

COMPARISON OF Mo COATING DEPOSITED BY TWAS AND APS SinplexPro THERMAL SPRAY TECHNIQUES

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ABSTRACT. The wear resistant Mo coatings were deposited using SmartArc Electric Arc Wire Spray System and advanced SinplexPro high throughput atmospheric plasma spray gun. The coatings were analyzed in terms of microstructure, mechanical properties and tribological characteristics, including wear rate and wear mechanism. It was shown that despite of the differences in deposition process principles, the properties of the coatings don't differ with respect to their functional properties. Both coatings reached comparable hardness, microhardness, wear resistance and coefficient of friction. The economic aspects remain the main argument for the recommendation of the most suitable thermal spray deposition technique for the application of molybdenum coatings.

KEYWORDS: APS, ASTM G-133, coating, COF, Mo, nanoindentation, sliding thermal spray, TWAS, wear.

1. INTRODUCTION

Thermally sprayed Mo coatings are widely used as surface treatment offering high wear and scuffing resistance. Due to their superior tribological behavior they are applied especially in sliding contact [1, 2]. To deposit the Mo-based coating, various thermal spray techniques can be utilized. As the coating's microstructure is dependent on the used thermal spray method the differences in the wear resistance and friction behavior can be also expected [3].

The atmospheric plasma spraying (APS) is the most widespread technique for thick coating deposition providing the possibility to spray a wide range of materials, including metals, hardmetals or ceramics with various functionalities, it is also usually utilized to deposit the wear and scuffing resistant Mo coatings. In addition to the examination of coatings sliding properties [2, 4, 5], the spraying of Mo was also used for studying the process-structure-property relationships and for creating so called "process maps" of thermal spraying [6, 7]. As various studies were previously published on available APS systems, there is a lack of information concerning the recently developed SinplexPro high throughput atmospheric plasma spray gun.

The twin wire electric arc spraying (TWAS) is a technique utilizing the material in the form of wires. The principle of the TWAS limited its use on the materials that are electrically conductive. That is why it is used primarily for spraying of Fe and Ni-based alloys, even though the wires with more complex compositions are also available [8]. The lower operating costs, as well as lower price of feedstock material in the form

of wire compared to powder, can make the TWAS technique desirable alternative to plasma spraying if it produces the Mo coatings with sufficient properties.

In the paper, the comparison of Mo coatings, sprayed by APS SinplexPro plasma torch and SmartArc Electric Arc Wire Spray System is done to evaluate the differences in the coatings microstructure, properties and deposition efficiency. The aim is to recommend the most suitable spraying system for the application of Mo coatings on the sliding surface of piston rings for the automotive industry.

2. EXPERIMENTAL

Feedstock material: Two kinds of feedstock material were used: (i) the pure (99.55%+) molybdenum powder Amdry 313X from Oerlicon Metco, agglomerated and densified, with (45–75 μm) size range for APS spraying and (ii) the pure molybdenum (99.9%+) wire W400.1 from Flame Spray Technologies, 1.6 mm diameter.

Spraying: The SinplexProTM plasma torch and the SmartArcTM TWAS spraying system, both from Oerlicon Metco, were used for spraying onto grid blasted (Al₂O₃, 0.8–1 mm grain size) carbon steel substrates (45x25x5 mm). The spraying parameters were previously optimized for reaching the highest coating quality. To evaluate the deposition efficiency, the consumption of feedstock material was measured during spraying of 1 mm thick coating onto the prototype part - piston ring spine Ø 120 mm, 280 mm long.

