Fabrication and evaluation of D-gun sprayed WC–Co coating with self-lubricating property

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A WC–Co coating with self-lubricating property was deposited by detonation gun (D-gun) process, using a commercial WC–Co powder doped with a MoS_2–Ni powder, under a proper spray condition. It is proved that the MoS_2 composition in the feed powder was kept, which is attributed to the protection of Ni around it, and its content is a little higher in the resulting coating. Evaluation on sliding wear property indicates that the MoS_2 composition plays an important role in lowering both coefficient of friction and wear rate for the resulting coating, which is confirmed by observations on wear track, as well as X-ray photoelectron spectroscope (XPS) results on worn surface. It suggests that the deposition of WC–Co coating with self-lubricating property by D-gun spray is feasible by controlling lubricant powder and spray conditions, which can exhibit higher sliding wear resistance.

KEY WORDS: ceramics, coatings, hardness, self-lubrication

1. Introduction

Thermal sprayed WC–Co coating, combining WC as the hard constituent and Co as the ductile binder, has good properties, in particular a high-wear resistance [1–3]. Numerous studies have been conducted to examine the relationship among feed powder characteristics, process conditions, microstructural parameters, and wear resistance of this coating [4–16]. Among them, more attention was paid on the improved wear resistance by nanostructured WC–Co coatings [9,12–14]. However, Usmani *et al.* [15], and Stewart *et al.* [16] reported disappointing sliding wear and abrasive wear resistance of nanostructured WC–Co coatings for the increased decarburization, which indicates that the achievement of superior wear resistance from nanostructured coatings would require an optimization of the powder preparation and a readaptation of the spray process.

One of the more promising ways to improve wear resistance for thermal sprayed coatings is through self-lubrication by doping lubricant in the coatings, which is cheaper and easier than the optimization for nanostructured coatings, but the biggest challenge to this goal is to retain the preexisting lubricant in feed powder from chemical reaction for the high temperature in thermal spray. In all thermal spray techniques, Detonation gun (D-gun) spray can minimize decomposition of the feed powder due to lower heat enthalpy and shorter duration involved in the depo-

sition. In addition, higher particle velocity during deposition provides resulting coatings several advantages such as lower porosity, higher bond strength, and hardness, which is better than those of the coatings deposited using other thermal spray method including plasma spray and HVOF [2]. The objective of this article is to report an achievement on depositing WC–Co coating with self-lubricating property by doping a common lubricant-MoS_2 using D-gun spray. In our work, a WC–Co powder doped with a MoS_2–Ni powder was deposited under a proper spraying condition. Then, the resulting WC–Co coating was characterized on structure including phase structure, element concentration, porosity, and roughness, as well as mechanical properties including hardness, fracture toughness, and adhesion. At last, the sliding wear property of the resulting WC–Co coating was evaluated by employing a sliding, reciprocating, and vibrating (SRV) tester, which is compared with that of a pure WC–Co coating deposited under the same condition.

2. Experimental procedures

A commercial WC–Co alloy powder (JK112, Shanghai Satellite Co. Ltd., Shanghai, China) with a nominal composition of 88 wt.% WC and 12 wt.% Co, and with size in range of 15–60 μm and an average 30 μm was employed in this work [17]. A MoS_2 powder (figure 1(a)) coated with Ni by chemical method in Beijing General Research Institute of Mining and

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Metallurgy was employed as doping powder for the resulting coating. The coated powder has a nominal composition of 22 wt.% MoS_2 and 78 wt.% Ni, with an average particle size of 50 μm, and an average thickness of Ni layer 5 μm, as shown in figure 1(b, c). The two powders were mixed with 10 wt.% of MoS_2–Ni for 24 h for deposition.

A D-gun spraying system ('ob'-type) was employed to deposit coating specimens. Acetylene was employed as

Figure 1. SEM images on morphology of MoS_2 (a) and MoS_2–Ni (b) powders and cross-section of MoS_2–Ni (b) powder (c).

fuel gas, while nitrogen as carrier gas to introduce the sprayed powders into the gun, as well as cleaning gas. In this work, the maintenance of MoS_2 composition as an important constraint, and the minimized decomposition of WC have to be considered for the resulting coating. To find the proper spray conditions, both the WC–Co coatings [17] and the MoS_2–Ni coatings were deposited and the effects of deposition parameters on their structures and properties were measured, respectively, by which the spray distance between the nozzle exit and substrate, and the oxygen-fuel ratio were chosen as 100 mm and 1.06, respectively, as an optimal combination for both powders. The other parameters were the same as those described in our former paper [17]. Two coating specimens were deposited onto steel substrates that were freshly grit-blasted before, one with the pure WC–Co powder, the other with the WC–Co powder containing MoS_2–Ni composition. The thickness range of as-sprayed coatings was 350–400 μm.

