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High-Performance Molybdenum Coating by Wire–HVOF Thermal Spray Process

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Abstract Coating deposition on many industrial components with good microstructural, mechanical properties, and better wear resistance is always a challenge for the thermal spray community. A number of thermal spray methods are used to develop such promising coatings for many industrial applications, viz. arc spray, flame spray, plasma, and HVOF. All these processes have their own limitations to achieve porous free, very dense, high-performance wear-resistant coatings. In this work, an attempt has been made to overcome this limitation. Molybdenum coatings were deposited on low-carbon steel substrates using wire–high-velocity oxy-fuel (W-HVOF; WH) thermal spray system (trade name HIJET 9610®). For a comparison, Mo coatings were also fabricated by arc spray, flame spray, plasma spray, and powder-HVOF processes. As-sprayed coatings were analyzed using x-ray diffraction, scanning electron microscopy for phase, and microstructural analysis, respectively. Coating microhardness, surface roughness, and porosity were also measured. Adhesion strength and wear tests were conducted to determine the mechanical and wear properties of the as-sprayed coatings. Results show that the coatings deposited by W-HVOF have better performance in terms of microstructural, mechanical, and wear resistance properties, in comparison with available thermal spray process (flame spray and plasma spray).

Keywords adhesion · microhardness · molybdenum · porosity · wear · wire–high-velocity oxy-fuel (W-HVOF)

Introduction

Molybdenum (Mo) is a widely used material in the thermal spray industry due to its promising wear and scuff resistance properties. Therefore, a coating of molybdenum is fabricated where a higher hardness and low friction coefficient are needed to offset the wear mechanisms. Molybdenum is used in many industrial applications, viz. bearings, seals, and shafts, as an overlay coating to prevent surface damage and degradation (Ref 1). Molybdenum coatings show low friction, excellent sliding, and wear resistance compared to uncoated hardened steel (Ref 1, 2). Thermal spray coatings of molybdenum and its alloys are used for many automotive parts due to their excellent tribological properties (Ref 1, 3).

In the past, molybdenum was deposited by the flame spraying method using Mo wire or powder. Flame spray is a widely used coating deposition method in the broad category of thermal spraying, in which molybdenum wire gets melted through a high-temperature flame and compressed air breaks the molten wire into several small droplets, resulting in splats formation and that builds up a coating. The only problem with this process is to have a high degree of oxidation. This oxidation degrades the performance of molybdenum coating and resulting in coatings to relatively have a short life (Ref 4). Plasma spray is often used to deposit molybdenum coatings (Ref 5-11). But some recent studies show that plasma-sprayed molybdenum coatings are relatively soft as its microhardness falls in the range of 300-500 HV, having porosity more than 5% and low wear resistance (Ref 12-15).

High-velocity oxy-fuel (HVOF) coatings are being used in many industries for coating deposition on various parts and components. The HVOF coatings offer a better advantage over air plasma-sprayed (APS) coatings.

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However, the HVOF coatings are applied using spray grade powders as the feedstock material. It is well known that spray grade powders are more expensive than spray grade wires used as a feedstock material. In the powder-HVOF process, powder particles travel in flame for a short time due to high particle velocity. Therefore, the possibility of having unmelted or semi-molten particles in the coating cannot be denied and these may increase porosity and reduce other mechanical properties of the coatings.

In the present study, molybdenum coating was deposited on the mild steel substrates using modified HVOF thermal spray system W-HVOF in order to obtain better coating properties (higher hardness, high adhesion strength, very low porosity, higher wear resistance) compared to coatings deposited by other available spray methods. Coating properties have been investigated and compared with arc, flame, and plasma-sprayed Mo coatings.

Experimental

Molybdenum wire (99.9% pure) 3.17 mm in diameter was used as a feedstock material for preparing the coating samples. The coatings were deposited onto low-carbon steel substrates of dimensions 80 × 50 × 3 mm^3. Prior to spraying substrates were cleaned with acetone for 5 min and grit-blasted with alumina (Al_2O_3 of 16 mesh size) in order to increase the surface roughness, so that it could improve the adhesion strength of the coating to the substrate. The grit blasting air pressure was 4.5 bars with a blasting angle of 90°. Subsequently, they were blasted with high-pressure air and mechanically cleaned to remove any remaining grit on the surface. The resultant surface roughness of the substrate was approximately Ra ~ 6.96 µm.

Mo coatings were deposited by a patented technology (*Patent number 214843, Indian Patent application number 2529/DEL/1997*) W-HVOF thermal spray system (trade name: HIJET 9610®), developed by the R&D unit of the MEC, Jodhpur, India. A schematic diagram of the gun and feeding of wire is shown in Fig. 1.

The W-HVOF system works on oxygen propane and liquefied petroleum gas (LPG). The present experiments were carried out using oxygen LPG as fuel. (Propane is not available in India.) The process parameters were previously optimized in order to achieve the dense microstructure, highest microhardness, and high deposition efficiency. Optimized spray parameters are listed in Table 1. The samples were prepared for (1) metallographic evaluation, (2) three-body dry abrasion wear testing, and (3) tensile bond strengthening of the coatings.

The modified HVOF thermal spray system (M/S Metallizing Equipment Company Jodhpur, India) uses wire as the feedstock, which directly affects the process economics and makes it a cheaper coating process because it is a well-known fact that the wires are cheaper than powders. As well, the operating cost of this process is lower than most of the other available thermal spray processes. The advancement of this system is that the temperature reaches the melting point of the wire and atomization is also high in the W-HVOF process, resulting in wire droplets are completely melted and there are no unmelted or semi-molten particles found in the coatings.

