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Effect of carbon on microstructure of $CrAlC_xN_{1-x}$ coatings by hybrid coating system

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Abstract: A systematic investigation of the microstructure of $CrAlC_xN_{1-x}$ coatings as a function of carbon contents was conducted. Quaternary $CrAlC_xN_{1-x}$ coatings were deposited on Si wafers by a hybrid coating system combining an arc-ion plating technique and a DC reactive magnetron sputtering technique using Cr and Al targets in the $Ar/N_2/CH_4$ gaseous mixture. The effect of carbon content on microstructure of $CrAlC_xN_{1-x}$ coatings was investigated with instrumental analyses of X-ray diffraction, X-ray photoelectron, and high-resolution transmission electron microscopy. The results show that the carbon content of $CrAlC_xN_{1-x}$ coatings linearly increases with increasing $CH_4/(CH_4/N_2)$ gas flow rate ratio. The surface roughness of the $CrAlC_xN_{1-x}$ coating layer decreases with the increase of carbon content.

Key words: CrAlC_xN_{1-x} coating; nanocomposite; microstructure; hybrid coating system

1 Introduction

CrN hard coatings are widely used for various tribological applications from automotive components to forming dies[1-5] due to their high hardness, good adhesion to steel substrate materials and good resistance to wear and corrosion[6-7]. Recently, researches on ternary or quaternary Cr-N based hard coatings have been extensively studied to improve their mechanical, thermal, and tribological properties, and operating temperature[8–9]. For the ternary Cr-X-N coatings, where X is one of various alloying elements such as Ti, Si, Al, Ta, Nb, Ni, B, and C[10–17], it is well understood that these improved properties are strongly related to not only the properties of adding elements but also the formation of unique microstructure such as nanocomposite or solid-solution. For the quaternary Cr-N based coatings such as Cr-Mo-C-N[18], Cr-Si-C-N[19], Cr-Al-Si-N[20], Cr-Mo-Si-N[21], and Cr-Al-C-N, however, it is still required to investigate the detailed microstructure for a more comprehensive understanding.

In Ref.[22], it was reported that quaternary

 $CrAlC_xN_{1-x}$ coatings have even better practical performance as compared to ternary coatings, and thus provide a better coating alternative under severe application conditions in the near future. This is principally due to the grain refinement, solution hardening and formation of amorphous carbon layer in the coatings. Nevertheless, the effect of carbon concentration on the microstructure and properties of $CrAlC_xN_{1-x}$ coatings needs to be investigated in detail.

In this work, the effect of carbon on the microstructure and properties of $CrAlC_xN_{1-x}$ coatings was investigated in detail. Also, the role of carbon on the improved properties of CrAlCN coatings was systemically discussed.

2 Experimental

2.1 Deposition

The $CrAlC_xN_{1-x}$ coatings were deposited on Si wafer substrates using a hybrid coating system, where an arc ion plating (AIP) was combined with a magnetron sputtering technique. An arc cathode gun for the Cr source and a DC sputter gun for the Al source were installed on each side of the chamber wall. A rotational

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substrate holder was located between two sources. The rotational speed of the substrate was 25 r/min. Both CH₄ (99.999% purity) and N₂ gas (99.999% purity) were injected near the substrate holder, and Ar gas (99.999% purity) was introduced into the sputter target holder to increase the sputtering rate. The purities of Cr and Al targets were 99.99%. Substrates of disk 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 installed inside the chamber, and then $CrAlC_xN_{1-x}$ coatings were deposited from arc and sputter source at a working pressure of 0.173 kPa. The deposition temperature was fixed at 300 °C. Typical deposition conditions for $CrAlC_xN_{1-x}$ coatings by the hybrid coating system are summarized in Table 1.

Table 1 Typical deposition conditions of $CrAlC_xN_{1-x}$ coatings by arc ion plating

Parameter	Value
Base pressure/Pa	6.67
Deposition pressure/Pa	1.73
Total gas rate/($cm^3 \cdot min^{-1}$)	80
Arc source	Cr (99.99%)
Sputter source	Al (99.99%)
Arc current for Cr target/A	50
Sputter current for Al target/A	2
Deposition time/h	1
Substrate temperature/°C	300
Typical coating thickness/µm	≤2
Rotational velocity of substrate/ $(r \cdot min^{-1})$	25

2.2 Characterization

The film thickness was measured by a field emission scanning electron microscope (FE-SEM). The composition of the films was analyzed by an electron probe microanalyzer (EPMA). X-ray photoelectron spectroscopy (XPS) was used to observe the chemical bonding status in the $CrAlC_xN_{1-x}$ coatings. The XPS spectra were obtained after removing the surface adatoms on the samples by sputtering with Ar⁺ ion for 360 s and the spectra were calibrated for the value of carbon peak C1s at 284.5 eV. The microstructure of the coating was determined by a field emission transmission electron microscope (FE-TEM). The other structural information on the components of the coatings was obtained from the analyses by the selected area diffraction pattern (SADP) and high-resolution transmission electron microscopy (HRTEM). The surface topography and average values of the surface roughness (R_a) of the coatings were examined with an

atomic force microscope (AFM, PSIA, XE-100)

3 Results and discussion

Fig.1 shows the compositional changes of Cr, Al, C, and N elements in three kinds of $CrAlC_xN_{1-x}$ coatings at fixed Cr arc current of 50 A and Al sputter current of 2 A. For three samples, the molar fractions of Cr and Al in the coatings are maintained at nearly constant values of 35.5% and 14.5%, respectively. And, C and N contents of the films can be controlled by varying flow rate of CH₄ to (CH₄+N₂) from 0 to 1 during the deposition. As a result, three samples with different carbon contents (CrAIN, CrAIC_{0.17}N_{0.83} and CrAIC) were prepared.



