Comparison of mechanical and tribological properties of CrBN coatings modified by Ni or Cu incorporation

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Abstract: To compare the merits of Ni and Cu, the mechanical and tribological properties of CrBN coatings modified by Ni or Cu incorporation were studied. The results demonstrated that the CrBN–Cu coatings presented a lower friction coefficient than CrBN and CrBN–Ni coatings owing to the improved lubrication effect of the CuO layer originating from the tribochemical reaction. However, the hardness decline due to Cu incorporation was much greater than that of Ni incorporation. Thus, the CrBN–Cu coatings exhibited a higher wear rate than the CrBN coating. In contrast, the plastic deformation enhancement induced by Ni incorporation exceeded the hardness decline. Therefore, the wear of CrBN–Ni coatings partially turned to plastic deformation to present a lower wear rate than that of the CrBN coating.

Keywords: CrBN coatings; friction; lubrication effect; wear; transmission component

1 Introduction

Helicopters are important transport modes for both civil and military use [1]. The bearings and hinges in the airscrew system are crucial transmission components to ensure the stable operation of the helicopter. To prolong the service life of transmission components, hard coatings have been widely used to prevent wear [2–5]. Transition metal nitride coatings incorporated with non-metal elements—such as C, Si, and B—present high hardness and good wear resistance owing to the reinforcement effect of the nanocomposite structure [6]. It has been discovered that as well as hardness, the plastic deformation ability or crack resistance is also an important property that strongly determines the wear resistance of coatings [7, 8]. Therefore, the development of hard and tough coatings has become the objective of researchers [9–11]. Many studies have

focused on the crack resistance modification of transition metal nitride coatings by tough metal incorporations, such as Ni [12, 13], Cu [14], Ag [15, 16], Au [17], Al [18], Nb [19], Ti/Al [20], and Cu/Cr [21]. As a result, the wear resistance of transition metal nitride coatings was enhanced accordingly [13–15].

Nevertheless, researchers have found that hardness and crack resistance are contradictory to a certain degree. For instance, Liu et al. [22] found that the crack propagation resistance (CPR) of AlCrSiN coating increased from 375 to 525 with 12.46 at% Ni incorporation but the hardness decreased from 27.5 to 21.6 GPa. Resultantly, the wear rate of the AlCrSiN coating increased from 4.2×10^{-7} to 6.0×10^{-7} mm³/(N·m). Our recent work also found that the toughness of CrSiN coatings increased from 5.91 to 6.85 MPa·m^{1/2} with Ni incorporation (2.4 at%) while the hardness of CrSiN coatings decreased from 28.9 to 26.9 GPa.

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Consequently, the wear rate of the CrSiN coating increased from 1.1×10^{-7} to 1.5×10^{-7} mm³/(N·m) [23]. Regarding Cu incorporation, Zhao et al. [24] noted that Cu incorporation of 10 wt% increased the crack extension force of TiCN coatings from 33.4 to 45.8 J/m² but decreased the hardness from 1,415 to 1,150 HV0.1. The wear loss increased from 0.006 to 0.0105 g. The above results demonstrate that the increment in crack resistance is generally achieved at the cost of reduced hardness and is therefore unable to ensure enhanced wear resistance. Thus, the balance between crack resistance and hardness is important, i.e., it is better to improve the crack resistance of the coating by slightly sacrificing hardness. However, the toughening degree among different tough metals in Refs. [12–19] is incomparable since these tough metals were not compared simultaneously in one article and the hardness decrement was not considered. Namely, it is difficult to distinguish which tough metal exhibits a superior synthetic strengthening effect. Thus, it is extremely necessary to simultaneously consider crack resistance and hardness of coatings to distinguish the advantages of different tough metals.

In this study, two tough metals, Ni and Cu, were chosen. A series of CrBN–Ni and CrBN–Cu coatings with similar Ni and Cu contents were deposited. Based on the comparison of plastic deformation and hardness, the individual advantage effect of Ni and Cu incorporation on the mechanical and tribological properties of CrBN coatings was elucidated.

