed the (CrAl)N and (CrAlSi)N coatings were deposited. The deposition parameters were listed as following: deposition temperature 260ºC, N_2 partial pressure1Pa, 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°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 Kα 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 boned to the coating leaker 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 the increase of N_2 pressure.

Table 1. Composition of (CrAlN) and (CrAlSi)N prepared under different N_2 partial pressure

Nitrogen partial Pressure(Pa)	Composition[at.%]				Al/(Cr+Al)	Al/(Cr+Al+Si)	Si/(Cr+Al+Si)
	N	Al	Si	Cr	(%)	(%)	(%)
(CrAl)N-1Pa	55.89	29.24	—	14.87	66.42	—	—
(CrAl)N-2Pa	55.68	29.89	—	14.43	67.44	—	—
(CrAl)N-4Pa	55.33	29.65	—	15.02	66.38	—	—
(CrAlSi)N-1Pa	53.59	29.04	4.31	13.06	—	62.57	9.29
(CrAlSi)N-2Pa	55.61	26.28	3.83	14.29	—	59.19	8.63
(CrAlSi)N-4Pa	56.12	24.37	3.69	15.82	—	55.54	8.41

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

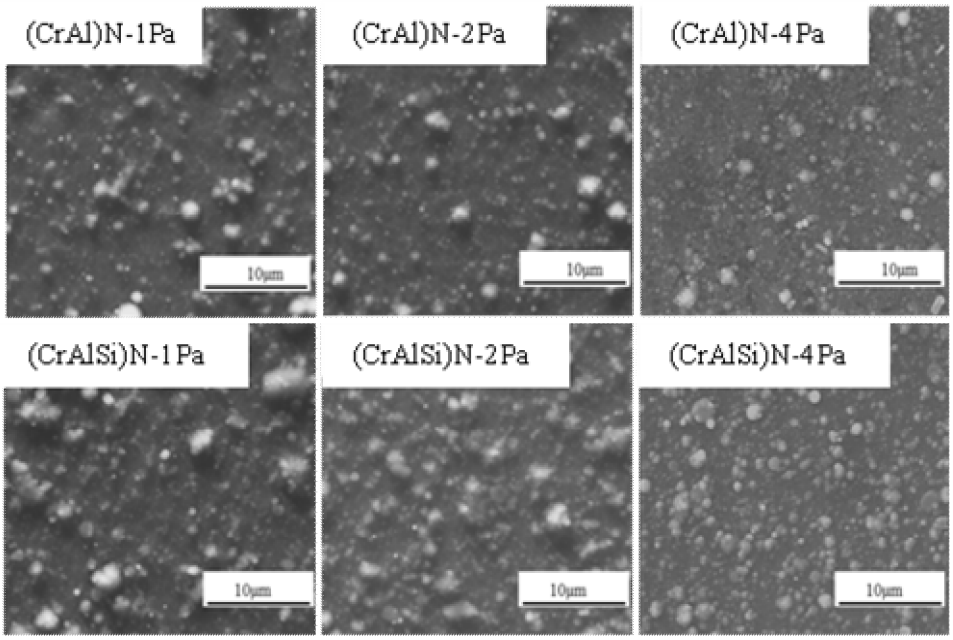

Fig.1 Surface morphologies of (CrAl)N and (CrAlSi)N coatings of different N_2 partial pressure

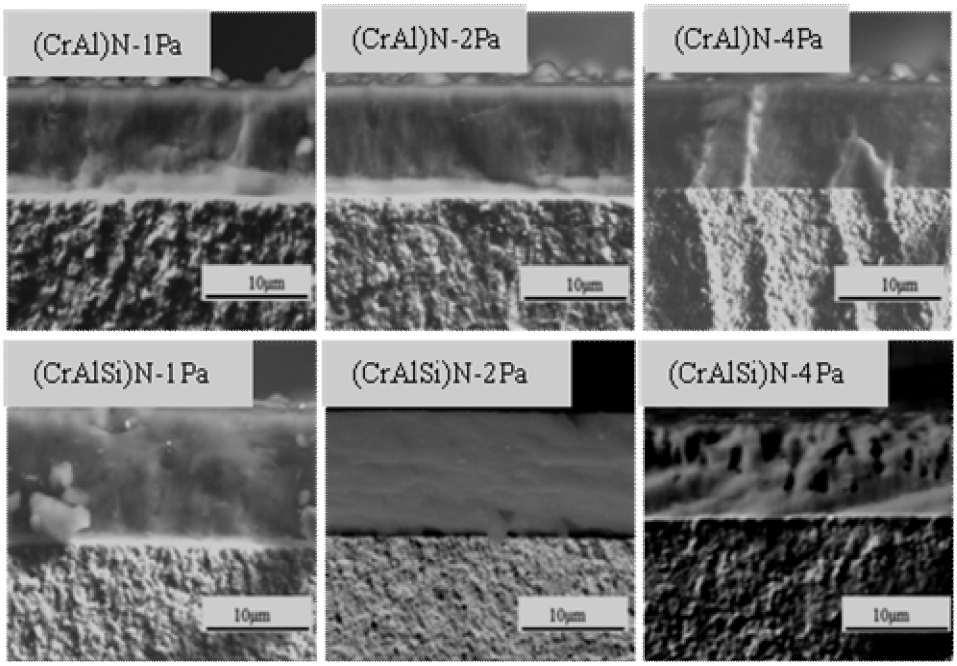

Fig.2 Cross-section morphologies of (CrAl)N and (CrAlSi)N coatings of different N_2 partial pressure

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 resputtered 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_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 B1structure. Critical content of AlN for B1/B4 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_2 pressure gave rise to significant decrease of grain size which was indicated by the increase of the FWHM.