Scanning electron microscopy (SEM; JSM 6401, JEOL, Tokyo, Japan) equipped with an energy dispersive spectrometer (EDS; Oxford, UK) was employed to study the powders, coatings, and worn surfaces, respectively. Equipments and details for characterizing structure including phase structure, porosity, and roughness, as well as mechanical properties including hardness, toughness, and adhesion for the resulting WC–Co coatings were described elsewhere [17]. Furthermore, X-ray Fluorescence Spectroscopy (XRF; MagiX Pro-PW2440, Philips, Netherlands) was employed to determine element concentrations in the resulting coating deposited with the WC–Co powder containing MoS_2–Ni composition by the sample with size of 30×30 mm^2 quantitatively.

A SRV tester (SRV III, Optimol, Munich, Germany) was employed to evaluate wear resistance property for the resulting coatings. A WC–Co ball (95 wt.% WC and 5 wt.% Co in composition, 10 mm in diameter, 1750 in Vickers hardness, data from Optimol) with a mirror-polished surface was oscillated against the stationary plates of the coating specimens. Before sliding wear test, both the coating specimen polished to Ra < 0.1 μm, and the counterpart were degreased with acetone. The tests were conducted with a normal load, 20 N, at an oscillating frequency of 20 Hz, amplitude of 1 mm, and a period of 30 min (total sliding distance 72 m), at room temperature (about 20 °C), and a relative humidity of 35%. By using a Form Talysurf Plus surface roughness tester (Rank Taylor Hobson, Leicester, England, UK), the cross-section areas of worn track on the coating specimens were obtained, which were used to calculate the wear volumes. On case of the WC–Co ball, the wear volume was calculated from the spot diameter of worn surface measured by optical microscope (Stemi 2000-C, ZEISS, Jena, Germany). Then, the wear rates for the sliding pair were acquired from the wear volumes
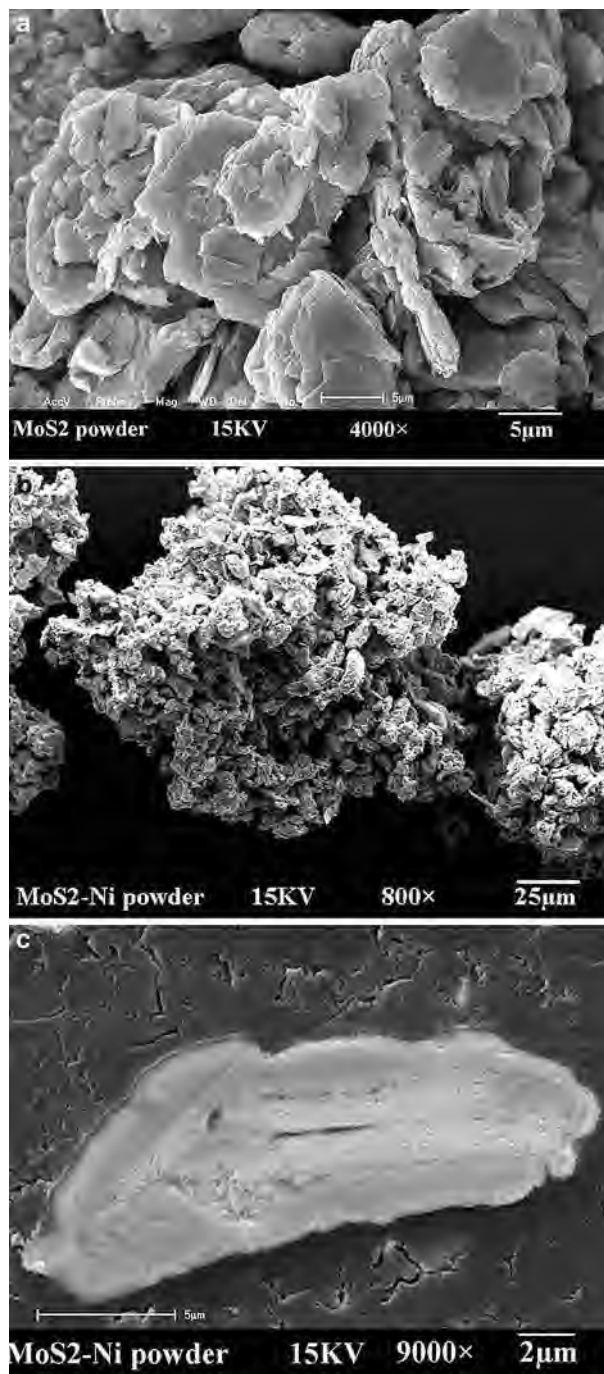
divided by load and sliding distance. The coefficient of friction and the wear rate were evaluated from the average values by three tests with 95% confidence interval for standard deviation for each sliding pair under the same condition. After sliding wear test, the tribofilm was surface analyzed by X-ray photoelectron spectroscope (XPS; Escalab 250, Thermo VG, CA, USA) operating at 150 W and 15 kV. The size of the X-ray probe was set at 500 μm, the thickness probed in XPS was about 5 nm with a exponential decay. The binding energy of C1s (284.6 eV) was used as the reference. In view of a possible contamination with carbon and oxygen on the surface, argon etching (Ar$^+$; 2kV, 4 μA; 0.3 nm/s) was performed for 30 s before XPS analysis.