2 Experimental

2.1 Coating deposition

The common material 45 steel was used as the substrate with two dimensions (big wafer: Φ 30 mm $\times$ 4 mm and small wafer: Φ 10 mm $\times$ 1 mm). The substrate wafers were placed on the sample holder in a closed-field unbalanced magnetron sputtering instrument (UDP-650, Teer Coatings Limited, UK) for coating deposition. When the base pressure in the chamber reached 2.0×10^{-6} Torr, coating deposition was performed, which comprised three procedures: i) ion cleaning by Ar⁺ plasma, ii) binding layer deposition, and iii) top layer deposition. During all of the above procedures, no heating was applied to the substrate. To ensure similar coating thicknesses of approximately 2.1 μ m, the deposition time decreased as the Ni (or Cu) target current increased. During deposition, an optical emission monitor (OEM) was used to automatically control the flow of N₂ by presetting at 50%. The Ni (or Cu) concentration in the CrBN–Ni (or CrBN–Cu) layer was adjusted by setting different currents of the NiCr (or Cu) target. The specific deposition procedures and the corresponding coating labels are listed in Tables 1 and 2. Structural and morphological characteristics were investigated using coatings on small wafers. Mechanical and tribological properties evaluations were performed using coatings on big wafers.

Table 1 Deposition processes and labels of CrBN–Ni coatings.

Process		Cr target current (A)	CrB ₂ target current (A)	NiCr target current (A)	Ar flow (sccm)	N ₂ flow	Bias voltage (V)	Revolving speed (rpm)	Time (min)
Ion cleaning	Ar ⁺ bombardment	—	—	—	50	—	–450	10	30
	Cr	4.0	—	—	50	—	–80	10	10
Binding layer	CrN	4.0	—	—	50	OEM 50%	–80	10	15
	(Ni)–CrBN gradient	4.0	0.0→2.0	0.0→Set point	50	OEM 50%	–80	10	15
Top layer	CrBN	4.0	2.0	Set point: 0.0	50	OEM 50%	–80	10	80
	CrBN–Ni–0.4	4.0	2.0	Set point: 0.4	50	OEM 50%	–80	10	75
	CrBN–Ni–0.8	4.0	2.0	Set point: 0.8	50	OEM 50%	–80	10	70
	CrBN–Ni–1.2	4.0	2.0	Set point: 1.2	50	OEM 50%	–80	10	65
	CrBN–Ni–1.6	4.0	2.0	Set point: 1.6	50	OEM 50%	–80	10	60
	CrBN–Ni–2.0	4.0	2.0	Set point: 2.0	50	OEM 50%	–80	10	55

Table 2 Deposition processes and labels of CrBN–Cu coatings.

	Process	Cr target current (A)	CrB ₂ target current (A)	Cu target current (A)	Ar flow (sccm)	N ₂ flow	Bias voltage (V)	Revolving speed (rpm)	Time (min)
Ion cleaning	Ar ⁺ bombardment	—	—	—	50	—	–450	10	30
	Cr	4.0	—	—	50	—	–80	10	10
Binding layer	CrN	4.0	—	—	50	OEM 50%	–80	10	15
	(Cu)–CrBN gradient	4.0	0.0→2.0	0.0→Set point	50	OEM 50%	–80	10	15
Top layer	CrBN	4.0	2.0	Set point: 0.0	50	OEM 50%	–80	10	80
	CrBN–Cu–0.4	4.0	2.0	Set point: 0.4	50	OEM 50%	–80	10	75
	CrBN–Cu–0.8	4.0	2.0	Set point: 0.8	50	OEM 50%	–80	10	70
	CrBN–Cu–1.2	4.0	2.0	Set point: 1.2	50	OEM 50%	–80	10	65
	CrBN–Cu–1.6	4.0	2.0	Set point: 1.6	50	OEM 50%	–80	10	60
	CrBN–Cu–2.0	4.0	2.0	Set point: 2.0	50	OEM 50%	–80	10	55

2.2 Structural characterizations

The chemical composition (Table 3) and the elemental bonding conditions of the coatings were determined by using X-ray photoelectronic spectroscopy (XPS, ESCALAB 250, Thermo Scientific, USA). An Ar⁺ etching was conducted for 4 min on the coating samples before XPS measurement. Additionally, an X-ray diffractometer (XRD, Ultima IV, Japan) was used to scan the diffraction angle θ from 20° to 80° to characterize the crystal phase in the coatings. Subsequently, the obtained XPS and XRD data were further processed using the software XPSPEAK41 and Jade 5, respectively. The morphologies of the coatings were observed using a field-emission scanning electron microscope (SEM, SIGMA 500, Zeiss,

Table 3 Chemical compositions of CrBN–Ni and CrBN–Cu coatings.