For a comparative study, the same Mo wire and Mo powder were also sprayed by arc spray (AS), flame spray (FS), plasma spray (PS), and powder-HVOF (PH) techniques, respectively. Spray conditions were fixed at the optimal parameters for arc, flame, plasma, and powder-HVOF spraying. Spray parameters for AS, FS, PS, and PH are listed in Tables 2, 3, 4, and 5, respectively. Top surfaces, cross-sectional morphologies, hardness, porosity, adhesion strength, surface roughness, and three-body dry abrasion results have been studied and compared.

All as-deposited coatings were tested and characterized in the R&D laboratory of MEC, India. Coated samples were cut and polished following a routine developed to analyze the microstructures and other properties. Cross sections of the samples were examined under the scanning electron microscope (Carl ZEISS Evo18, equipped with backscatter electron detector (BSC)) and EDS analysis (Oxford Instruments, UK). X-ray diffraction (PANalytical Empyrean Series 2, Netherlands) was used to identify the phases present in powder and in the coating. The diffraction angle (2θ) ranges from 20° to 80°. A 0.05° step size and a 2 s dwell time per step were employed. The microhardness was examined with a Vickers microindenture (Shimadzu HMV-G-21ST, Japan) as per ASTM-E384 under a load of 300 g (HV0.3), and fifteen measurements were taken on the coated sample. Porosity measurements were made with a standardized batch routine with the QSMIAS 4.0 Metallurgical Image Analysis System as per ASTM-E2109 method B. Coating deposition efficiency (DE) was calculated as per ISO 17836:2017.

The surface roughness of the as-sprayed coatings was measured using surface roughness tester (MITUTOYO Model SJ-210, Japan). A diamond stylus was traversed across the as-sprayed coating with a cutoff length $\lambda c = 0.8$ mm and traversal speed 0.5 mm/s as per ISO 4287: 2015. Each coated sample was measured at five random locations with the average and standard deviation of the Ra values being quoted. The adhesion strength of the coating was tested using INSTRON Digital Tensile Bond Testing Machine (Model: 5969 USA) according to ASTM-C633. Three-body dry abrasion tests were conducted as per ASTM-G65 to see wear characteristics of the Mo coatings.

Fig. 1 Schematic of the gun and wire feeding system

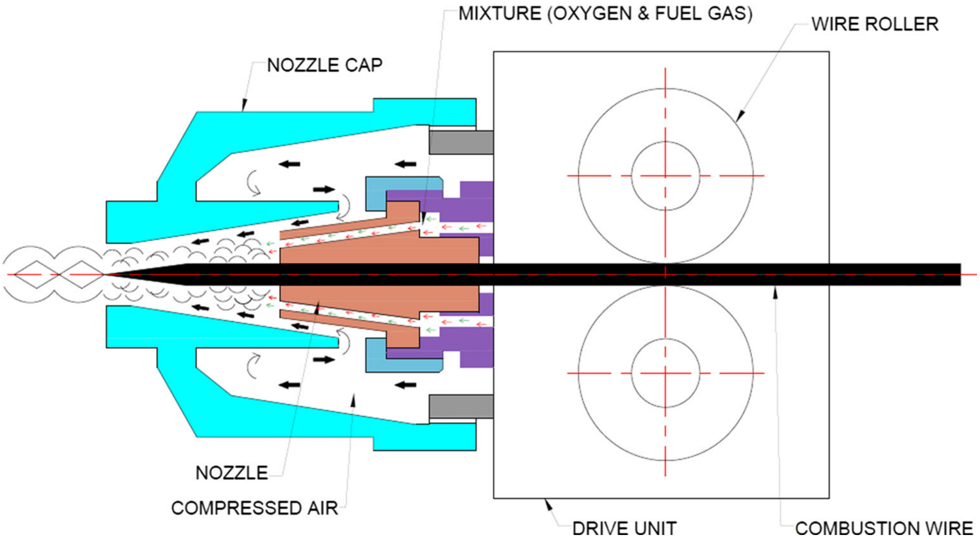

Table 1 Optimized spray parameters for the W-HVOF-sprayed Mo coatings

Spray parameters	Values
Oxygen flow	200-230 slpm
LPG flow	40-50 slpm
Air flow	550-650 slpm
Spray distance	6, inches
Wire and size	Molybdenum, 3.17, mm
Wire feed rate	52 cm/min (45, gm/min)

slpm standard liter per minute

Table 2 Spray parameters for arc-sprayed Mo coatings

Spray parameters	Values
Voltage	40, V
Current	150, A
Air pressure	5, kg/cm^2
Spray distance	6, inches
Wire and size	Molybdenum, 3.17, mm
Wire feed rate	288, cm/m

slpm standard liter per minute

Table 3 Spray parameters for flame-sprayed Mo coatings

Spray parameters	Values
Oxygen flow	28.2 slpm
Acetylene flow	11.75 slpm
Air flow	600 slpm
Spray distance	4, inches
Wire and size	Molybdenum, 3.17, mm
Wire feed rate	52, cm/m

slpm standard liter per minute

Table 4 Spray parameters for plasma-sprayed Mo coatings

Spray parameters	Values
Primary gas Ar	38 slpm
Secondary gas H	6-7 slpm
Carrier gas Ar	4.5 slpm
Voltage	66, V
Current	600, A
Spray distance	4, inches
Powder feed rate	40, gm/min

slpm standard liter per minute

Results and Discussion

Coating Microstructures

The cross-sectional and their corresponding top surface micrographs of the as-sprayed coatings by WH, AS, FS, PS, and PH spraying are shown in Fig. 2. The average coating thicknesses deposited by five different processes (WH, AS, FS, PS, and PH) were found to be 237, 400, 350, 415, and 304 microns, respectively. Variations in coating thicknesses can be correlated with a feed rate of feedstock material. However, maximum DE was observed in the W-HVOF process than AS, FS, and PS. DE for all five WH, AS, FS, PS, and PH spray processes was found to be 58, 56, 42, 20, and 45%, respectively. Higher DE in the WH could be because of no loss of the molten droplet and the complete melting of wire feedstock.