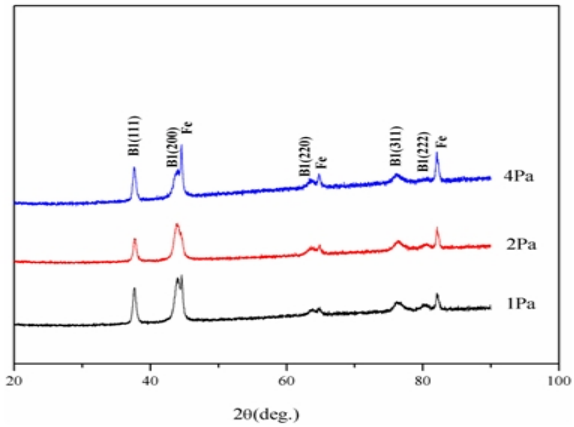

Fig.3 XRD patterns of as-deposited of (CrAl)N coatings of different N_2 partial pressure

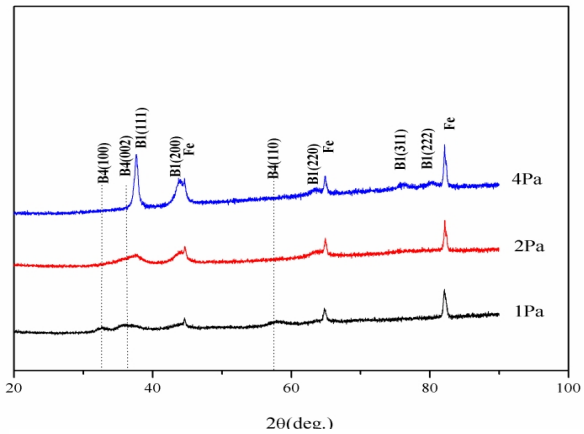

Fig.4 XRD patterns of as-deposited of (CrAlSi)N coatings of different N_2 partial pressure

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_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_2 pressure during the preparation of the coatings caused the thinner oxide films. The incorporating of element silicion into the coatings made the oxide films thinner. Moreover the increased N_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_2 pressure and (CrAlSi)N of 1Pa N_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_2 pressure of 2Pa or 4Pa show no change of thickness. For (CrAl)N and (CrAlSi)N of 1Pa N_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_2 pressure inhibited the interdiffusion and eliminated the accumulation of element Cr in the interface.

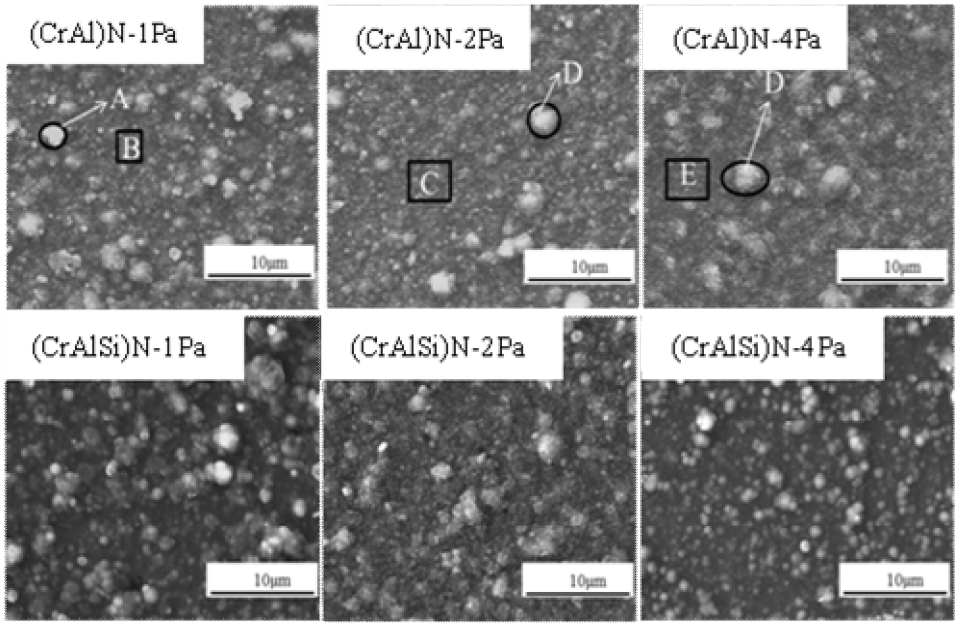

Fig.5 Surface morphologies of (CrAl)N and (CrAlSi)N coatings oxidized at 900°C for 50h

