Water-lubricated tribological behavior of WC-Ni coatings deposited by off-angle HVOF spraying

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The off-angle thermally sprayed coatings generally present noticeable degradation in coating feature and characteristic, such as density, microhardness and/or toughness. A critical spray angle was previously suggested for different thermal spray techniques, e.g. HVOF of 45°, wire arc spraying of 60°, plasma spraying of 50° or 45°, primarily based on degree of the degradation benchmarked on that of normal angle. In this study, the feasibility of off-angle HVOF spraying of WC-Ni coatings is clarified directly by wear performance under water lubrication, since reported wear test results seem to be controversial. It is found that, the coating porosity is almost tripled with an upper limit within 3% as reducing the spray angle from 90° to 30°, while the maximum variation in the WC phase retention is about 13.6%, and about 11.7% in both microhardness and elastic modulus, and about 26.4% in indentation fracture toughness, respectively. As compared to a reported dry abrasive wear test showing that specific wear rate of HVOF WC-Co coatings at a spray angle of 30° was nearly doubled to that of 90° within 10^{-4} - 10^{-5} mm³/Nm, our water-lubricated wear test shows a comparably low specific wear rate below 10^{-7} mm³/Nm with about 30% maximum variation for WC-10Ni coatings off-angle sprayed with respect to that of normal spray angle. A notable reduction in friction coefficient is confirmed for off-angle sprayed coatings at 30° and 45°. The improved tribological behavior is mainly attributed to the higher porosity with well-dispersed micro-pores facilitating a better water lubrication, as well as the mostly retained mechanical properties of off-angle coatings due to controlled porosity in a certain range. The off-angle sprayed WC-Ni coatings down to the spray angle of 30° are applicable in tribological applications due to improved fluid lubricating characteristic.

Keywords: Thermal spray; Spray angle; WC-Ni; Coefficient of friction; Wear resistance; Water lubrication

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1. Introduction

Off-angle spraying is indispensable for thermal spray technologies in industrial practice to coat components of complicated shape [1-3]. It has been reported that off-angle thermal spray may lead to notable degradation of coatings features and characteristics, for surface features mainly including higher porosity (lower density) and cracking [1,5], and for surface characteristics including lower microhardness [1,4,5], lower fracture toughness [2,5] or less compressive residual stress [4,5], respectively. Among the different thermal spray technologies, high-velocity oxy-fuel (HVOF) spraying has advantage in the off-angle spraying capable of obtaining denser coatings over other techniques such as plasma spraying and wire arc spraying, as a result of the higher velocity of powders accelerated by the HVOF spray flame [1]. Since the plasma spray and wire arc spray processes are associated with low velocity of sprayed powders, the deposited coatings suffered great oxidation due to the high-temperature heating of sprayed powders with longer dwelling time in the flame, and the limited oxidation during HVOF spraying may be a dominant factor to obtain a relatively denser coating preferably for spraying non-oxide ceramic-metallic composite coatings [6-10]. For instance, for deposition of WC based composite coatings, HVOF sprayed WC-12Co coatings may reach a porosity of about 3% [1] whereas the plasma sprayed WC-12Co coatings could reach about 15% [4]. Consequently, a critical spray angle was suggested for the different thermal spray techniques, i.e. HVOF spraying no less than 45° [4], arc spraying no less than 60° [1], plasma spraying no less than 50° [1] or 45° [3], since substantial rise in porosity and/or degradation in coating characteristics occurred below such a spray angle.

