Wear and Corrosion properties of CrSiCN coatings deposited by cathodic arc deposition process

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Abstract. In this study, three CrSiN based coatings were fabricated using cathodic arc deposition (CAD) technique. CrSiCN coatings were obtained by using metal plasma activated CAD process to decompose the C_2H_2 and N_2 reactive gas. The analyzed CrSiCN coatings were obtained with higher hardness and smooth surface. With addition of Si (8.7 at.%) and C (41 at.%) in the coatings, the hardness increased to Hv3300 which is resulted from the addition of CrCN and CNx new phases. Tribological test shows the coefficient of friction of CrSiCN down to 0.2 was observed with the addition of Si and C, related to hardness and smooth surface. However, the corrosion resistance of the CrSiN coating is better than that of CrSiCN coating in the 1M H_2SO_4 solution at room temperature.

1. Introduction

Traditionally, CrN coatings are characterized by superior corrosion and oxidation resistance as compared to TiN coating. However, CrN coating is not as hard as TiN coating. By adding Si element into the CrN coating, CrSiN coatings have appeared better mechanical properties, tribological properties, and thermal stability [1-9]. CrSiN coatings, featured with nanocomposite structure that comprises nanocrystalline and amorphous phases, can be a potential material for tool applications. Previous studies have shown that the corrosion resistance of the CrSiN coatings was further improved by using cathodic arc deposition technology with pulsed current input [10]. The interfacial electrical resistance of CrSiN coatings deposited on AISI 304 stainless steel substrates similar with the blank substrate was confirmed. The improved corrosion behavior can be obtained by using the pulsed current of 90/120 and 90/150 A via cathodic arc deposition process [10]. Generally, the formation of nanocomposite structure and fine grain size can mainly contribute to the improved properties of the

CrSiN coatings. Carbon (C) is known to further reduce the friction coefficient and improve wear resistance of the coatings. Recently, CrSiCN coating was to be a potential coating as well [11-14]. The alloying effects from Si and C on the structure and properties of the CrSiCN coatings were to be investigated. The CrSiN or CrSiCN coatings were usually deposited via physical vapor deposition methods, especially magnetron sputtering techniques [14]. However, cathodic arc deposition (CAD) is known to be a vital technique to deposit hard coating on the cutting tools. In this study, CrSiN and CrSiCN coatings by using CAD process with different C_2H_2 and N_2 mixture as a reactive gas were compared in the field of the wear and corrosion properties.

2. Experimental

The CrSiN and CrSiCN coatings were deposited on AISI 304 stainless steel and tungsten carbide coupons in a cathodic arc deposition system (CAD). Two circular cathodic arc sources (dia. 150 mm) were installed face to face in the chamber, with a distance to substrate holder of 150 mm apart. One Cr target and one $Cr_{80}Si_{20}$ target were used as cathodic arc sources during the coating depositions. Prior to depositions, the chamber was pumped down to a base pressure below 1.0×10^{-3} Pa. Then the substrates were cleaned by Ar+ glow discharged plasma at 1.3 Pa using a dc bias voltage of −800 V for 30 min. As for the coatings, layered structure containing Cr/CrN/CrSiN and Cr/CrN/CrSiN/CrSiCN was designed to insure the best adhesion with the substrate. Different ratio of C_2H_2 and N_2 mixture gas was introduced to form CrSiN and CrSiCN coatings via different flow rate. Scanning electron microscopy (SEM; model JOEL JSM-5600) was carried out to observe the surface morphology of the various samples. Chemical compositions of the coatings were measured using energy dispersive X-ray spectroscopy (EDS). A surface roughness measurement meter was used to measure the surface roughness of the coating. The hardness H was obtained using a Vicker's Hardness Tester under the different load of 0.01 to 0.05Kg. The tribological properties of the coatings were evaluated using a conventional ball-on-disc tribometer without any lubricant under a normal load of 5 N with a 6-mm diameter WC ball as a counterpart material. The corrosion resistance of the coated AISI304 stainless steel was investigated by in corrosive medium of 1M H_2SO_4 solution to simulate the aggressive aqueous environment. The electrode potential was scanned from −0.8 to 0.8 V at the scanning rate of 1.0 mV/s.