3. Results and discussion

3.1. Coating structure, composition, and mechanical properties

The cross-section of the resulting coating deposited with the WC–Co powder containing MoS$_2$–Ni composition is shown in figure 2. This coating exhibited very dense structure with few small pores. The gray layers were proved to be comprised of three elements Mo, S, and Ni by EDS measurement on black regions in backscattered electron image with a higher magnification (figure 2(b)). Moreover, it is interesting to find a wide variety of carbide size in the coating, as well as the excellent cohesion not only between WC grains (white grains) and Co binder (gray part), but also between layer of Mo, S, and Ni (black part indicated by arrow), and Co binder in figure 2(b).

XRD patterns confirm the existence of MoS$_2$ composition in not only the feed powder, but also the resulting coating (figure 3). There are several peaks for MoS$_2$ phase on case of the feed powder, while only a peak (2θ = 40.516) was detected for the resulting coating, no peak from oxide of MoS$_2$ or other phase was found. Furthermore, no peak for W$_2$C phase can be found on case of the resulting coating; both Co and Ni were undetectable, which can be attributed to their amorphous or nano-crystalline states [18]. Table 1 shows comparison between the feed powder and the resulting coating on chemical composition. An impurity from Cr was detected on case of the coating, which may originate from the feed powder. It is found that the ratio of Mo/S in the resulting WC–Co coating is lower than that in the feed powder as the lightest element C is undetectable by XRF, which influence the result of element S. It can be also found that contents of both WC and Co in the resulting coatings are a little lower than those in the feed powder, while both MoS$_2$ and Ni a little higher, which may come from the different deposition efficiency between the two powders. The MoS$_2$ content is calculated as 2.8 wt.% for the resulting
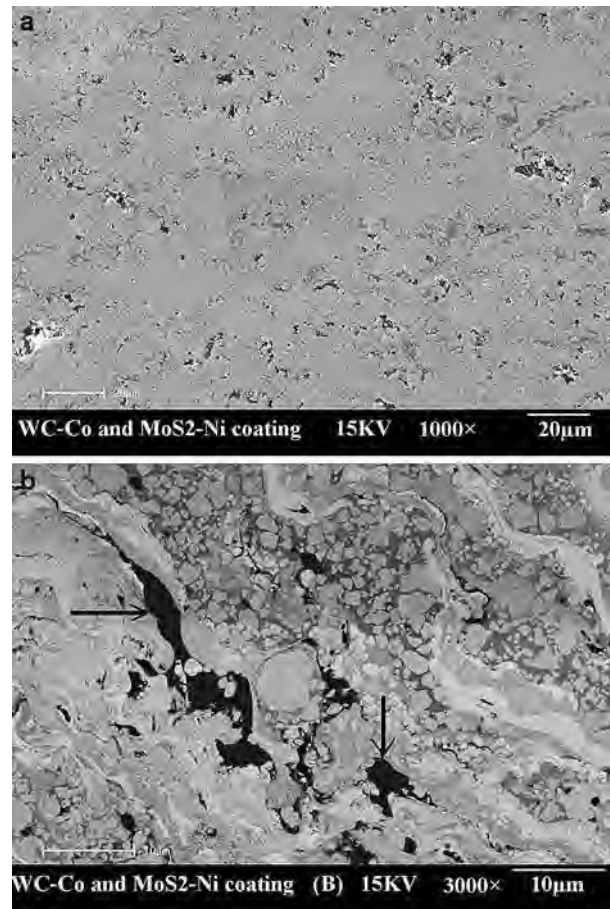