Note that, for practical applications, the coating performance should be a direct criterion to assess the applicability of these coatings. However, coating performance is not fully explored in relation to the spray angle even though the degradation in off-angle sprayed coating features and characteristics are thought to be detrimental to the final performance. In this aspect, the porosity, hardness and toughness etc. should be concerned and understood as a sum of surface integrity parameters that have a combined effect on the high performance of components [11]. Up to date, wear resistance has been evaluated for the feasibility of off-angle spraying in few publications. Despite the reduced hardness and

compressive residual stress of off-angle sprayed coatings, Strock et al. [4] firstly reported an unexpected wear resistance enhancement for off-angle HVOF sprayed WC-CoCr coatings in comparison with that of normal angle sprayed coatings during dry fretting wear test against NiAl-bronze alloy or AISI 4340 steel wear pair under a load of 1.8 MPa and a frequency of 300 Hz for 8 h or 16 h. The exceptional wear response was attributed to more uniformly distribution of phases across the coating surface at off-angle spraying, and the enhanced wear resistance of off-angle sprayed coatings also caused greater wear of the wear pairs. More recently, Houdkova et al. [5] confirmed poorer wear behavior of off-angle HVOF sprayed hardmetal coatings evaluated by a dry sand/rubber wheel test under low-stress condition with a load of 22 N and a sliding distance of 1.436 m, where significant reduction in wear resistance was observed at less than 45° for WC-17Co coatings and less than 60° for Cr₃C₂-NiCr coatings, with a high wear rate of nearly doubled for WC-Co and over doubled for Cr₃C₂-NiCr as comparing the 30° sprayed coating to that of normal angle. Recalculating the reported data, the specific wear rate could be estimated to within a range of 10⁻⁴-10⁻⁵ mm³/Nm. The authors recommended a maximum 30° diversion from the normal angle for WC-Co and 15° diversion for Cr₃C₂-NiCr coatings, i.e. the critical spray angle is 60° for WC-Co coatings and 75° for Cr₃C₂-NiCr coatings based on the wear performance evaluation.

Systematic investigation is still necessary to clarify the influence of off-angle spraying scheme on the surface features and characteristics of thermally sprayed coatings and correlate them to the resultant performance under specific working conditions. Subsequently, the criterion based on coating performance could be established to evaluate feasibility of the off-angle spraying for coatings in industrial application. On this motivation, tribological behavior of off-angle HVOF sprayed WC-Ni coatings are explored in this study under water lubrication condition taking into account variations in coating features and characteristics under the off-angle spraying scheme. Water lubrication wear is frequently considered for components using WC-based cemented carbides material either in bulk or coating form, such as wear pairs of mechanical seals using water as coolant and lubricant [12-14]. The WC phase transformation in the coatings is analyzed along with the changes in porosity, hardness and toughness as varying the spray angle from 90° to 30°. A

comparable wear resistance of all sprayed coatings is observed at a very low specific wear rate below 10^{-7} mm³/Nm against high hardness WC-9Ni cemented carbide wear pair. The wear response of off-angle sprayed coatings with lower friction coefficient is discussed in correlation with the changes in the surface integrity parameters as well as the interactions between them since they have a combined effect on the final performance [11].

2. Experimental

The substrates for HVOF spraying experiments were 17-4PH precipitation strengthening martensitic stainless steel rectangle bars with a size of $12 \times 12 \times 60$ mm³. The substrates were cleaned with acetone, and then the surface to be coated was blasted with alumina grits of 60# mesh. WC-10Ni powders in diameter of +15-45 μ m were used as feedstock material. The feedstock powders were pretreated by heating up to 120 °C kept with 30 min followed cooling to room temperature in an electrically drying oven and then loaded into the powder feeder of HVOF system. An EvoCoat HVOF system equipped with Woka-610-Si HVOF spray gun on which the powders were fed into the HVOF flame with two laterally fixed inlets using N₂ as carrier gas. The HVOF process of off-angle spraying is schematically shown in Fig. 1, where the spray angle α is varied from 30° to 90° in this study. During spray process, the spray gun installed on a 6-axis robot is programmed to move with multiple sets of passes along the length of the steel substrate to deposit a coating of thickness about 200 μ m, where each set of passes consists of partial overlapping 4 passes with a pitch of 5 mm between the parallel passes. No forced cooling was conducted during spraying. The surface temperature of samples was monitored with infrared temperature meter and was not higher than 200 °C at the termination of program for each set of passes. Such a surface temperature was controlled by compressed air cooling during an interval time of within 30 seconds between each set of passes. The typical spray parameters are summarized in Table 1.