Coatings	Cr (at%)	B (at%)	N (at%)	O (at%)	Ni (at%)
CrBN	34.32	6.72	40.48	18.48	—
CrBN–Ni–0.4	27.20	10.88	37.33	20.24	4.35
CrBN–Ni–0.8	28.79	9.85	35.65	18.43	7.28
CrBN–Ni–1.2	21.44	10.49	30.79	24.74	12.54
CrBN–Ni–1.6	19.56	15.79	29.52	22.51	12.62
CrBN–Ni–2.0	20.37	10.67	24.37	24.97	19.62
Coatings	Cr (at%)	B (at%)	N (at%)	O (at%)	Cu (at%)
CrBN–Cu–0.4	25.75	8.94	45.79	15.82	3.70
CrBN–Cu–0.8	24.37	10.23	42.82	15.74	6.84
CrBN–Cu–1.2	21.57	9.69	35.80	19.68	13.26
CrBN–Cu–1.6	19.09	8.30	30.67	25.89	16.05
CrBN–Cu–2.0	19.06	8.42	29.51	23.95	19.06

Germany). The transmission electron microscopy (TEM) samples of CrBN–Ni–0.8 and CrBN–Cu–0.8 coatings were prepared via hand polishing and Ar⁺ polishing in succession. Subsequently, the lamella was observed using a transmission electron microscope (TECNAI G2 S-TWIN F20, USA).

2.3 Mechanical property characterizations

Based on the approach proposed by Oliver and Pharr [25], the mechanical properties, including hardness (H) and Young's modulus (E) of the coatings were measured by nano-indentation tests using a dynamic ultra-micro hardness tester (DUH211S, Shimadzu, Japan). During the test, the penetration displacement was maintained at 200 nm, with a constant loading speed of 1.4632 mN/s. For each coating, at least ten test points were chosen to minimize the data scattering. The average values of hardness (H) and Young's modulus (E) were calculated based on these ten measurements and are listed in Table 4. It is known that H/E reflects elastic strain to failure while H^3/E^2 is proportional to plastic deformation resistance, to a certain degree. Thus, the ratios of H/E and H^3/E^2 were also calculated. In addition, the crack resistance of the coatings was evaluated based on the plastic deformation capacity (D_p), which was calculated by dividing the residual depth by the maximum depth. The residual and maximum depths were extracted from the loading–unloading curves.

2.4 Evaluation of tribological properties

Friction tests of SiC balls (Φ 8 mm) sliding against the

Table 4 Mechanical properties of CrBN–Ni and CrBN–Cu coatings

Coatings	H (GPa)	E (GPa)	H/E	H^3/E^2 (GPa)	D_p (%)	Decreasing rate of H (%)	Rising rate of D_p (%)
CrBN	38.4 ± 3.8	346 ± 7	0.111	0.473	40.1 ± 1.1	—	—
CrBN–Ni–0.4	36.3 ± 2.2	347 ± 18	0.105	0.398	44.6 ± 2.5	5.5	11.2
CrBN–Ni–0.8	31.7 ± 0.8	294 ± 12	0.108	0.367	44.4 ± 1.8	17.4	10.0
CrBN–Ni–1.2	31.5 ± 2.6	324 ± 14	0.097	0.297	50.5 ± 1.6	18.0	25.9
CrBN–Ni–1.6	26.3 ± 1.7	295 ± 22	0.089	0.209	52.5 ± 0.7	31.5	30.9
CrBN–Ni–2.0	22.4 ± 0.8	264 ± 16	0.085	0.160	54.3 ± 1.1	41.7	35.4
Coatings	H (GPa)	E (GPa)	H/E	H^3/E^2 (GPa)	D_p (%)	Decreasing rate of H (%)	Rising rate of D_p (%)
CrBN–Cu–0.4	31.4 ± 0.6	318 ± 7	0.099	0.307	46.5 ± 0.9	18.2	16.0
CrBN–Cu–0.8	20.8 ± 0.6	254 ± 10	0.082	0.139	53.1 ± 1.4	45.8	32.4
CrBN–Cu–1.2	19.7 ± 0.9	262 ± 20	0.075	0.111	53.5 ± 0.7	48.7	33.4
CrBN–Cu–1.6	13.6 ± 0.5	217 ± 16	0.063	0.054	60.3 ± 1.3	64.6	50.4
CrBN–Cu–2.0	11.5 ± 0.3	190 ± 8	0.060	0.042	61.0 ± 0.7	70.1	52.1