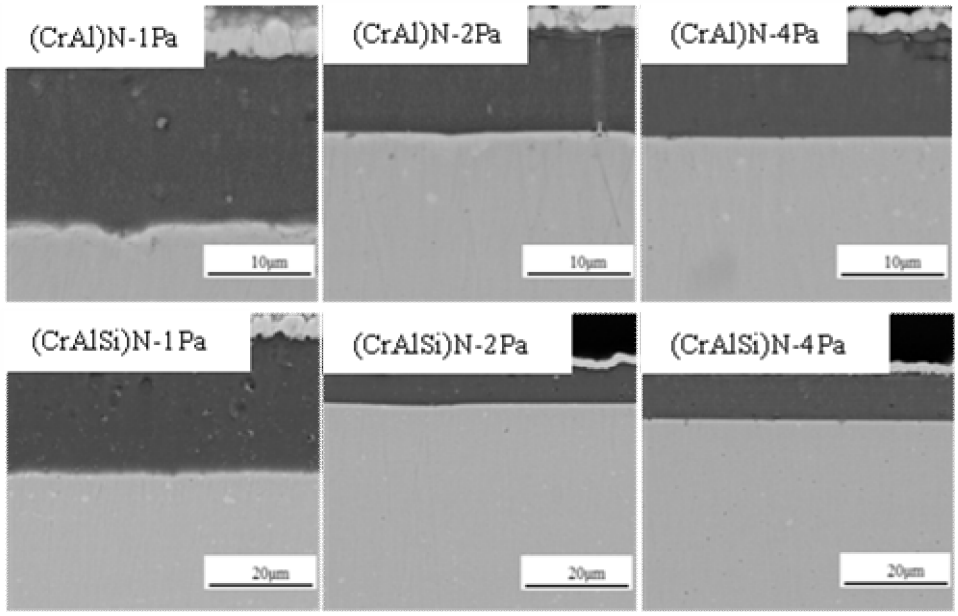

Fig.6 Cross-section morphologies of (CrAl)N and (CrAlSi)N coatings oxidized at 900°C for 50h

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 Al_2O_3 and Cr_2O_3 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 N_2 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 N_2 pressure was conductive to the stability and oxidation-resistance for the coatings.

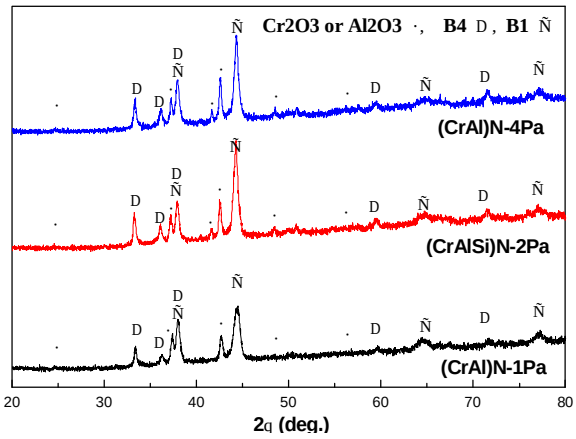

Fig.7 XRD patterns of (CrAl)N coatings after oxidation at 900 °C for 50h

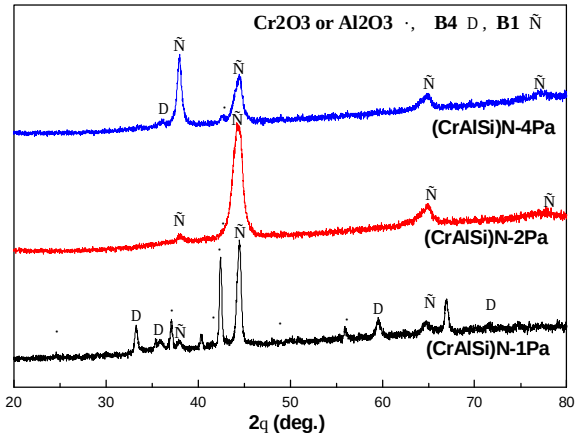

Fig.8 XRD patterns of (CrAlSi)N coatings after oxidation at 900 °C for 50h

Summary

The incorporation of element silicon into (CrAl)N and the increase of N_2 presure 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

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References

[1] B. Navinšek, P. Panjan, I. Milošev: Surface & Coatings Technology Vol. 97 (1997), p. 182

[2] S.K. Pradhan, C. Nouveau, A. Vasin, et al.: Surface & Coatings Technology Vol. 200 (2005), p. 141

[3] Y.C. Chim, X.Z. Ding, X.T. Zeng, et al.: Thin Solid Films Vol. 517 (2009), p. 4845

[4] H.Y. Lee, W.S. Jung, J.G. Han, et al.: Surface & Coatings Technology Vol. 200 (2005), p. 1026

[5] K.C. Baek, C.Y. Seo, K.B. Heo, et al.: Materials Science Forum Vol. 706-709 (2012), p. 2589

[6] Y. Makino: Surface & Coatings Technology Vol. 193 (2005), p. 185.