Characterizations of coated samples mainly include two aspects, i.e. surface features and surface characteristics, as categorized for surface integrity parameters which should be well controlled for components to achieve a high performance [11]. In this study, the surface features including surface roughness, porosity, metallurgical microstructure as well as phase structure were analyzed for coatings obtained under different spray angles, and

surface characteristics were measured including microhardness, elastic modulus, and indentation fracture toughness. The cross-sectional morphology of coatings was observed by using a Zeiss SUPRA55 field emission scanning electron microscope. Based on the SEM image analysis, the porosity of coatings was calculated with a set of images at a magnification of 200 according to the conventional method adopted for cemented carbide bulk material as well as coatings [15,16]. Furthermore, the porosity down to a submicron range was also resolved on images at a magnification of 5000-15000 and compared with the above-mentioned porosity analysis. Microhardness under different loads was also measured comparatively at 100 g and 300 g load with 10 s dwelling time, on the cross section of coatings using a HXD-1000TM Vickers indentation tester and each value was averaged over 10 measurements. The surface roughness of coatings was measured on a Kosaka ET4000AK surface profilometer. The phase structure was analyzed using X-ray diffraction measurement with Cu $K\alpha$ radiation on a SHIMADZU XRD-600 diffractometer. Elastic modulus of the coatings was measured by using a non-contact approach developed in our lab based on advanced ultrasonic technique by which both transverse and longitudinal waves through the coatings are simultaneously recorded in a single water-immersed ultrasonic probe. And then, the measured velocities of transverse and longitudinal waves were used to calculate the Poisson ratio and elastic modulus of coatings, similar to a recent study where the two wave velocities are measured separately via a laser ultrasonic method [17]. In this way, Poisson is derived from the measurement, other than empirically assumed in conventional method [18]. The coating fracture toughness was obtained by eq. (1) employing a Vickers indentation method [19] under a load of 49 N,

$$K_{IC} = 0.016 \frac{P}{a^{\frac{3}{2}}} \left(\frac{E}{H} \right)^{\frac{1}{2}} \quad (1)$$

where P is the indentation load, a the averaged half-length of the crack extended along indent diagonal, E the elastic modulus of coatings measured by the ultrasonic technique and H the microhardness of coatings under 300 g load. Tribological behaviors of coated samples were evaluated on MRH-3A ring-on-block tribometer with the ring half-immersed in deionized water. The coated rectangular bars were cut into the block samples with a size of $12 \times 12 \times 20 \text{ mm}^3$ by electrical discharge machining and the coating surfaces were

mirror polished to a surface roughness of Ra value of about 0.015 μm . The wear test of bulk WC-9Ni ring pressured against block coating samples were carried out at a load of 200 N for 5 h, where the ring rotation speed of 200 rpm led to a tangential friction speed of 0.5 m/s at the contact interface between the ring and block samples. The bulk WC-9Ni cemented carbide ring has an average Vickers microhardness of 1100HV measured under both 100 g and 300 g load.

3. Results

3.1 Phase structure

Fig. 2 shows the XRD patterns of the WC-10Ni coatings obtained by the HVOF spray at the different spray angles. The XRD data were normalized by the intensity of diffraction peak at $2\theta = 35.6^\circ$ from WC (100) diffraction plane. It can be seen that the relative intensity of W_2C diffraction peak is enhanced for the coatings deposited at smaller spray angles. In addition, small diffraction peaks from metallic W and WC_{1-x} phases are also identified in XRD patterns for all the coatings except that the enhancement in the peak intensity with reducing the spray angle is not obvious as compared to that of W_2C . The results reveal that the thermal spray at smaller angles promotes decomposition of WC into carbon-deficient phases to some extent.