Very dense and microcrack-free coating microstructures were observed in the coatings deposited by WH in

Table 5 Spray parameters for powder-HVOF-sprayed Mo coatings

Spray parameters	Values
Oxygen flow	250 slpm
LPG flow	60-65 slpm
Air flow	550-600 slpm
Spray distance	7, inches
Powder feed rate	40, gm/min

slpm standard liter per minute

comparison with coatings deposited by AS, FS, PS, and PH process. It is evident from the SEM micrographs that low porosity and crack-free microstructures can be considered as a first structural indicator for other mechanical properties like microhardness, surface roughness, adhesion, and wear. Coating porosities were measured by the image analyzer having QSMIAS 4.0 Metallurgical Image Analysis System. Seven sites from each cross section were taken into account for the porosity measurements. The porosity of the coatings deposited by WH, AS, FS, PS, and PH was found to be < 0.7, 4.52, 5, 4, and 3-4%, respectively. The WH-sprayed coating exhibited a good microstructure due to the accumulation of the high-speed molten particles onto the substrate with higher DE and resulting in coatings that are very dense, porous free and well bonded to the substrate. Such quality coating properties cannot be achieved by AS, FS, PS, and PH processes as results have shown. It is reported that the HVOF coating possesses minimum porosity due to high-impact velocity compared to other thermal spray technique (Ref 16); thus, in the present work, the wire is used as feedstock material in the HVOF process in order to achieve better coating properties.

The lamellar structure of the plasma-sprayed Mo coating is formed by the deformation of molten droplets when impacting the substrate. Plasma-sprayed Mo coating has large porosities, cavities, and microcracks in comparison with WH and FS coatings. It is due to the entrance of fuel gases in small porosity areas, which were formed between the lamellar structure of the plasma-sprayed Mo coating (Ref 17, 18). At the time of cooling, residual internal stresses are generated in flattened droplets results microcracks formation in the coatings. The same phenomenon occurs in the flame spray process. But in the W-HVOF process due to the high-velocity impact of molten particles on the substrates resulting in no formation of such microcracks in the coating.

In general, the coating roughness decreases if the droplet sizes are very fine during the coating deposition. Low splash fraction and increasing direction angle of the overspray due to high-impact particle velocity are also key factors of low surface roughness. The surface roughness of the all five as-sprayed coatings by WH, AS, FS, PS, and PH was measured as Ra = 2.83 µm, Ra = 9.81 µm, Ra = 5-7 µm, Ra = 5.36 µm, and Ra = 8.63 µm, respectively.

To investigate the internal structure of the as-sprayed coatings, Fig. 3 shows the coating microstructures at higher magnification. Clearly, it can be observed from the micrographs that W-HVOF coatings have fine, dense structure with less porosity and free from internal microcracks, as shown in Fig. 3(a). However, microcracks can be seen in the powder-HVOF coating in Fig. 3(e). Arc and plasma-sprayed coating has a lamellar structure, as shown in Fig. 3(b) and (d).

The microhardness measurement was carried out on the as-sprayed coatings. The average of 10 identical hardness readings is taken along the cross section of each sample. It was observed that WH-sprayed Mo coating has a high hardness (928 ± 15 HV) in comparison with FS and 2 times higher than PS and powder-HVOF Mo coating. Such higher hardness has been reported by Modi and Calla (Ref 4) in the first phase of development of W-HVOF. The average hardness, porosities, surface roughness, and DE values of the Mo coatings are summarized in Table 6. The hardness of the WH-sprayed coating found to be 3 times higher than recently studied Mo coatings and 2 times higher than $MoSi_2$-Mo plasma-sprayed coatings (Ref 13, 14). Higher hardness in WH-sprayed can be correlated with the porosity level in the coatings which is less than 0.70% and improvement of the splat particle cohesion due to increase velocity and temperature of the in-flight particles and lower oxide content in the as-sprayed coating.

Adhesion Strength of the Coatings

Adhesion strength is an important factor in thermal spray coatings because it is directly related to the performance and durability of the coating as it directly influences the fatigue life of the coating. The adhesion strength of the coatings was investigated by the tensile test using INSTRON Digital Tensile Bond Testing Machine UTM, Model: 5969, USA. The adhesion strength of the as-sprayed coatings by the five different processes (WH, AS, FS, PS, and PH) was found to be 55.10 ± 3.0, 52.0 ± 2.0, 50.20 ± 3.5, 41.0 ± 3.2, and 44.0 ± 3.0 MPa respectively. The compressive residual force at the interface is known to prevent the formation of thickness cracks and improve adhesion strength (Ref 19). In addition due to the high velocity of spraying, better adhesion strength could be achieved (Ref 20). The high velocity of the spraying, very low porosity, and the residual compressive stresses in the coating could be a possible reason for better bonding in the WH-sprayed Mo coating.