coatings in an ambient environment (at room temperature and 50% humidity) were conducted using a homemade unidirectional sliding tribometer. The detailed structure and operation principle of the homemade tribometer are described in our previous study [26]. To compare the friction behavior of CrBN–Ni (or CrBN–Cu) coatings with different Ni (or Cu) contents, a constant load (2 N), sliding velocity (0.1 m/s), and sliding distance (1,000 m) were used. The initial mean contact pressures of the tribo-pairs were calculated based on the Hertz contact model and varied in the range of 0.517–0.657 GPa. These contact pressures are comparable to the actual bearing contact pressure. The friction coefficient of the tribo-pairs could be automatically calculated from the friction force collected by the tribometer. Conversely, the wear resistance of the coatings was evaluated by the wear rate, which was obtained by dividing the wear volume (V) by the load (2 N) and the sliding distance (1,000 m). The V of the coatings after the tribotest was measured using a white light interferometer (Contour GT-K, Bruker, Germany). To analyze the friction and wear mechanism, the morphologies of the wear tracks on the coatings were observed using a SEM (FEI Quanta 200 FEG, USA). Meanwhile, the corresponding chemical compositions were determined via energy dispersive spectra (EDS).

3 Experimental

3.1 Microstructures and morphologies of coatings

The chemical compositions of the CrBN–Ni and CrBN–Cu coatings are listed in Table 3. As the current

of the NiCr (or Cu) target increases from 0.4 to 2.0 A, the Ni (or Cu) concentration in the CrBN–Ni (or CrBN–Cu) coatings gradually increases. Specifically, the concentration of Ni increases from 4.35 to 19.62 at% while Cu increases from 3.70 to 19.06 at%. Moreover, the corresponding Ni and Cu concentrations under the same target current are very close. Specifically, the mechanical and tribological properties of CrBN–Ni and CrBN–Cu coatings deposited under the same target current are comparable.

The variations in the crystal patterns of the CrBN–Ni and CrBN–Cu coatings are illustrated in Fig. 1. Except for the diffraction peak at 44.5° correlating to the Fe phase from the 45 steel substrate (JCPDS 06-0696), the diffraction peaks of CrN(111), CrN(200), and CrN(220) at 36.7° , 43.1° , and 62.5° , respectively, are found (JCPDS 11-0065), which demonstrate the face-centered cubic structure. However, the intensity variation of CrN(111) as a function of Ni or Cu content is different. As seen in Fig. 1(a), the intensity of CrN(111) in the CrBN–Ni coatings varies slightly. In contrast, the intensity of CrN(111) in CrBN–Cu coatings decreases strongly, which could be observed from the CrN(111) shoulder peak in the CrBN–Cu–2.0 coating.

The Ni 2p, Cu 2p, and B 1s core level XPS spectra of the coatings are illustrated in Figs. 2 and 3, respectively, to analyze the bonding conditions of the Ni, Cu, and B elements, of which no information was obtained from the XRD results. As seen in Figs. 2(a) and 3(a), the major Ni–Ni bond and major Cu–Cu bond are presented around 853.0 and 932.7 eV, respectively [27]. Additionally, additional Ni–O and Cu–O bonds are

Fig. 1 XRD patterns of (a) CrBN–Ni and (b) CrBN–Cu coatings.

Fig. 2 (a) Ni 2p and (b) B 1s core level XPS spectra of CrBN–Ni–0.4, CrBN–Ni–1.2, and CrBN–Ni–2.0 coatings.