The dependence of WC retention on the spray angle is given in Fig. 3, where the WC retention after new phase formation in the coatings was defined similar to that in a previous study [20], and calculated using the following equation based on the intensity of the strongest peak of the main phases, i.e. I_{WC} represents the integrated intensity from the diffraction peak at $2\theta = 35.6^\circ$ for WC (100), $I_{\text{W}_2\text{C}}$ at $2\theta = 39.4^\circ$ for W_2C (102), I_{W} at $2\theta = 41.6^\circ$ for W (110), and $I_{\text{WC}_{1-x}}$ at $2\theta = 42.9^\circ$ for WC_{1-x} (200), respectively.

$$I_{\text{ret.WC}} = \frac{I_{\text{WC}}}{I_{\text{WC}} + I_{\text{W}} + I_{\text{W}_2\text{C}} + I_{\text{WC}_{1-x}}} \quad (2)$$

Therefore, the decomposition of WC is evaluated by the retention ratio of WC content in coatings. The WC retention ratio decreased as reducing the spray angle, from about 81% at 90° to 70% at 30° , with a rapid reduction in the range of less than 60° .

3.2 Morphological characterization

Fig. 4 shows the deposition rate, surface roughness, and porosity of WC-10Ni coatings obtained by the HVOF spraying at different spray angles. The deposition rate is obviously

reduced as the spray angle decreases, from a value of about 20 μm per each set of passes at the spray angle of 90° to about 10 μm per passes at 30° . The rapid linear decrease is observed at spray angles less than 60° . As reducing the spray angle from 90° to 30° , the average surface roughness is slightly lowered from a Ra value of 3.4 to 3.1 μm . Along with decrease in the spray angle, the coating porosity is doubled from a value of about 0.8% to 1.6% as estimated from the SEM images at with a low magnification of 200. As for the porosity data obtained from analyzing higher magnification images, the porosity increases more rapidly with reducing the spray angle from a value of about 0.6% at 90° to about 2.6% at 30° . It is revealed that, image analysis at the different magnifications image led to different porosity at the same spray condition, i.e. the value is higher for the higher magnification at 30° but becomes lower at 60° and 90° , and similar at 45° . Moreover, the standard deviation of porosity is higher as obtained from the images of the higher magnification. This difference may be understood by the fact that the analysis area in the coatings at 10000 magnification is about 50 times smaller than that of images at 200 magnification when the same number of images was used for analyzing the porosity, and at the same time more tiny pores in the submicron range can be identified at the higher magnification. Thus, it is also implied that a variation in the density of submicron pores between the smallest spray angle of 30° and the larger spray angle of 60° and 90° . It is confirmed that, dependence of deposition rate and surface roughness on spray angle presents a decreasing tendency and an increasing tendency is observed for the porosity.

Typical SEM images of the coatings in the 10000 magnification are presented in Fig. 5, for the WC-10Ni coatings sprayed at different angles from 30° to 90° , respectively. Small pores mainly below 1-2 μm can be clearly observed, whereas the submicron range porosity is hardly to be counted in the common method based on metallographic images of 100 or 200 magnification [16]. In accordance with the difference in the coating porosity on different magnifications (Fig. 4), WC-10Ni coatings show a relatively low porosity at 90° and 60° and a notable increase in the porosity at 45° and 30° , and particularly formation of small pores in submicron size is significant at the smaller spray angles.

3.3 Mechanical characterization

Fig. 6 shows the Vickers microhardness of WC-10Ni coatings deposited at the

different spray angles, measured at the different loads of 100 g and 300 g respectively. The microhardness increases with increasing the spray angle. At spray angle of 90°, the average coating hardness at the two loads is very close, i.e. about 1115HV_{0.1} and 1116HV_{0.3}, respectively. Note that, the microhardness of coatings obtained with the lower load are higher than that of measured under the higher load, and the difference seems to be bigger at the smaller spray angles. The microhardness measurements have an indent diagonal length of about 12-14 µm for 1000-1200HV under the load of 100 g and about 22-24 µm for 1000-1100HV under the load of 300 g. The changes in the coatings porosity and phase transformation due to varying the spray angles directly affect the microhardness in a way that, both enhanced decomposition of WC phase and micro-pores formation reduce the measured values at the higher load of 300 g since more submicron pores and more carbon-deficient phases of lower hardness were covered by the larger indent area under the higher load in comparison with that of 100 g. It is also indicated that, from the fact of no difference in the measured values under the loads of 100 g and 300 g for coatings at normal angle spraying, influence of coating porosity on the microhardness is negligible when the porosity is no more than 1%, and above the critical value increase in the coating porosity due to off-angle spraying [Fig. 4(c)] reduce the coating microhardness.