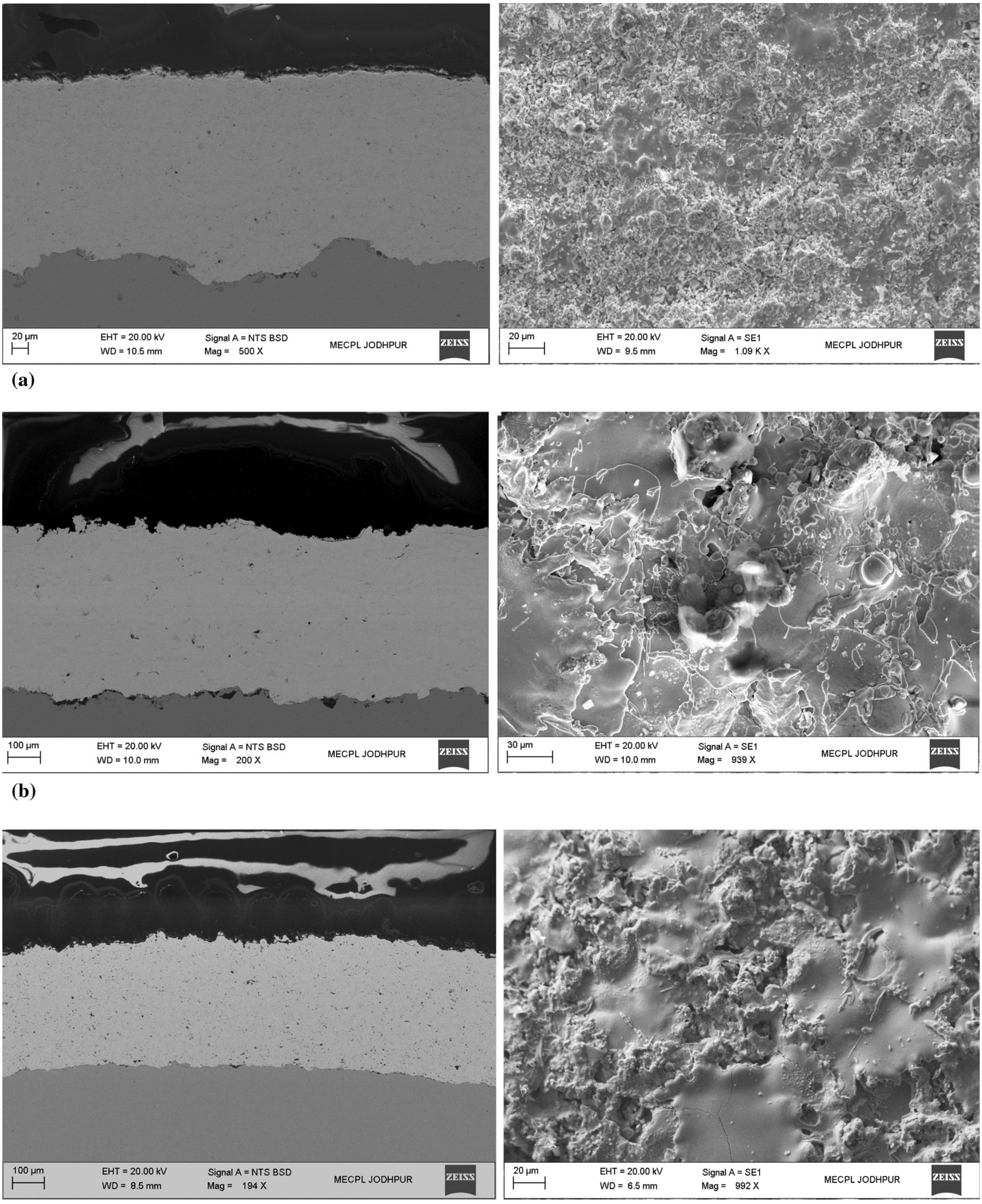

Fig. 2 Cross sections and corresponding top surfaces of the as-sprayed coatings deposited by five different processes (a) W-HVOF, (b) arc spray, (c) flame spray, (d) plasma spray, and (e) powder-HVOF