Fig. 3 (a) Cu 2p and (b) B 1s core level XPS spectra of CrBN–Cu–0.4, CrBN–Cu–1.2, and CrBN–Cu–2.0 coatings.

also found, which result from absorbed oxygen. For the B element, a strong B–N bond around 190.3 eV accompanied by a weak B–O bond is observed in Figs. 2(b) and 3(b). This demonstrates that Ni (or Cu) is mainly bonded with Ni (or Cu) while B is mainly bonded with N. To confirm the nano-composite structure of CrN crystal and amorphous phase, the selected area electron diffraction (SAED) and high resolution

transmission electron microscopy (HRTEM) images of CrBN–Ni–0.8 and CrBN–Cu–0.8 coatings are illustrated in Fig. 4. As seen in Figs. 4(a) and 4(d), a binding layer, with a thickness of approximately 250 nm between the Si substrate and top layer, is observed. Based on the HRTEM images in Figs. 4(c) and 4(f), large CrN crystal grains (around 10 nm) are present in the CrBN–Ni–0.8 coating but small CrN crystal grains

Fig. 4 (a) Cross-sectional morphology of (b) SAED and (c) HRTEM image of CrBN–Ni–0.8 coating and (d) cross-sectional morphology of (e) SAED and (f) HRTEM image of CrBN–Cu–0.8 coating.

(around 5 nm) are present in the CrBN–Cu–0.8 coating. In addition, the CrN crystal grains with different lattice plane distances (0.239 and 0.207 nm) could be distinguished in Figs. 4(c) and 4(f). The lattice plane distances of 0.239 and 0.207 nm are correlated to CrN(111) and CrN(200) (JCPDS 11-0065), which are consistent with the diffraction rings shown in Figs. 4(b) and 4(e). Moreover, the weak diffraction rings of CrN(220), CrN(311), and CrN(222) are presented in Figs. 4(b) and 4(e).

The surface morphologies of the CrBN–Ni and CrBN–Cu coatings are shown in Figs. 5 and 6. It can be seen that the surface morphology of the CrBN coating becomes smooth and compact after Ni incorporation. Moreover, the boundaries of the column clusters are reduced but can still be seen clearly in Fig. 5. However, after Cu incorporation, it is difficult to observe the boundaries of the column clusters in Fig. 6.

Fig. 5 Surface morphologies of (a) CrBN, (b) CrBN–Ni–0.4, (c) CrBN–Ni–0.8, (d) CrBN–Ni–1.2, (e) CrBN–Ni–1.6, and (f) CrBN–Ni–2.0 coatings.

Fig. 6 Surface morphologies of (a) CrBN–Cu–0.4, (b) CrBN–Cu–0.8, (c) CrBN–Cu–1.2, (d) CrBN–Cu–1.6, and (e) CrBN–Cu–2.0 coatings.

3.2 Mechanical properties of coatings

The hardness (H) and Young's modulus (E) of the coatings are listed in Table 4. Overall, the hardness of CrBN decreases after Ni and Cu incorporation.

However, the decreasing rate of hardness by Ni incorporation is much lower than that by Cu incorporation. With increasing Ni content from 4.35 to 19.62 at%, the hardness decreases from 36.3 to 22.4 GPa. The maximum rate of decrease is 41.6%. In contrast, with increasing Cu content from 3.7 to 19.06 at%, the hardness decreases from 31.4 to 11.5 GPa. The maximum decreasing rate reaches 70.1%. The ratios of H/E and H^3/E^2 also show the decreasing trend as that of hardness. In addition, the D_p is listed in Table 4. Although the decreasing rate of hardness by Cu incorporation is very high, the plastic deformation ability is reinforced from 40.1% to 61.0% by Cu incorporation.