Figure 2. SEM images on cross-section of the WC–Co coating containing MoS$_2$–Ni composition; second electron image (a), and backscattered electron image with higher magnification (b).
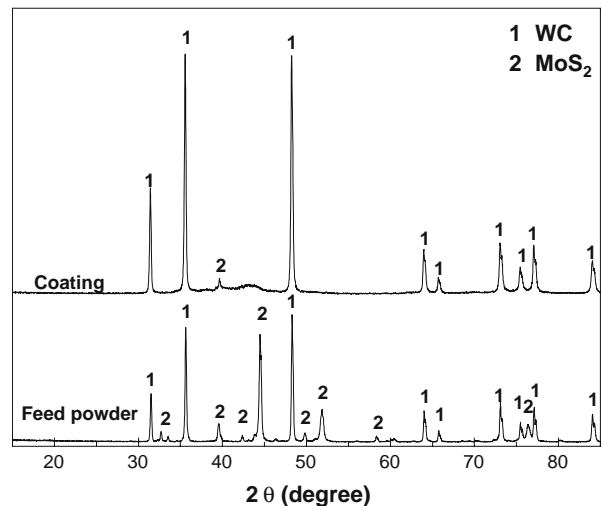

Figure 3. XRD patterns for the feed powder and the resulting coating containing MoS$_2$ composition.

WC–Co coating by element Mo. It is also found that Ni content in the resulting coating is higher than that in feed powder, which is not clear.

Combining SEM, XRD, and XRF results mentioned above, it is confirmed that the premise of this coating

Table 1.

Comparison on element concentration between feed powder and the resulting coating.

Element	Concentration (wt.%)	
	Powder	Coating
S	0.88	1.48
Cr		0.16
Co	10.80	10.38
Ni	7.80	11.46
Mo	1.32	1.68
W	74.34	73.85

system, a solid lubricant phase-MoS_2 distributed in the WC–Co coating has been fulfilled. The maintenance of MoS_2 phase in the resulting coating can be mainly attributed to the protection of Ni. It has been reported that thermal sprayed particle in flight stage reaches higher temperature at its surface than at its center [18,19]. On case of the MoS_2 powder coated with Ni, it is assumed that the nickel around the powder was molten, which dissolved and protected the MoS_2 composition in the spray process. In addition, the character of D-gun spray plays another important role on the maintenance of MoS_2 composition in the resulting coating. The maximum temperature of detonation torch is much lower than that of the plasma spray flame. Furthermore, the heating time for particles in the detonation torch was very short and the heat transfer between the detonation wave and the particles was very limited, due to high-velocity flow [20]. These characters make it possible that MoS_2 composition exists in the resulting coating and adheres with other parts well in the splat by nickel.

The porosity, surface roughness of the WC–Co coating containing MoS_2 composition are 3.0%, 5.57 μm, respectively, which are almost the same as those of the pure one deposited under the same spray condition. On the other hand, the hardness, fracture toughness, and adhesion of the WC–Co coating containing MoS_2 composition are reported in table 2, which are very near to those of the pure one.

3.2. Sliding wear behavior and mechanism

Table 3 shows the coefficients of friction and wear rates of the WC–Co coating containing MoS_2 composition and the pure one sliding against the WC–Co ball.

Table 2.

Hardness, toughness, and adhesion of the pure WC–Co coating (coating 0) and the WC–Co coating containing MoS_2 composition (coating 1).

	Hardness (kg/mm^2)	Toughness (Mpa/m^2)	Adhesion (Mpa)
Coating 0	1094 ± 100	9.6 ± 1.0	132 ± 10
Coating 1	1070 ± 134	9.2 ± 1.6	130 ± 11

Table 3.