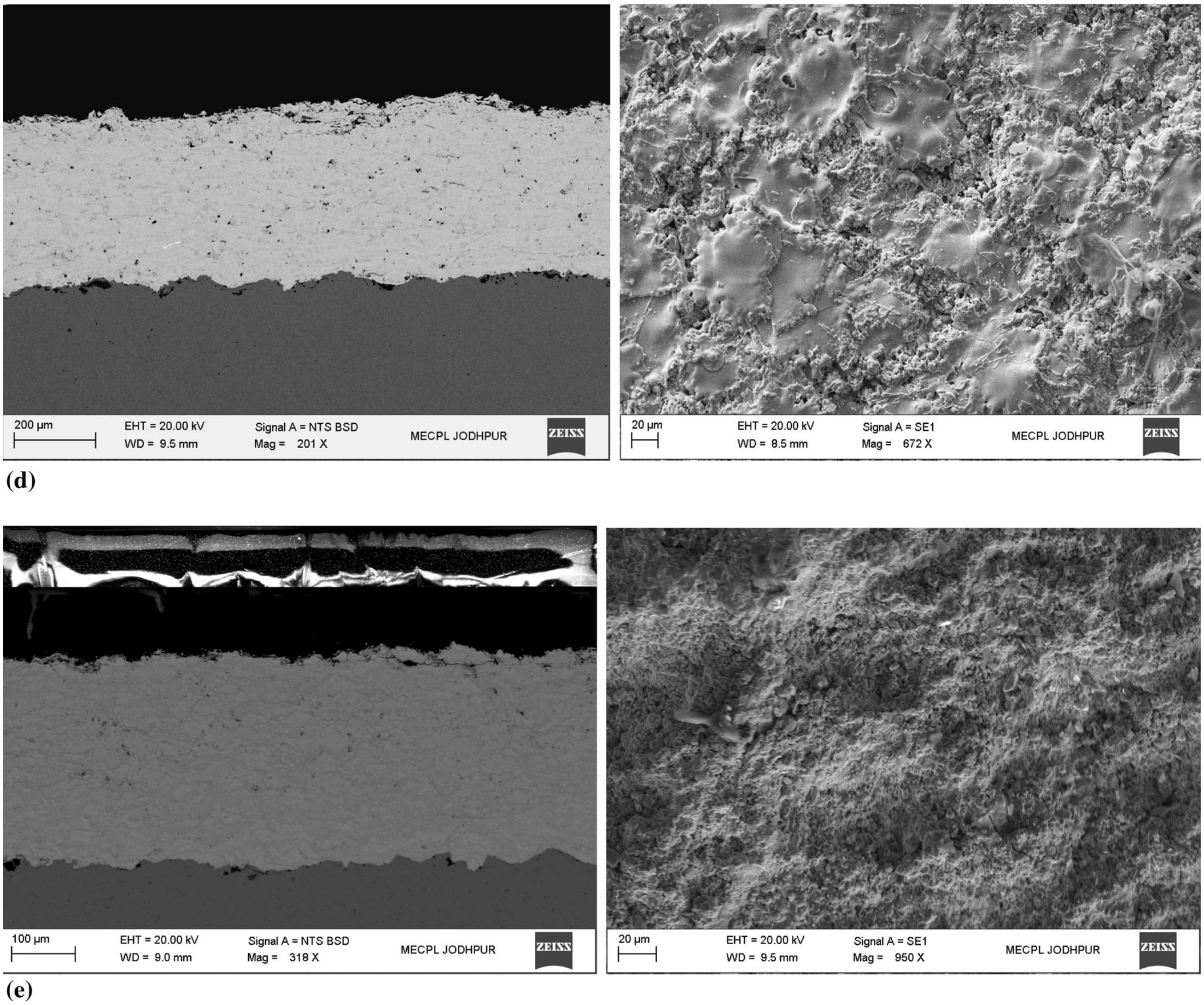

Fig. 2 continued

Dry Abrasion Test

To examine wear characteristics of all as-sprayed coatings, three-body dry abrasion tests were conducted as per ASTM-G65. Alumina (80 meshes) was used as abrasive media with a fixed flow rate of 300 gm/min. Wheel rotation was set at 100 rpm. All coatings were tested at a load of 50 N. A schematic of the test setup is shown in Fig. 4. All coatings were tested for 200 cycles.

After the dry abrasion test, weight loss results are shown in Fig. 5. It can be seen that plasma-sprayed Mo coating has shown higher wear rates in comparison with other respective coatings. W-HVOF-sprayed Mo coating shows superior wear-resistant characteristics. However, flame-sprayed Mo coatings also show a better wear-resistant property than AS, PS, and PH but lower than W-HVOF. Figure 6 shows the samples after the test. It can be seen that after test conducted at the same wear conditions, arc- and plasma-sprayed Mo coatings fully worn out and substrate surfaces appeared. It can be attributed that the wear rate depends on factors such as microstructure, the hardness of the coating, and oxide content in the coating. Analysis of oxygen content in all as-sprayed coatings has been discussed in the next section. In general, hardness is the most critical factor affecting wear resistance. However, internal factors such as ductility and the presence of pores also affect the wear properties.

To analyze the wear resistance of the coatings, worn surfaces of the coatings were investigated. These micrographs are showing the sample conditions after the end of testing. Figure 7 shows scanning electron microscopic images of all molybdenum coatings treated at 50 N under