Fig. 7 shows the elastic modulus of the coatings at the different spray angles, respectively. The elastic modulus measured by the ultrasonic method present a general increase trend with increasing the spray angle. The value at the smallest spray angle of 30° is about 331 GPa, and almost linearly increased to about 345 GPa at 45° and 363 GPa at 60° with respect to the spray angle value, and the increase is slow down with further increase in the spray angle, i.e. to about 375 GPa at 90°. The K_{IC} , representing the resistance of coatings to fracture cracking propagation, is shown in Fig. 8. It is confirmed that, the K_{IC} decreased gradually with decreasing spray angle, with a value in the range of about 6.7-9.1 MPa·m^{1/2}.

3.4 Wear performance

Fig. 9 shows the specific wear rate of the coatings obtained at different spray angle. All the coatings possess a relatively low specific wear rate below 10⁻⁷ mm³/Nm, though a slight decrease of wear rate is observed as increasing the spray angle. In the present

water-lubricated wear test, the specific wear rate of the coating sprayed at 30° is found to be about $6.5 \times 10^{-8} \text{ mm}^3/\text{Nm}$ and slightly reduced to about $5.6 \times 10^{-8} \text{ mm}^3/\text{Nm}$ for the coating sprayed at 45° , about $5.3 \times 10^{-8} \text{ mm}^3/\text{Nm}$ at 60° and about $5.0 \times 10^{-8} \text{ mm}^3/\text{Nm}$ at 90° , respectively. The corresponding friction coefficients of WC-10Ni coatings as well as the surface roughness before/after wear test are presented in Fig. 10, respectively, for deposited at the different spray angles. It is confirmed that, a general decrease tendency of friction coefficient is observed with reducing the spray angle. The friction coefficient curves present a maximal value at the beginning of wear test during running-in stage, and decrease gradually down to a smaller value during a steady stage which starts from 2000-7000 s dependent on the spray angle, except for the case of normal angel sprayed where no clear steady stage was observed but a relatively stable coefficient of 0.15 found during 9000-15000 s followed by a slow reduction to a value similar to that of 60° sprayed coatings at the end of wear test up to 18000 s. Moreover, the coatings obtained at the spray angle of 90° presents the higher friction coefficient over the other three cases with a maximal value of about 0.25 during initial stage of test period. For the coatings deposited at spray angle of 60° , the friction coefficient starts with a maximal value of 0.20-0.25 within running-in stage and the steady stage begins at about 4000 s with a value of 0.12-0.15. The lowest friction coefficients are found at the smaller spray angles of 30° and 45° , with a maximum value of 0.15-0.20 during running-in stage lasting about 2000-3000 s followed by a steady stage with a value of 0.10-0.12 up to about 6000s, and then with a further drop in the value to 0.08-0.10. It is also noted that, relatively smooth friction coefficient curves with less fluctuation in the value are found for the coatings sprayed at the angle of 90° , whereas a certain fluctuation of friction coefficients is observable for the coatings off-angle sprayed. The surface roughness increased after wear test to about 0.025-0.03 μm from the original 0.013-0.015 μm , and for the off-angle sprayed coatings roughness is slightly higher [Fig. 10(b)]. The typical surface morphologies of wear track on the coatings obtained at the different spray angles are presented in Fig. 11, respectively. It is shown that, all the coatings mainly underwent a mild abrasive wear process with some small and shallow parallel ploughing scratches presented on the surface. This wear morphology is similar to that of bulk WC-Ni mild abrasive wear accompanied with some adhesive wear under dry sliding

against a softer bearing steel wear pair in our previous study [21]. Note that, in the present study, much more mild abrasive wear is obtained with a low specific wear rate 1 order less due to well water lubricated condition.

