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Microstructures, mechanical properties, and tribological behaviors of Cr–Al–N, Cr–Si–N, and Cr–Al–Si–N coatings by a hybrid coating system

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Abstract

Cr–Al–N, Cr–Si–N, Cr–Al–Si–N coatings were successfully deposited on WC–Co substrates by a hybrid coating system combining an arc ion plating technique using Cr target, and a magnetron sputtering method using Al and Si targets under N_2/Ar atmosphere. XRD, HRTEM, and XPS analyses revealed that the synthesized Cr–Al–N coatings consisted of solid-solution (Cr,Al)N crystallites, and the Cr–Si–N and Cr–Al–Si–N coatings with Si content of ~9 at.% were fine composites consisting of (Cr,Si)N and (Cr,Al,Si)N crystallites, respectively, embedded in an amorphous Si_3N_4/SiO_2 matrix. The hardness values of the Cr–Si–N (~35 GPa) and the Cr–Al–Si–N (~55 GPa) coatings were significantly increased compared with those of CrN (~23 GPa) and Cr–Al–N (~25 GPa) coatings. Besides, the average friction coefficients of the Cr–Si–N (~0.30) and the Cr–Al–Si–N (~0.57) coatings with Si content of about 9 at.% were largely decreased compared with those of CrN (~0.50) and Cr–Al–N (~0.84) coatings. A comparative study on microstructural characteristics among Cr–Al–N, Cr–Si–N, and Cr–Al–Si–N coatings is reported in this paper.

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Keywords: Cr–Al–N; Cr–Si–N; Cr–Al–Si–N; Mechanical properties; Tribological behaviors

1. Introduction

Chromium nitride (CrN) coatings have been widely used as protective coatings for various tribological forming and casting applications [1,2], because the coatings have high hardness as well as good wear-resistance due to its low friction coefficient. CrN coatings also show excellent corrosion-resistance under severe environmental condition [3] and good oxidation-resistance [4]. Recently, ternary Cr–X–N coatings, where X is the alloying element such as Ti [5,6], Al [7,8], Si [9,10], B [11], C [12,13], Ta [14,15], Nb [16], and Ni [17], etc., have been actively investigated to improve the properties of CrN coatings. Among these ternary systems, Cr–Al–N films have higher hardness (25–32 GPa) than that of CrN coatings, and have much improved oxidation-resistance up to 900 °C due to the formation of stable oxidation barrier of Al_2O_3 layer by migrated Al atoms to surface region [18,19]. Besides, Cr–Si–N coatings based on nanocomposite consisting of nanosized CrN crystallites and an amorphous SiN_x phase have been explored [20,21] to improve the hardness and tribological properties. More recently, quaternary Cr–Al–Si–N coatings start to be explored since it could become multi-functional coatings having superhardness (≥40 GPa), excellent oxidation- and wear-resistance. To our knowledge, no previous research was found in the literatures on the quaternary Cr–Al–Si–N coatings up to the present. For these reasons, we investigated the microstructure, mechanical properties, and tribological behaviors of quaternary Cr–Al–Si–N coatings compared with ternary Cr–Al–N and Cr–Si–N coatings.

In this work, Cr–Al–N, Cr–Si–N, and Cr–Al–Si–N coatings have been deposited on WC–Co substrates using the hybrid coating system of arc ion plating and magnetron sputtering

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Table 1
Typical deposition conditions for CrN, Cr–Al–N, Cr–Si–N, and Cr–Al–Si–N coatings by the hybrid coating system

Variable		CrN	Cr–Al–N	Cr–Si–N	Cr–Al–Si–N
Arc	Cr target current	55 A	55 A	55 A	55 A
Sputter	Al target current	–	1.4 A	–	1.4 A
	Si target currents	–	–	0–2.2 A	0–2.2 A
N_2 : Ar ratio					2 : 1
Base pressure					2.7×10^{-3} Pa
Working pressure					4.0 Pa
Substrate temperature					300 °C
Substrate to target distance					300 mm
Substrate rotation speed					25 rpm
Typical coatings thickness					~2 μm

techniques. The relationship among microstructure, mechanical properties, and tribological behaviors of Cr–Al–N, Cr–Si–N, and Cr–Al–Si–N coatings was comparatively investigated.