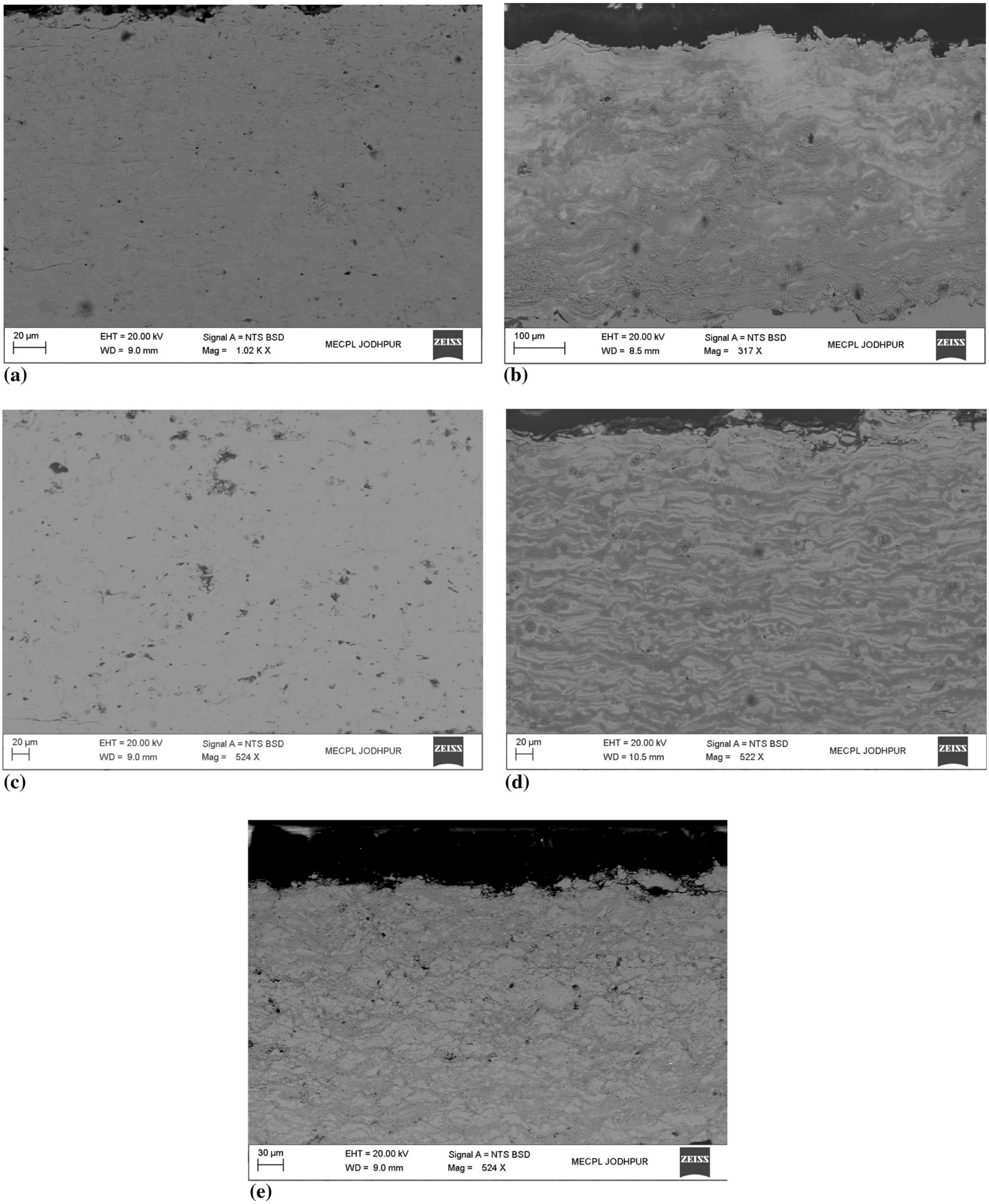

Fig. 3 Internal microstructures of the as-sprayed coatings deposited by five different processes at higher magnification (a) W-HVOF, (b) arc spray, (c) flame spray, (d) plasma spray, and (e) powder-HVOF

Table 6 Properties of as-sprayed Mo coatings

Coating properties	Coating process				
	W-HVOF	Arc spray	Flame spray	Plasma spray	Powder-HVOF
Microhardness at 300 gm load (HV)	928 ± 15 HV	400 ± 13 HV	660 ± 16 HV	383 ± 15 HV	384 ± 15 HV
Porosity	0.70%	4.52%	5%	4%	3-4%
Surface roughness Ra	2.83 μm	9.81 μm	5-7 μm	5.36 μm	8.63 μm

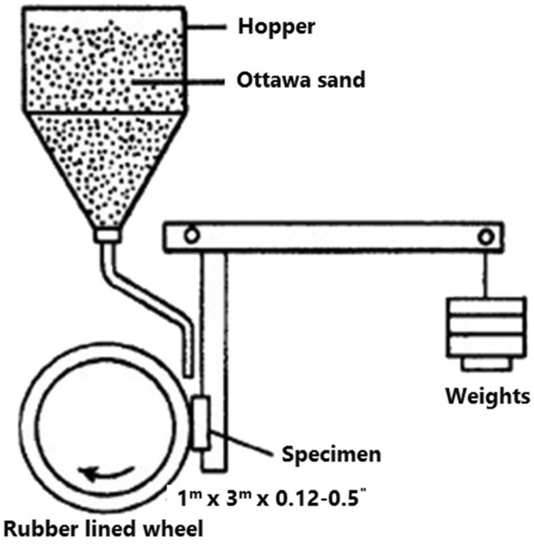

Fig. 4 A schematic of three-body dry abrasion test (ASTM-G65)

the same dry conditions. A wear scar can be seen on the worn surface of coatings as shown in Fig. 7 (a), (c), (e), (g), and (i), and corresponding Fig. 7(b), (d), (f), (h), and (j) shows pits, cracks, and splat fractures, at higher magnification.

As displayed in Fig. 7, pits, cracks and splat fractures, plastic deformation were found with their own different morphologies. After the wear test substrate surface can be identified in AS and PS samples and depth of the wear scar for the AS-, PS- and PH-sprayed coatings were higher than observed in WH and FS coatings as shown in Fig. 7(c), (g), and (i).

A coating's microstructure, hardness, and its friction characteristics affect the wear properties of a coating and environmental condition is also a factor (Ref 21). The microstructures of the molybdenum coatings deposited by different thermal spray processes (Fig. 7) indicate that porosity and inter-splat cracks are present. Severe stresses are generated in the coating during the friction with counterface. This stress causes inter-splat cracking, splat separation, and fracture, ultimately causing material loss and delamination.

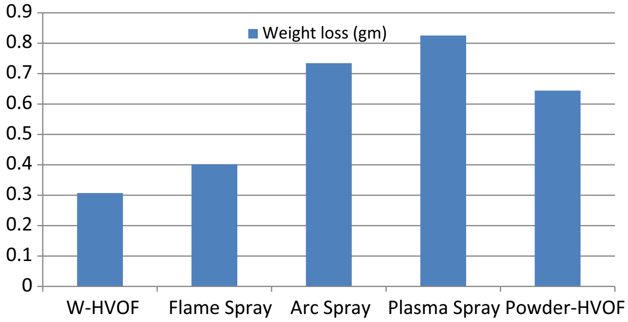

Fig. 5 Change in weight after the dry abrasion test

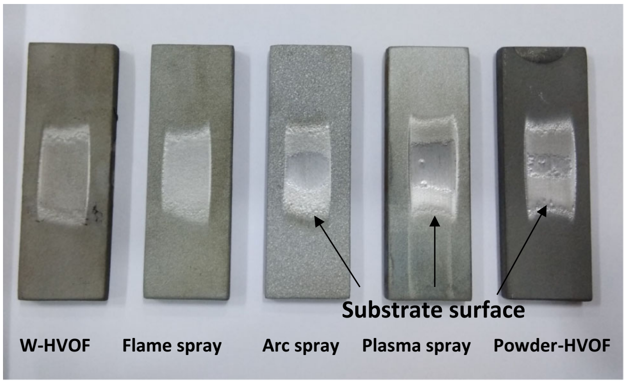

Fig. 6 Samples after the dry abrasion test showing wear scars

The wear properties of a material often depend on its hardness. As mentioned earlier, highly dense coating with low porosity (< 1) may provide a high hardness (Table 6). During dry abrasion testing of the as-sprayed molybdenum coatings, the abrasive media may penetrate into the available porosity in the coating. Due to this, the material is removed from the coating surface by plowing action (as shown in arc- and plasma-sprayed samples).