4. Discussion

4.1 Oxidation during off-angle spraying of WC-Ni coating

Formation of C deficient phases such as WC_{1-x} , W_2C or W has been also observed in WC-Co coatings during HVOF spraying [18,20]. Dobler et al. [22] reported that increasing the oxygen/fuel ratio of HVOF process may promote the oxidation of stainless steel coatings. In a previous numerical study of the particles oxidation during plasma spray of metallic coatings, it was indicated that the metal particle oxidation during in-flight is reciprocal to particle velocity and diameter square [23]. In addition, controlling the substrate at the relatively low temperature may also reduce particles oxidation [24,25]. Note that, in this study it is clearly found that, the oxidation/decomposition of WC phase in the sprayed coatings is notably affected by merely changing the spray angle while keeping the other spraying parameters constant, i.e., reduction of spray angle led to enhancement in the decomposition of WC phase. All the factors mentioned above, including oxygen/fuel ratio, particle size and velocity, and substrate temperature can be excluded in the present experimental setup. It is thus clear that, only the geometric factor of off-angle spraying scheme may interpret the different retention degree of WC phase in the off-angle sprayed coatings in comparison with that of normal angle.

Three regions are concerned where oxidation may occur: the core region of oxy-fuel flame or plasma jet, the free jet portion of the spray plume and the surface region of the substrate [26]. Swank et al. [27] studied the HVOF sprayed Inconel coating and concluded that oxidation of in-flight powders in the flame was limited and the oxidation predominantly proceeded on the substrate. Hackett and Settles [28,29] also pointed out that the particles exposure time in the oxidizing atmosphere during the period of deposition onto substrate are longer than that of flight in the center of flame. Hackett et al. [30] confirmed that bulk airflow was induced in the vicinity of the HVOF plume along the direction of its axis. The oxygen in the airflow was mixed with the plume, leading to increase of oxygen concentrations at a certain distance downstream from the nozzle exit of spray gun. Korpiola

et al. [31] measured the oxygen concentrations in HVOF plume using electrolyte oxygen probe by which oxygen concentration increased in an HVOF plume with increasing distance from the nozzle exit. The incorporation of oxygen into the flame near the deposited substrate surface should be significant due to gas dynamic flow, i.e. more entrained gas from ambient atmosphere in this region. It is implied that the oxidation of WC phase mainly took place during the periods of in-flight powders approaching to the substrates and splats deposition/deformation to form coating, different from other thermal spray technologies such as plasma spray with higher temperature and lower velocity of sprayed powders where the significant oxidation occurred during whole in-flight period of powders with longer dwelling time in the high-temperature flame.

Therefore, enhanced oxidation of WC phase leading to formation of WC_{1-x} , W_2C and W phases in the coatings at smaller spray angles is understood that, on one hand, due to smaller spray angle the particles flight is extended near the substrate surface, i.e. prolonged exposure time in the region of large amount of air entrained, and on the other hand, a thinner layer deposition per pass is obtained by off-angle spraying [Fig. 4(a)] by which more passes are needed to achieve a coating with similar final thickness and enhanced oxidation reaction is then promoted by the prolonged exposure time as well as longer accumulative heating history. Moreover, in WC-Ni system reaction between WC phase and oxygen at the high temperature may release gaseous products [32], which likely contribute to formation of the finely distributed pores of submicron range in the off-angle deposited WC-Ni coatings.