2. Experimental

2.1. Deposition

The Cr–Al–N, Cr–Si–N, and Cr–Al–Si–N coatings were deposited on WC–Co and Si wafer substrates using the hybrid coating system, where the AIP method was combined with a magnetron sputtering technique. Arc cathode guns for Cr source and dc sputter gun for Al and Si sources were installed on each side of the chamber wall. A rotational substrate holder was located between the sources. Ar gas (99.999%) was introduced into the sputter target holder to increase the sputtering rate and N_2 gas (99.999%) was injected near the substrate holder. Purities of Cr, Al and Si targets were 99.99%. The WC–Co substrates of the disc type (20 mm in diameter and 3 mm in thickness) were cleaned in an ultrasonic cleaner using acetone and alcohol for 20 min. The substrates were cleaned again by ion bombardment using a bias voltage of −600 V under Ar atmosphere of 32 Pa for 15 min. The substrates were heated by resistant heaters set inside the chamber, and then the coatings were deposited from arc and sputter sources at a working pressure of 4 Pa. The deposition temperature was fixed at 300 °C. Typical deposition conditions for Cr–Al–N, Cr–Si–N, and Cr–Al–Si–N coatings by the hybrid coating system are summarized in Table 1.

Table 2
Chemical composition of the CrN, Cr–Al–N, Cr–Si–N and Cr–Al–Si–N coatings

	Elements		
	Cr (at.%)	Al (at.%)	N (at.%)
CrN	50	–	50±2
Cr–Al–N	33	17	50±2
Cr–Si(3 at.%)–N	47	–	50±2
Cr–Si(6.5 at.%)–N	43.5	–	50±2
Cr–Si(9.3 at.%)–N	40.7	–	50±2
Cr–Si(11 at.%)–N	39	–	50±2
Cr–Si(12.5 at.%)–N	37.5	–	50±2
Cr–Al–Si(4.5 at.%)–N	34	10.5	50±2
Cr–Al–Si(8.7 at.%)–N	31.7	9.2	50±2
Cr–Al–Si(9.8 at.%)–N	30.2	9	50±2
Cr–Al–Si(12.4 at.%)–N	29	8.8	50±2
Cr–Al–Si(16 at.%)–N	26.5	7	50±2

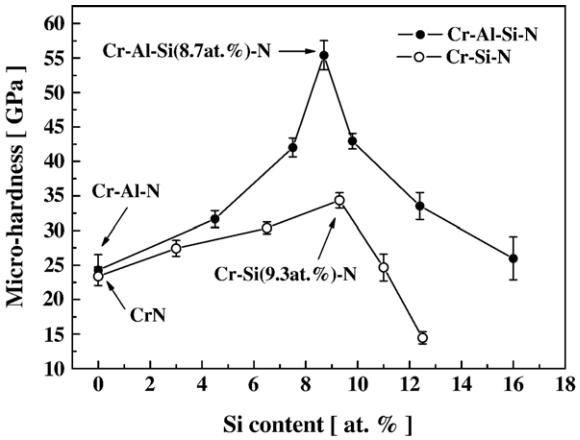

Fig. 1. Microhardness of the Cr–Si–N and Cr–Al–Si–N coatings as a function of Si content.

2.2. Characterization

The coating thickness was measured using a scanning electron microscopy (SEM, Hitachi, S-4200) and a stylus (α-STEP) instrument. Compositional analyses of the coatings to determine the contents of Cr, Al, Si and N were carried out by electron probe microanalyzer (EPMA, Shimadzu, EPMA 1600). Chemical compostions of the various coatings are shown in Table 2. The crystallinity of the Cr–Al–Si–N coatings was analyzed with X-ray diffractometer (XRD, PHILIPS, X'Pert-MPD System) using CuKα radiation. X-ray photoelectron spectroscopy (XPS, VG Scientifics, ESCALAB 250) was also performed to study the bonding status in the Cr–Si–N and Cr–Al–Si–N coatings. The XPS spectra were obtained after removing the surface layer of samples by sputtering with Ar^+ ions (3 keV) for 3 min and the spectra were calibrated for the value of carbon peak C 1s at

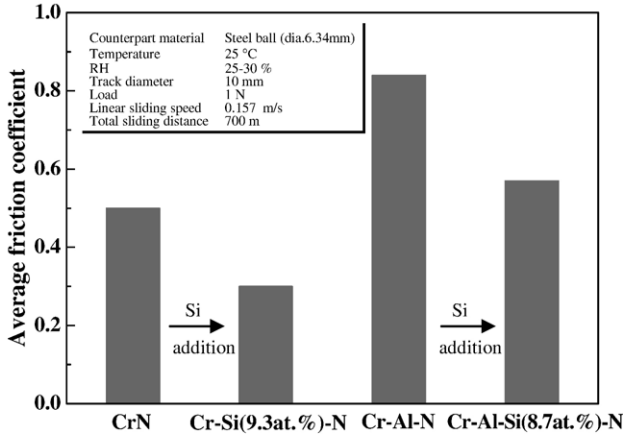

Fig. 2. Average friction coefficients of CrN, Cr–Si(9.3 at.%)–N, Cr–Al–N, and Cr–Al–Si(8.7 at.%)–N coatings against steel ball.