Comparison between the pure WC–Co coating (coating 0) and the WC–Co coating containing MoS_2 composition (coating 1) on coefficient of friction and wear rate.

	Coefficient of friction	Wear rate (10^{-7} mm^3/N m)	Wear rate (10^{-7} mm^3/N m) (Ball)
Coating 0	0.502 ± 0.010	8.514 ± 0.833	0.804 ± 0.077
Coating 1	0.445 ± 0.015	6.149 ± 0.764	0.704 ± 0.071

It can be found that the MoS_2 composition in the WC–Co coating plays an important role on decreasing both parameters. The coefficient of friction decreases from 0.502 to 0.445, comparing the pure WC–Co coating and the other one containing MoS_2 composition, while, the wear rate decreases from 8.51 to 6.15 (10^{-7} mm^3/N/m). In addition, the MoS_2 composition in the WC–Co coating also plays an important role on wear rate for the WC–Co ball. It can be recognized that the wear rate of the WC–Co ball sliding against WC–Co coating containing MoS_2 composition is also lower.

To analyze the improved sliding wear property of the WC–Co coating containing MoS_2 composition, worn surface after tests were observed and compared with that of the pure one, as shown in figure 4. It is apparent that groove is shallower for the WC–Co coating with MoS_2 composition. It is supposed that the wear particles produced in the sliding process are comprised of WC, Co, MoS_2, and Ni or some of them, which underwent crushing, compaction, and smearing at the contact area between tested material/counter body, leading to the diminution of their size, due to the developed shear stresses. Omitting any chemical reaction, the WC grain as very hard phase is detrimental to both the coating and the ball, which can result in groove on their surface. The other three compositions, especially the MoS_2 phase can decrease the shear stress, which results in the lower coefficient of friction and wear rate. The examination on worn surface of the WC–Co coating containing MoS_2 composition by XPS confirms this point. Figure 5 shows the XPS analysis results of Mo 3d, S 2p, W 4f, and C 1s, respectively. According to NIST X-ray Photoelectron Spectroscopy Database [21], it is found that the binding energy peak of Mo at 228.3 and 230.85 eV correspond to MoS_2, which coincides with the detected binding energy of S at 162.4 eV, no oxides of Mo exist. These results indicate that the MoS_2 with lamellar structure in the coating was not converted into its oxide due to the lower temperature from thermal effect of friction and stress of compression or shear. So, the friction-reducing effect of MoS_2 composition last for the whole sliding process, which results in the improved wear resistance with its continuous appearance. Furthermore, it is clearly indicated that the chemical state of tungsten can be deduced to be WC only, for its binding energy peak at 31.2 and 32.6 eV combining the value of C at
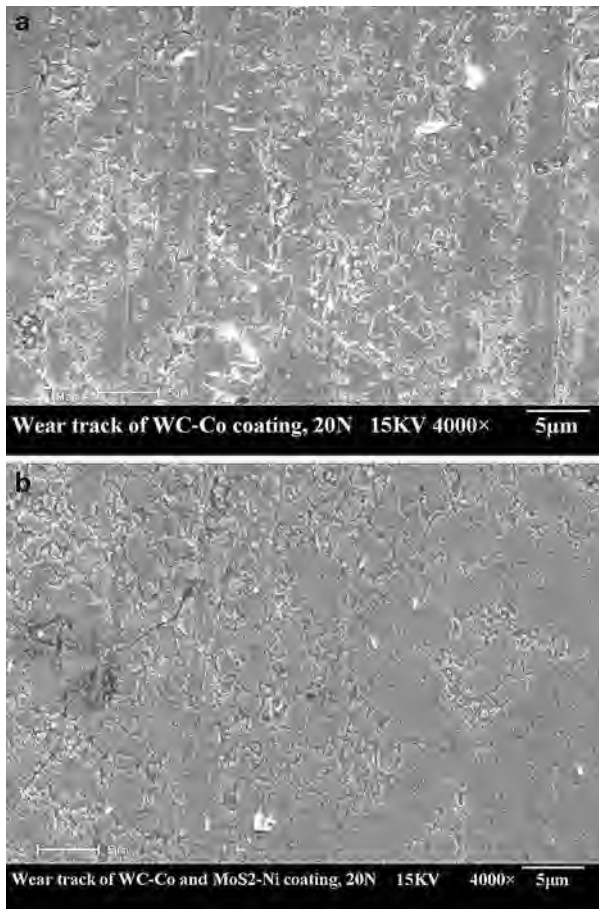
Figure 4. SEM morphologies of wear surface of the WC–Co coatings against WC–Co ball under normal load of 20 N; (a) pure WC–Co coating, (b) WC–Co coating containing MoS$_2$ composition.