4.2 Influence of off-angle spraying on coating features and characteristics

As categorized as two aspects of surface integrity parameters, surface features of HVOF WC-Ni coating samples concerned here include surface roughness, porosity, microstructure in addition to the phase structure of WC decomposition at the different spray angles, and the surface characteristics include microhardness, elastic modulus, and indentation fracture toughness; consequently, both the surface features and characteristics as well as their interactions should be considered to interpret the final tribological behavior [11]. The comparative study confirmed that, the spray angle notably affect the coating feature and characteristics. Specifically, taking into account the results for the lowest spray

angle of 30° benchmarked on that of 90°, it is found that the largest change in these surface integrity parameters is from the porosity. The porosity of the coatings is doubled as estimated from 200 magnification images and tripled from the higher magnification images, indicating that number of micro-pores is preferably enhanced at the off-angle spray [Fig. 4(c)]. The variations in the other feature and characteristic aspects of off-angle sprayed coatings are in correlation with the porosity change except for a lower relative change in comparison with that of normal angle. The retention of WC phase based on the relative XRD diffraction peak intensity is reduced by 13.6% (Fig. 3), and for the maximal change in the microhardness is observed under 300 g load by a reduction of only 11.7% (Fig. 6), and the elastic modulus reduced by 11.7% (Fig. 7) and indentation fracture toughness by 26.4% (Fig. 8), respectively.

As for the surface roughness, coating porosity and deposition rate of off-angle HVOF spraying of WC-Ni coatings, the present result is generally in agreement with that of HVOF sprayed WC-Co coatings using fine powders ($-10+2\mu\text{m}$) [1], i.e., smaller spray angle leads to lower surface roughness, higher porosity and lower deposition rate, among them the porosity and deposition rate are more significantly changed. It is understood that at smaller angles the tangential component of velocity of accelerated powders onto substrate surface during deposition increased and simultaneously the vertical component decreased, and the melted/semi-melted powders are easy to rebound or be taken away from the surface by the flame [33]. Moreover, the reduced normal impact force of the splat onto the coated surface may also contribute to a higher porosity in addition to the gaseous products from the oxidation reaction, and lead to a lower cohesion reducing the microhardness and indentation fracture toughness to some extent.

4.3 Wear performance of HVOF WC-Ni coatings at off-angle spraying

Specific wear rates of these the coatings are relatively low under water-lubricated condition, being the order of $10^{-7} \text{ mm}^3/\text{Nm}$ against bulk WC-Ni cemented carbide (Fig. 9). Therefore, high performance of off-angle HVOF sprayed WC-Ni coatings can be thus ensured as the above mentioned surface features and characteristics of coated samples are produced in the controllable range. The lower friction coefficients of coatings at the smaller spray angles is believed to result from better water lubrication condition with moderately

higher coating porosity of well-dispersed micro-pores. The improvement in tribological behavior with reduced friction coefficient with higher porosity is analogous to the observed lubricant pocket effect of intentionally patterned surfaces with small dimples under [34,35]. Note that, in the present case, the coating porosity is controlled no more than 3% and then the reduction in the microhardness, elastic modulus and toughness is minimized as mentioned in Section 4.2. As a result, the deterioration effect of the slight reduction in the mechanical properties on wear resistance could be compensated by the improved lubrication leading to a lower friction force at the interface in comparison with that of normal spray angle. In our previous study for wear resistance on surface modified bulk WC-Ni cemented carbide under unlubricated condition, it is revealed that the abrasive wear of WC-Ni originates from generation of pull-off carbide particles or fragmentation on the friction interface, while adhesive wear from the preferential removal of metallic binder phase under deformation and protrusion from between the much harder carbide phase [21]. It is found that, the bonding strength between WC harder phase and metallic phase is crucial for the wear performance. The pull-off of carbides particles could be mitigated as the friction force is reduced at the lower friction coefficient. Nevertheless, a larger fluctuation is observed for the lower friction coefficient of the off-angle sprayed coatings (Fig. 10). It is implied that, the probability of pull-off of carbide grains is still higher for the off-angle sprayed coatings as compared to the normal angle sprayed coatings, where both increased porosity and decomposition of WC into more brittle WC_{1-x} and W_2C phases could weaken the interface bonding of WC gains and Ni binder at the local region, as inferred from the slightly reduced microhardness and toughness. Therefore, the coating features and characteristics during off-angle spraying present the competing effects on the wear performance, i.e., lower friction force facilitated by improved water lubrication from porosity, but higher wear rate by abrasive wear with more pull-off of WC grains from porosity and brittle phase. Based on the results of the present study, it is indicated that off-angle spraying is applicable for wear-resistant cemented carbide based coatings under fluid lubricating condition. It also inferred that, measures to generate a certain porosity and simultaneously strengthen the bonding between WC grains and metallic binder is a solution to further improve the coatings wear performance.