3. Results and Discussion

Fig. 1 shows the surface morphologies of the deposited CrSiN and CrSiCN coatings on WC-8%Co substrates with different C_2H_2 and N_2 mixture gas. It is clearly observable that the deposited CrSiN and CrSiCN coatings were dense structure, however, macroparticles emitted from the target were seen on the surface. Macroparticles are liquid or solid debris particles that are produced at cathode spots. Their presence is the most severe limitation to cathodic arc deposition technology. From the Fig. 1, the

size of the macroparticles emitted from the metal targets was in the range up to $1\,\mu m$ which was related to the poison phenomena by introducing C_2H_2 and N_2 mixture gas in this study. Table 1 shows the surface roughness of the coatings. The C_2H_2 seems to reduce the size and quantity of the macroparticles. Therefore, the surface roughness of the CrSiCN coating ($0.06\,\mu m$) is smoother than that of CrSiN coating ($0.11\,\mu m$). The compositions of the coatings were analyzed by EDS as shown in Table 1. The higher C_2H_2 and N_2 mixture gas ratio leads to the higher C/N ratio in the coatings. However, Si content in the coatings exhibits a reverse trend of decreasing amount as the C_2H_2 gas increases. Previous study [10] shows the XRD patterns of the CrSiN coatings with (1 1 1), (2 0 0) orientation can be clearly indicated a fcc B1 NaCl-type crystal structure. As Si/(Cr+Si) concentration is about 18%, the CrSiN coating is exhibited a network structure which is comprises of CrN and SiNx phases [2]. Similar, the incorporation of Si and C in the coating may also induce phase transformation of crystalline fcc B1 NaCl-type structure (CrN, CrCN) and amorphous SiNx and CNx phase due to Si and C concentrations are high enough in this study.
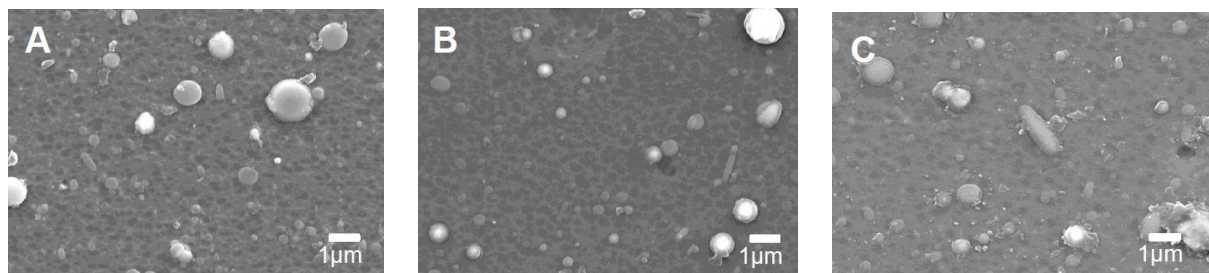

Figure 1. Surface morphologies of the coatings, A:CrSiN, B: CrSiCN, C_2H_2 and N_2 mixture gas ratio 1:1, C: CrSiCN, C_2H_2 and N_2 mixture gas ratio 3:1.

Table 1. Composition of the studied coatings analyzed by EDS

sample	C_2H_2/N_2 ratio	Cr (at.%)	Si (at.%)	N (at.%)	C (at.%)	Roughness (Ra, μm)
A-CrSiN	0/1	45.23	10.24	44.53	--	0.11
B-CrSiCN	1/1	31.28	8.70	18.50	41.53	0.06
C-CrSiCN	3/1	33.43	5.18	7.93	53.45	0.06

Fig. 2 shows the hardness of the CrSiN and CrSiCN coatings obtained by Vicker's hardness measurement under different loading rate. The hardness of the samples, related to the increasing indenter depth with increasing load, is the combination of hardness of coating and substrate. The higher hardness is obtained by lowering the indenter load. The hardness of the CrSiN coatings was found to be Hv2850 at the load of 0.01Kg. Similar work was achieved that the highest hardness of the CrSiN coating was observed for the Si content around 7-10 at.% [9]. Both CrSiCN coatings increased

its hardness with C introduced in the coatings. Apparently, the main effect can be anticipated by the solid solution hardening due to the substitution the Cr atom site for Si and C atom site. The hardness of the CrSiCN coating further increased to maximum values of Hv3300 (sample C) and Hv3000 (sample B), as the C increased to 41 and 53 at.%, respectively. Similar work by examining the XPS and TEM results [9, 14], a complete phase separation of CrN, CrCN nanocrystalline and SiNx and CNx amorphous phases has been achieved in CrSiN and CrSiCN coating, respectively. Therefore, it can be concluded that the hardness enhancement of CrSiCN coating is from the effects of solid solution hardening by CrCN nanocrystalline and the interface strengthening by SiNx and CNx.