3.3 Tribological properties

Figure 7 presents the variation in the friction coefficient as a function of sliding distance. After a rising running-in period, the friction coefficient reaches a steady period. For CrBN–Ni coatings, the influence of Ni incorporation on the friction coefficient is weak. The friction coefficient of the CrBN–Ni coatings varies in the range of 0.45–0.55 (Fig. 7(a)). However, as seen

in Fig. 7(b), Cu incorporation has a strong effect on decreasing the friction coefficient. The lowest friction coefficient reaches 0.25. By averaging the friction coefficient during the steady period, the mean-steady friction coefficient was obtained and is presented in Fig. 8(a). It is clear that the low concentrations of Ni and Cu incorporations (3.70–7.28 at%) both reduce the friction coefficient of the CrBN coating. Specifically, the friction coefficient of CrBN decreases from 0.527 to 0.480 and from 0.527 to 0.263 upon Ni and Cu incorporation, respectively. The Cu incorporation shows a better decreasing effect on the friction coefficient in comparison to Ni incorporation. Nevertheless, when the Ni and Cu concentrations increase to 12.62 and 16.50 at%, respectively, the mean-steady friction coefficient increases to 0.513 and 0.404, respectively.

The variations of CrBN–Ni and CrBN–Cu coating wear rates as a function of target current are both presented in Fig. 8(b). The wear rate of the CrBN coating is $7.42 \times 10^{-7} \text{ mm}^3/(\text{N} \cdot \text{m})$. After Ni incorporation, the wear rate decreases, regardless of the Ni concentration. Specifically, the CrBN–Ni coating wear rate varies

Fig. 7 Variation of friction coefficient as a function of sliding distance for (a) CrBN–Ni coatings and (b) CrBN–Cu coatings.

Fig. 8 (a) Mean-steady friction coefficient and (b) coating wear rate of CrBN–Ni and CrBN–Cu coatings.

in the range of 5.14×10^{-7} – 6.81×10^{-7} mm³/(N·m). Conversely, the CrBN–Cu coating wear rate increases gradually from 6.09×10^{-7} to 1.12×10^{-6} mm³/(N·m).

4 Discussion

4.1 Microstructure and morphology

As seen in Fig. 1, the effect of Ni incorporation on the crystallinity of CrN(111) is slight. In contrast, the crystallinity of CrN(111) decreases gradually with increasing concentration of Cu incorporation. Chang et al. [28] reported that the diffraction peaks of the CrN phase in the CrAlN coating moved to a small angle after Cu incorporation since Cu, as a three-dimensional (3D) transition metal element, possibly caused lattice distortion. Thus, the weakened intensity of the CrN(111) peak with increasing Cu content in this study could be attributed to the same reason. Moreover, the weakened effect of Cu incorporation on the diffraction peak of metal nitride coatings has been reported in Ref. [29–31]. In addition, no Ni, Cu, or BN crystals were found in the XRD results. It is indicated that Ni, Cu, and B might exist in the form of an amorphous phase, which was confirmed by the corresponding Ni–Ni, Cu–Cu, and B–N bonds in the XPS results. From another point of view, the HRTEM images in Figs. 4(c) and 4(f) directly observe the CrN crystal and amorphous matrix. Thus, the CrBN–Ni and CrBN–Cu coating structures are both nano-composite structures comprising CrN crystals and amorphous matrices.

Considering the variation in the CrN(111) diffraction peak in the CrBN–Ni and CrBN–Cu coatings, the incorporation of Ni has a slight influence on CrN crystal growth but the incorporation of Cu limited the growth of CrN crystals. This could be proved directly by the large CrN crystal grains (around 10 nm) in the CrBN–Ni–0.8 coating and the small CrN crystal grains (around 5 nm) in the CrBN–Cu–0.8 coating. Namely, with increasing Cu content, the portion of the amorphous phase in the CrBN–Cu coating gradually increases. For this reason, it is difficult to see the boundaries of the column cluster on CrBN–Cu–1.2, CrBN–Cu–1.6, and CrBN–Cu–2.0 coatings due to amorphization. In contrast, the surface morphologies of all CrBN–Ni coatings still show the boundaries of the column cluster.