5. Conclusions

The effects of spray angle have been investigated for HVOF WC-10Ni coating on the tribological behavior, through characterizing the surface features and characteristics of coated samples. There are main conclusions as follows.

- (1) The major change in the surface features and characteristics of coatings due to off-angle spraying is found to be porosity as reducing the spray angle from 90° to 30°, with a variation up to 300% benchmarked on that of normal angle spray. In comparison, the minor changes are observed in surface roughness, phase composition, microhardness and indentation fracture toughness within a range of 10-30%, respectively.
- (2) The deposition rate and surface roughness decreased at the smaller spray angles, while the porosity increased accordingly. The enhanced porosity may result from gaseous product during oxidation of WC phase as well as reduced impact force normal to the substrate surface at the off-angle spraying.
- (3) The WC phase transformation to W_2C and WC_{1-x} of HVOF sprayed WC-10Ni coatings could be enhanced to some extent at off-angle spraying, mainly attributed to the characteristic process of HVOF spraying by which the high velocity of powders minimizes oxidation in the flame and dominant oxidation reaction occurs in the region near to and/or on the deposited surfaces with more entrained ambient gas.
- (4) The surface features and characteristics of off-angle sprayed coatings have a combined influence on the final wear performance. The better lubrication condition of higher porosity with more micro-pores in the coatings deposited at lower spray angles leads to a mitigated friction force, while the reduction in the microhardness and fracture toughness is minimized within a maximum porosity no more than 3%.
- (5) All the WC-Ni coatings sprayed at different spray angles presented a comparably low specific wear rate below $10^{-7} \text{ mm}^3/\text{Nm}$ and the small spray angle down to 30° are applicable in tribological cases with water lubrication.

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Table 1 Typical parameters of HVOF spray for WC-10Ni coatings

Kerosene flow	22.7 l/h
Oxygen flow	811 NLPM
O/F ratio (λ)	1.11
Spray distance	350 mm
Spray speed	300 mm/s
Track pitch	5 mm
Spray angle	30°, 45°, 60°, 90°
Carrier gas N ₂ flow	7 NLPM
Powder flow	75 g/min
Shielding gas N ₂ flow	2000 L/h

Figure Captions

Fig. 1 Spray scheme of HVOF process with varying incident angle

Fig. 2 XRD patterns of WC-10Ni coatings deposited at the different spray angles

Fig. 3 Dependence of WC peak ratio from WC-10Ni coatings on the spray angle

Fig. 4 Dependence of the deposition rate, porosity, and surface roughness on the spray angle for HVOF sprayed WC-10Ni coatings: (a) deposition rate, (b) surface roughness, (c) porosity

Fig. 5 Microstructure of WC-10Ni coatings deposited at the different spray angles: (a) 30°, (b) 45°, (c) 60° and (d) 90°

Fig. 6 Microhardness, measured respectively under 100 g and 300 g load, of WC-10Ni coatings deposited at the different spray angles

Fig. 7 Elastic modulus of WC-10Ni coatings deposited at the different spray angles

Fig. 8 Fracture toughness of WC-10Ni coatings deposited at the different spray angles

Fig. 9 Specific wear rate of WC-10Ni coatings deposited at the different spray angles

Fig.10 Friction coefficient of WC-10Ni coatings deposited at the different spray angles and the corresponding surface roughness before/after ring-on-block wear test under water lubrication: (a) friction coefficient and (b) surface roughness R_a

Fig.11 Morphology of wear surfaces on WC-10Ni coatings after ring-on-block wear test under water lubrication: (a) 30°, (b) 45°, (c) 60° and (d) 90°

Fig. 1

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