283.3 eV, no information from WO$_3$ was found, which also confirms the low temperature during the sliding process.

It is interesting to find a lower coefficient of friction and a lower wear rate appear on the WC–Co coating containing MoS$_2$ composition sliding against WC–Co ball, which predict it possible to decrease both parameters further on the WC–Co coating containing higher MoS$_2$ content. However, it should be noted that wear is such a complex process that many factors can influence it [22]. The effects of MoS$_2$ content on the hardness and toughness of the WC–Co coating have to be considered on this case. Further work for WC–Co coatings containing higher MoS$_2$ contents on structure, mechanical properties and wear resistance is in progress to confirm this.

4. Conclusion

A WC–Co coating was deposited by a WC–Co powder doped with a MoS$_2$–Ni powder by D-gun process under a proper spray condition, which was characterized on structure including phase structure, element concentration, roughness, and porosity, mechanical properties including Vickers hardness, fracture toughness and adhesion, and sliding wear property. It is found possible to dope lubricant-MoS$_2$ in WC–Co coating by this method. The MoS$_2$ content in the resulting coating is a little higher than that in the feed powder. It is also found that the MoS$_2$ composition in the WC–Co coating can decrease coefficient of friction sliding against
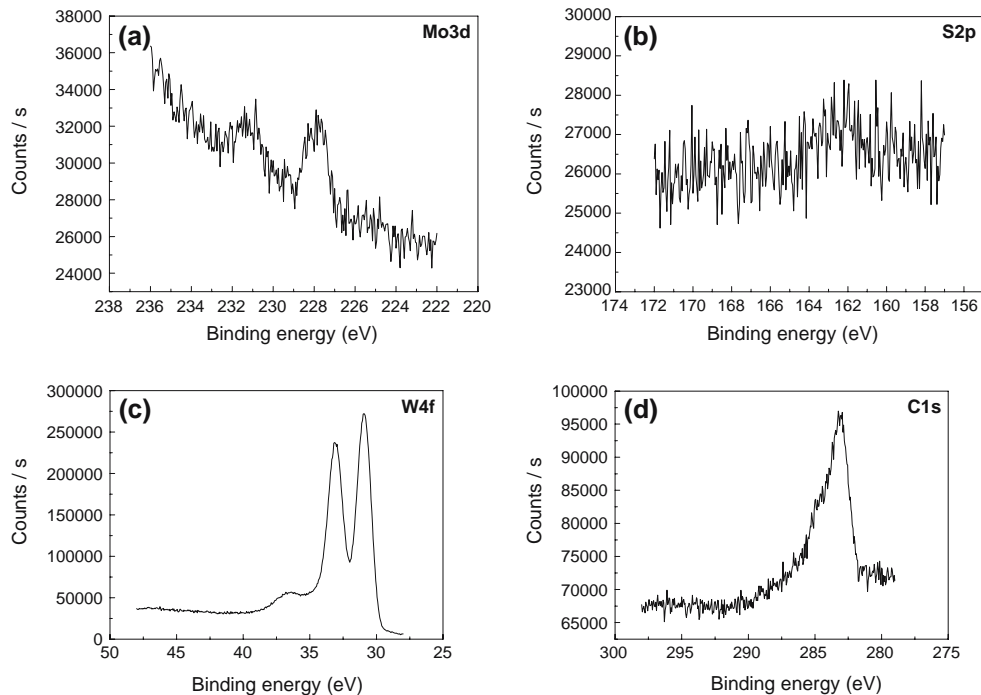

Figure 5. XPS spectra of Mo 3d (a), S 2p (b), W 4f (c), and C 1s (d) on the worn surface of the WC–Co coating containing MoS$_2$ composition.

WC–Co ball, decrease wear rates for both the coating and the ball. The results in this preliminary study promise that the envisioned deposition of WC–Co coating with self-lubricating property is feasible by controlling the feed powder and deposition condition, and the resulting coating can exhibit higher sliding wear resistance.

Acknowledgments

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