Fig.1 Molar fractions of $CrAlC_xN_{1-x}$ coatings with *x*=0, 0.17, and 1 (Carbon and nitrogen contents were controlled by varying flow rate ratio of CH₄ to (CH₄+N₂) gas

In Ref.[22], it is shown that the diffraction peaks position of $CrAlC_x N_{1-x}$ coatings are shifted to the lower angles as the carbon content increases. It is explained by two phenomena: the formation of solid solution by the incorporation of carbon atoms into (Cr, Al)N crystal lattice, and residual stress caused by differences in the thermal expansion between the substrate and the coatings. Also, the diffraction peak intensity is reduced and a peak broadening phenomenon is observed as the carbon content increases. It is worth mentioning that this phenomenon is very similar to that of Cr-Si-N coatings whose microstructure is nano-composite[11]. Therefore, the cross-sectional HRTEM images, selected area diffraction patterns (SADP), and dark-field TEM images for CrAlN, CrAlC_{0.17}N_{0.83} and CrAlC coatings were observed to investigate the detailed microstructure. As shown in Figs.2(a) and (b), the CrAlN coatings have crystalline phase of columnar structure. With increasing carbon contents, however, а nanocomposite microstructure consisting of crystallines and amorphous phase is found from $CrAlC_{0.17}N_{0.83}$ coatings (Figs.2(c) and (e)), which is very similar to that of CrSiN coatings. In Fig.2(c), the crystalline and amorphous phases can be



Fig.2 Cross-sectional HRTEM images with selected area diffraction patterns (SADP) of CrAlN (a), $CrAlC_{0.17}N_{0.83}$ (c) and CrAlC (e) coatings and corresponding dark-field TEM images of CrAlN (b), $CrAlC_{0.17}N_{0.83}$ (d) and CrAlC (f) coatings, respectively

distinguished from each other by the lattice fringe contrast. Moreover, CrAlC coatings mostly consist of amorphous phase (Figs.2(e) and (f)). Evidently, a relatively large columnar microstructure of CrAlN coatings is refined with carbon addition by forming a nanocomposite microstructure like that of Cr-Si-N coatings.

In order to clarify chemical bonding status of Cr, Al, C and N in $CrAlC_xN_{1-x}$ coatings, X-ray photoelectron spectroscopy (XPS) was carried out. Fig.3(a) shows XPS spectra near the binding energies of C1s for $CrAlC_xN_{1-x}$ coatings with various carbon contents. The peak intensity gradually increases with an increase of the carbon content. The C1s spectrum in Fig. 3(a) shows C—N (286.6–287 eV) and C—C (284.1–284.6 eV) peaks[23], respectively. For the $CrAlC_{0.17}N_{0.83}$ coatings, the spectra of carbon can be splitted into those of C—N and C—C (Fig.3(b)). And, only C—C bond is observed in the case of CrAlC. This result indicates that carbon atoms exist as amorphous carbon (a-C) phases because no carbon crystalline phase is indicated by HRTEM (Fig.2) and previous XRD result in Ref.[22].

The surface roughness of CrAlN, CrAlC_{0.17}N_{0.83} and CrAlC coatings layers was determined by atomic force microscopy (AFM) and compared in terms of the average surface roughness value (R_a). Fig.4 shows AFM images of CrAlC_xN_{1-x} coatings layers of different carbon contents. The average surface roughness of CrAlC_xN_{1-x}



Fig.3 XPS peaks of C1s measured on CrAlN, $CrAlC_{0.17}N_{0.83}$ and CrAlC coatings (a) and detailed spectral profiles of $CrAlC_{0.17}N_{0.83}$ coatings (b)

coatings was calculated from AFM images of a selected area 3 μ m×3 μ m. CrAlN layer shows a rough morphology (R_a =7.83 nm) with a shape of facet grains. However, CrAlC_{0.17}N_{0.83} layer shows a surface roughness of R_a =6.02 nm, and CrAlC layer has a smoother surface of R_a =4.22 nm. These results can be explained with the results in Fig.2. From the HRTEM images, it is shown that the grains size of CrAlC_xN_{1-x} coating is reduced with increasing carbon content of the films and coatings become an amorphous microstructure with increasing carbon contents. Therefore, the decrease in the surface roughness with increasing carbon contents can be understood by the amorphization of the films.

4 Conclusions

1) A systematic investigation of the microstructure of $CrAlC_xN_{1-x}$ coatings as a function of carbon contents is conducted. Quaternary $CrAlC_xN_{1-x}$ coatings are deposited on Si substrate by a hybrid coating system combining an arc-ion plating technique and a DC reactive magnetron sputtering technique using Cr and Al targets in the $Ar/N_2/CH_4$ gaseous mixture. The carbon



Fig.4 AFM images and corresponding average surface roughness of different coatings: (a) CrAlN, R_a =7.83 nm; (b) CrAlC_{0.17}N_{0.83}, R_a =6.02 nm; (c) CrAlC, R_a =4.22 nm

content of $CrAlC_xN_{1-x}$ coatings is controlled with increasing flow rate ratio of CH_4 to CH_4+N_2 gas.

2) The microstructure of $CrAlC_xN_{1-x}$ coatings is nanocomposites consisting of nano-sized Cr(Al, N) crystallines surrounded by amorphous carbon phase. Also, surface becomes smoother by the microstructural changes of $CrAlC_xN_{1-x}$ coatings from polycrystalline to amorphous structure.

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