4.2 Mechanical properties

As seen in Table 4, the hardness of the CrBN coating decreases after Ni and Cu incorporation. It is known that Ni and Cu are soft metals, which have a hardness of approximately 0.2 and 0.1 GPa, respectively [32]; this explains the reduced hardness of the CrBN coatings. However, the rate of decreasing hardness from Cu incorporation is stronger than that from Ni incorporation. This is primarily owing to the relatively lower hardness of Cu (0.1 GPa) compared to Ni (0.2 GPa). The second reason is the decline of the reinforcement effect from the nanocomposite structure. It has been reported that when only a few monolayers of amorphous layer existed as the interfacial layer between crystals, the grain boundary sliding block formed a strong interface between the amorphous and crystal phases, thus leading to an increase in hardness. However, at a high amorphous phase fraction, the separation between crystals increases, leading to a decrease in hardness due to the large degradation of coherence between the amorphous layer and crystals [33]. As discussed before, the portion of the amorphous phase in the CrBN–Cu coating gradually increases with increasing Cu content. Thus, the reinforcing effect from the nanocomposite structure is weakened due to a greater portion of the amorphous matrix in the CrBN–Cu coatings. Similar results were obtained for metal nitride coatings, such as TiSiN [34], CrSiN [35], and CrBN [36].

It is worth noting that, for the above two reasons, the D_p of CrBN coating increases from 40.1% to 61.0% for CrBN–Cu–2.0 coating, which is higher than the value of 54.3% for the CrBN–Ni–2.0 coating. The variations in hardness and plastic deformation capacity D_p can affect the corresponding tribological properties, which will be discussed in the next section.

4.3 Tribological properties

It is worth noting that at similar Ni or Cu concentrations, all of the CrBN–Cu coatings present a lower friction coefficient than the corresponding CrBN–Ni coatings. Three reasons contribute to this result. The first is hardness. As presented in Table 4, the hardness of the CrBN–Cu coating is much lower than that of the CrBN–Ni coating at a similar Ni or Cu concentration. This indicates that the roughness peak is easily worn to decrease roughness, as shown in Fig. 9(a). The

second reason is the plastic deformation capacity, D_p . The higher D_p of the CrBN–Cu coating in comparison to the CrBN–Ni coating can lower the roughness peak due to plastic deformation, as shown in Fig. 9(b). The 3D profiles and wear track contours on CrBN–Ni–0.8 and CrBN–Cu–0.8 are illustrated in Fig. 10. It can be seen that with a sharp roughness peak, the CrBN–Ni–0.8 coating presents a rougher wear track than that on the CrBN–Cu–0.8 coating, verifying the above two reasons. The third reason is the lubrication layer generated from the tribochemical reaction, which could be proved by the high oxygen content from the EDS results. Based on the EDS results, Cr, B, Ni, and Cu could all be oxidized. It is worth noting that the Cr and B contents in the wear tracks of the CrBN–Ni and CrBN–Cu coatings deposited at the same NiCr or

Cu target currents are similar. This implies that the lubrication effects of boron and chromium oxides are almost the same. In contrast, the different oxide types, i.e., NiO and CuO, are deemed to have a major role in reducing the friction coefficient of CrBN–Cu coatings in comparison to CrBN–Ni coatings, as shown in Fig. 8(a). According to the Gibbs free energies ΔG_f^{298} of Eqs. (1) and (2), Ni and Cu could be oxidized during the friction test.

$$\Delta G_f^{298} = -423.4 \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta G_f^{298} = -259.4 \text{ kJ} \cdot \text{mol}^{-1}$$

The lubricating capacity of the above metallic oxides could be determined by their ionic potential, based on the crystal chemistry principle described by Erdemir [37]. As Ref. [37] reported, the ionic potentials of NiO and CuO were 2.8 and 4.0. Their friction coefficients were inversely proportional to the ion potential. Specifically, the friction coefficient of NiO varied in the range of 0.35–0.60, while CuO presented the lowest friction coefficient of 0.18–0.22. In contrast, chromium oxides exhibited a friction coefficient of approximately 0.4 but the friction coefficient of boron oxides varied in the range of 0.50–0.85 [38, 39]. In

Fig. 9 Schematic diagrams of (a) wear and (b) plastic deformation of roughness peak.

Fig. 10 3D profiles and contours of wear tracks on (a, b) CrBN–Ni–0.8 and (c, d) CrBN–Cu–0.8 coatings.

addition, Cu and CuO, exhibiting good lubricating properties, have been widely used as solid lubricants [40]. Liu et al. [41] reported that the average friction coefficient of MoCuN coatings decreased as the Cu content increased as more Cu and CuO lubrication layers formed. Thus, under the combination of the above three reasons, the CrBN–Cu coatings present a lower friction coefficient than the corresponding CrBN–Ni coatings.