Fig. 3 shows the coefficient of friction (COF) value of the CrSiN and CrSiCN coatings sliding against a WC–Co ball. In dry sliding tests, the CrSiN coating exhibited a similar COF of 0.5 to that of the previous work (COF=0.56) [9]. The COF value of CrSiCN coatings was decreased to 0.2 when the Si% was decreased below to 8.7 at.% and C% increased above to 41 at.%, respectively. Unlike CrSiN coating, the COF decreased obviously with the addition of Si and C, which can have a beneficial impact on the wear resistance. The decrease in the COF is mainly related to the increase of the hardness and smooth surface which is attributed to CrCN and CNx phases, acted as lubricant phase in the coatings. However, some peaks of COF during the wear test may be accompanied with crack of the coating due to the increase of the hardness. A better wear resistance of the CrSiCN coated tungsten carbide obtained is the potential application for the tools.
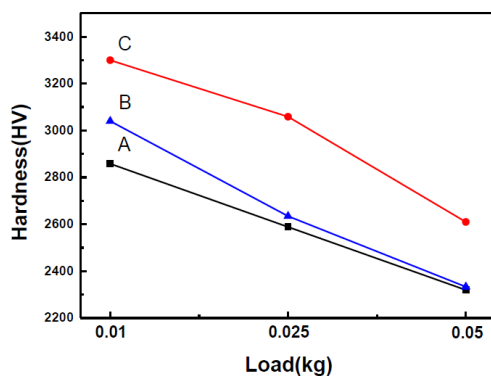

Figure 2. The hardness of the CrSiN and CrSiCN coatings obtained by Vicker's hardness measurement under different loading rate.
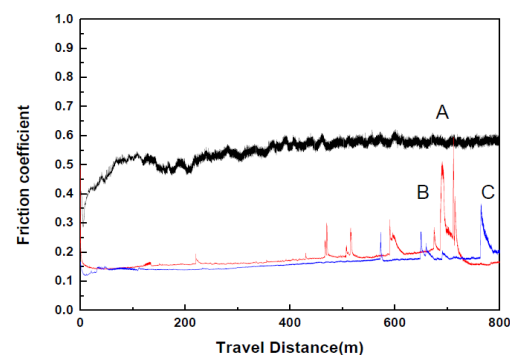
Figure 3. The coefficient of friction (COF) value e of the CrSiN and CrSiCN coatings sliding against a WC–Co ball.

Polarization tests were carried out using 1M H_2SO_4 solution at room temperature. The polarization curves (Ecorr. vs. Icorr.) of CrSiN and CrSiCN coated AISI 304 stainless steels are shown in Fig. 4. Compared with the coated specimens, the potentiodynamic polarization curves of CrSiN coating showed a more positive corrosion potential and a lower current density than those of the CrSiCN coated AISI 304 stainless steel substrate. Generally, Icorr commonly utilized as an index of corrosion

rate is determined by the extrapolation of cathodic Tafel lines. In this study, a significantly reduced Icorr was observed for the CrSiN coating as compared to CrSiCN coatings. The CrSiN treated specimen had an evident enhancement on the corrosion resistance as compared to the CrSiCN coated specimens. With the complete phase separation of CrN nanocrystalline and SiNx amorphous phases, the CrSiN are well protected by the amorphous SiNx matrix. The strengthened interfaces can effectively limit the diffusion paths of the corrosive medium. For the CrSiCN coating, it is expected that higher amount of C element causes the less protection in the coatings. A better corrosion resistance of the CrSiN coated AISI 304 stainless steel obtained demonstrates that this coating can work as a protective barrier against the acid environment.
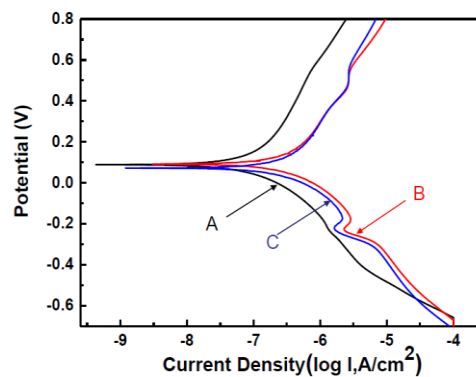

Figure 4. Polarization tests of CrSiN and CrSiCN coated AISI304 stainless steel carried out in 1M H_2SO_4 solution at room temperature.

4. Conclusions

In this study, three CrSiN based coatings were fabricated using cathodic arc deposition technique. By plasma decomposed C_2H_2 gas, additions of C to CrSiN were used to modify the microstructure and properties of the coatings. The analyzed CrSiCN coatings were obtained with higher hardness and smooth surface. With addition of Si (8.7 at.%) and C (41 at.%) in the coatings, the hardness increased to HV3300 may result from the formation of CrCN and CNx new phases. Tribological property of the coefficient of friction down to 0.2 was observed with the addition of Si and C, related to hardness and smooth surface. However, the corrosion resistance of the CrSiN coating is better than that of CrSiCN coating in the 1M H_2SO_4 solution at room temperature.

5. Acknowledgement

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