Analysis of Oxygen Content in the As-Sprayed Coatings

Table 7 shows the EDS analysis of all as-sprayed Mo coatings deposited by five different thermal spray processes WH, AS, FS, PS, and PH. It has been observed that oxygen

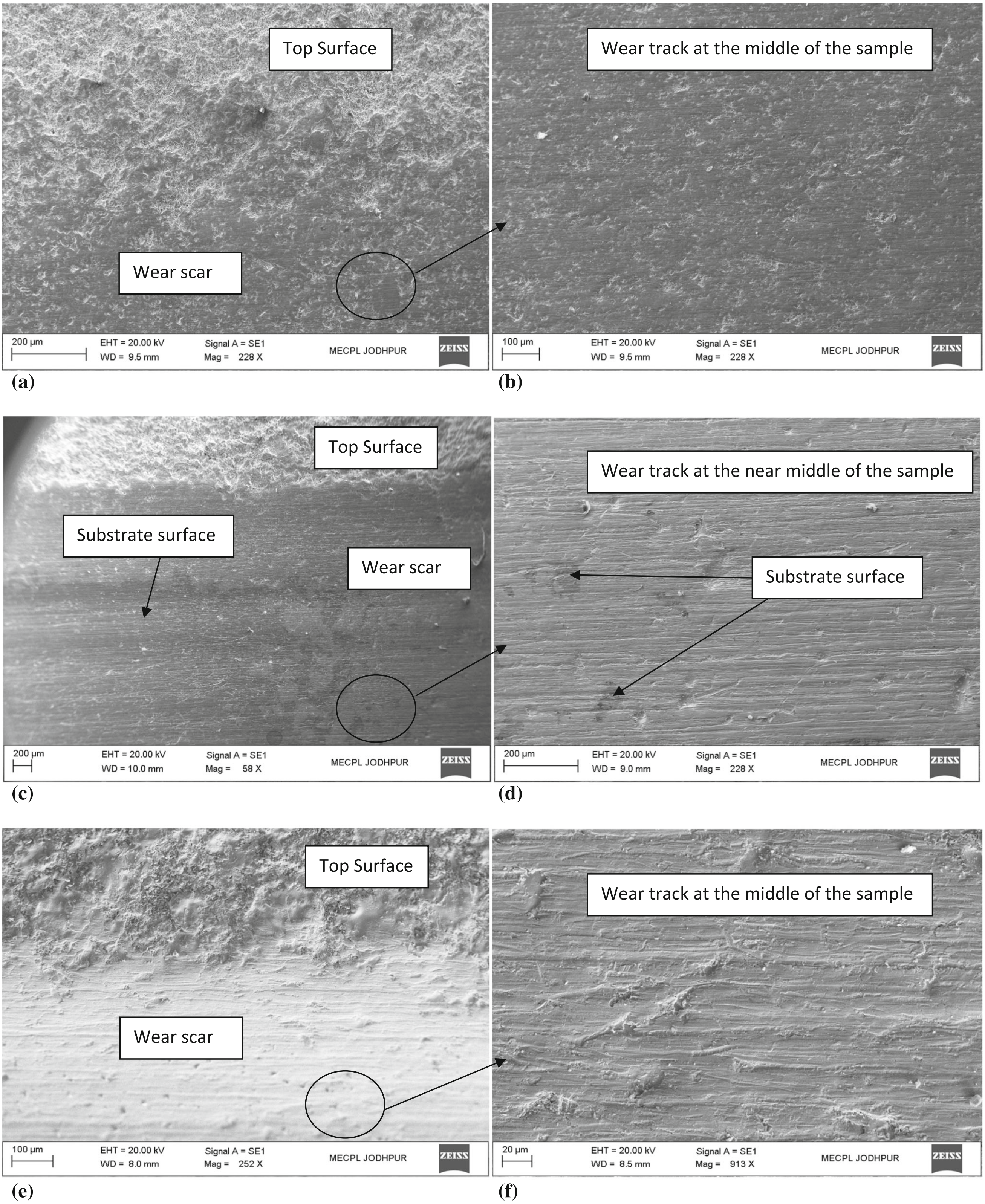

Fig. 7 SEM micrographs of the worn surface of the coatings deposited by (a, b) W-HVOF, (c, d) arc, (e, f) flame, (g, h) plasma spraying, and (i, j) powder-HVOF