In addition, when the incorporation contents of Ni and Cu are low ($\text{Ni} \leq 7.28 \text{ at\%}$ and $\text{Cu} \leq 6.84 \text{ at\%}$), the friction coefficients of CrBN–Ni–0.4, CrBN–Ni–0.8,

CrBN–Cu–0.4, and CrBN–Cu–0.8 decrease in comparison to those of the CrBN coating (0.527). In contrast, when the incorporation contents of Ni and Cu are high ($12.54 \leq \text{Ni} \leq 19.62 \text{ at\%}$ and $13.26 \leq \text{Cu} \leq 19.06 \text{ at\%}$), the friction coefficients of CrBN–Ni–1.6, CrBN–Ni–2.0, CrBN–Cu–1.6, and CrBN–Cu–2.0 increase slightly. The major reason for this variation in friction coefficient with increasing Ni (or Cu) content is the adhered debris. As shown in Figs. 11(b) and 11(c), buckling debris could be observed on the wear track of the CrBN coating. In contrast, the wear tracks of CrBN–Ni–0.8 and CrBN–Cu–0.8 coatings shown in Figs. 12

Fig. 11 (a–c) SEM images of wear track and (d, e) EDS analyses of spectrum A and spectrum B of CrBN coating.

Fig. 12 (a–c) SEM images of wear track and (d, e) EDS analyses of spectrum A and spectrum B of CrBN–Ni–0.8 coating.

and 13 present smooth adherent debris, leading to a lower roughness and the lowest friction coefficient. As seen in Figs. 14 and 15, a greater portion of wear tracks is covered by wear debris and some buckling debris is still observed on the wear tracks of CrBN–Ni–1.6 and CrBN–Cu–1.6 coatings, which is believed to increase the roughness, thus leading to a further increase in the friction coefficient.

As listed in Table 4, the hardness of the CrBN coating decreases after Ni incorporation but D_p increases. Under such circumstances, CrBN–Ni coatings would encounter more plastic deformation rather than wear.

It can clearly be seen that, for CrBN–Ni coatings, the rising rate of D_p is close and even higher than the decreasing hardness rate. This implies that the wear caused by the hardness decrease could be reduced by the increase in D_p . This explains why the CrBN–Ni coating exhibits a lower wear rate than the CrBN coating. In contrast, for CrBN–Cu coatings, the increasing rates of D_p are all lower than the decreasing hardness rate. This means that the wear caused by the hardness decrease cannot be reduced by the increase in D_p . This contributes to the gradual increase in the wear rate of CrBN–Cu coatings. Therefore, the difference

Fig. 13 (a–c) SEM images of wear track and (d, e) EDS analyses of spectrum A and spectrum B of CrBN–Cu–0.8 coating.

Fig. 14 (a–c) SEM images of wear track and (d, e) EDS analyses of spectrum A and spectrum B of CrBN–Ni–1.6 coating.

Fig. 15 (a–c) SEM images of wear track and (d, e) EDS analyses of spectrum A and spectrum B of CrBN–Cu–1.6 coating.

in wear rate between CrBN–Cu and CrBN–Ni coatings deposited at the same target current becomes large, as shown in Fig. 8(b).

5 Conclusions

To compare the influence of different tough metals on the mechanical and tribological properties of CrBN coatings. CrBN–Ni and CrBN–Cu coatings containing different and similar Ni/Cr contents were deposited. Some conclusions were obtained based on mechanical and tribological characterizations.

1) The hardness of the CrBN coating gradually decreased after incorporation owing to the soft features of Ni and Cu. The decreasing hardness rate due to Cu incorporation is stronger than that by Ni incorporation.

2) Due to the lubrication effect of Cu and CuO, CrBN–Cu coatings presented a lower friction coefficient than those of CrBN–Ni coatings.

3) Ni incorporation could decrease the wear rate of CrBN coatings due to the enhanced plastic deformation ability, even with decreasing hardness.

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