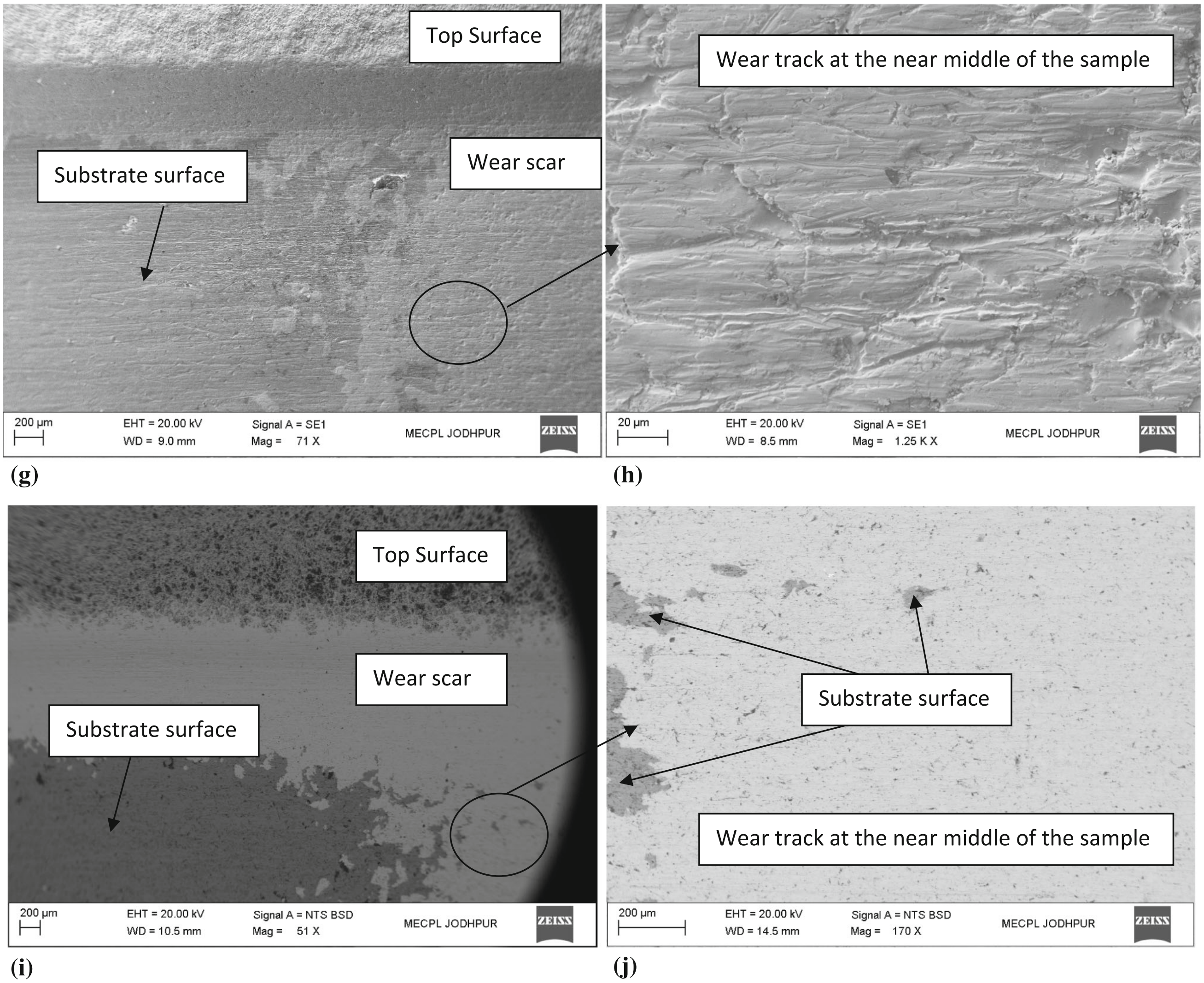

Fig. 7 continued

is present in all as-sprayed five coatings, but in different weight percentage as 10.3, 33.9, 13.9, 29.1, and 16.5, respectively. Maximum oxidation has occurred in the PS coating and minimum oxidation in W-HVOF. This can be attributed to the high particle velocity which reduces the dwell time of particles within the flame and reduces in-flight oxidative processes. This corroborates that both in-flight particle oxidation and post-depositing surface oxidation contribute to the overall coating oxidation.

In certain high-temperature applications, the oxide phase can initiate coating failure in the form of microcracks and decrease inter-splat cohesion bonding, because this coating shows high wear rate. Thus, lower oxide content in the coating is beneficial to improve the cohesion bonding between the splats. The poor cohesion of the oxide particles with the surrounding metallic/oxide particles is the primary cause of bond failure of molybdenum coatings (Ref 22). The relative movement occurs between the oxide and metallic phase because the oxide and metal phases have different densities (Ref 23).

Plasma-sprayed Mo coatings are less susceptible to failure caused by oxides. Thermal-sprayed Mo coatings can be used successfully in more demanding applications, such as the higher efficiency, high power engines typical of current automotive technology if oxidation content can be controlled in the coating.

Oxidation in the coating alters the microhardness and the wear performance of the coating (Ref 4). The presence of this oxide layer in the molten droplet or splat may also lead to porosity in the coating microstructure, as the oxide layer, which is already solid when it hits the substrate, may debond from the substrate surface, thus leaving a gap between the already deposited splat and the incoming splat (Ref 23). Moreover, the oxide layer thus deposited may come out during subsequent processing of the coating because it lacks sufficient cohesion with the matrix,

Table 7 Elemental analysis in as-sprayed Mo coatings

Coating process Elements	W-HVOF	Arc spay	Flame spray	Plasma spray	Powder-HVOF
Oxygen, wt.%	10.3	33.9	13.9	29.1	16.5
Molybdenum, wt.%	89.7	66.0	86.0	70.8	83.4
Total	100	100	100	100	100

resulting in a high wear rate. Therefore, AS and PS coatings show low wear resistance and W-HVOF coating shows high wear resistance performance.

Conclusions

Molybdenum coatings were fabricated on a low-carbon steel substrate by five different thermal spray processes W-HVOF, arc, flame, APS, and powder-HVOF; and their microstructure, mechanical properties, and tribological properties were investigated and compared. The coating deposited by W-HVOF has promising dominant properties in terms of microstructural, mechanical, and tribological, in comparison with coatings deposited by arc spray (AS), flame spray (FS), plasma spray (PS), and powder-HVOF (PH) spraying. W-HVOF opens the scope for the users to use the metallic wires in HVOF rather than using the expensive powders and thus makes it a most economical thermal spray system to achieve promising coating properties for many industrial applications. W-HVOF coatings exhibited very dense microstructure, very high hardness (928 ± 15HV), very low porosity (< 0.7), smooth surface (Ra $\sim$ 2.83 µm), and obviously very good wear resistance and adhesion strength 55.10 ± 3.0 MPa. Oxygen content in the coating influences the coating properties such as high wear rate and low cohesion bonding. Such high hardness, very low porosity, and high wear resistance make this coating a good candidate for anti-scuff coating on piston rings.

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