Microstructure evaluation: The scanning electron microscope (SEM) EVO MA25 from Zeiss with LaB6 thermal filament and equipped by EDX detector SDD

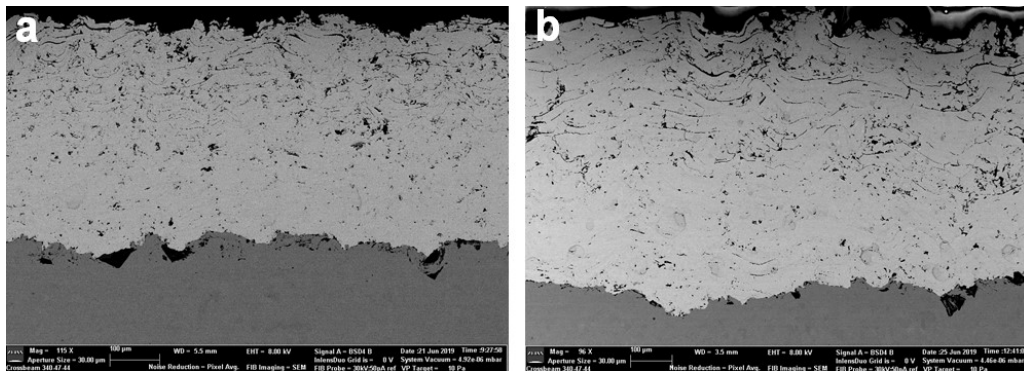


FIGURE 1. The SEM of Mo coatings sprayed by a) APS and b) TWAS technique

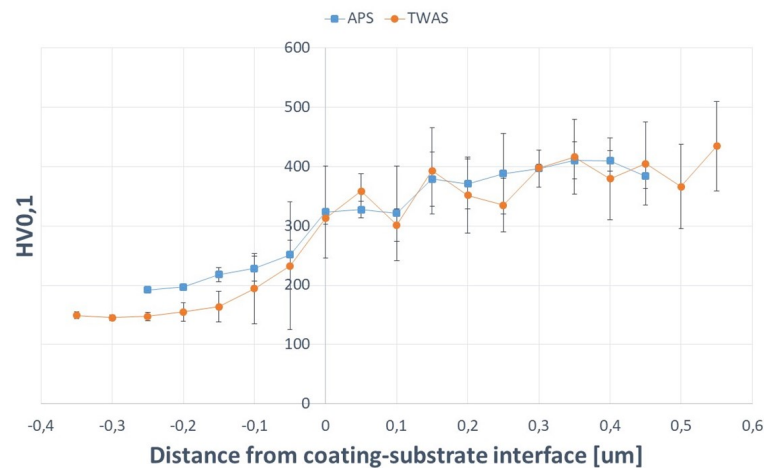


FIGURE 2. The coatings microhardness depth profile

X-Max 20 Oxford Instruments was used to evaluate the microstructure of the coating on the cross-sections. The phase compositions were analysed by X-ray diffraction (XRD), using D8 Discover diffractometer with 1D detector and $\text{CoK}\alpha$ radiation. The obtained diffraction patterns were subjected to quantitative Rietveld analysis performed in TOPAS 4.2 [9] in IPP ASCR.

Coating properties evaluation: The adhesion tests were realized in accordance with ASTM C633-13 [10]. For each value, at least 3 measurements were done. Surface roughness was measured in accordance with EN ISO 4288 [11]. For each value, at least 3 measurements were done. The surface hardness HR 15N was measured on the gently ground surface of coatings. For each value, at least 5 measurements were done. Microhardness HV0.3 was measured in the middle of coatings cross-sections. For each value, at least 7 measurements were done. Microhardness depth profile HV0.1 was measured on the coating's cross sections in 0.05 μm steps. For each value, at least 3 measurements were carried out in one depth. The instrumented hardness was measured in RTI UWB using the NanoTest Vantage testing device from Micro Materials company, equipped with Berkovich indenter, by 5 N testing load, 200 mNs^{-1} loading rate, 10 s dwell period at maxi-

imum load, 20 indents were performed 10 μm below the surface and 20 indents 100 μm above the interface. The sliding wear resistance was measured by Ball-on-flat test, in accordance with ASTM G-133 [12], using 6 mm diameter. Cr-steel ball counterpart; 25 N load, 50 Hz frequency; 1000 s test duration. During the test, the coefficient of friction was recorded. The coatings sliding wear resistance K [mm^3/Nm] was determined from the wear tracks profile measurements. The average value of three ASTM G-133 tests on each sample is reported.

3. RESULTS AND DISCUSSION

The microstructure of the APS and TWAS sprayed coatings is shown in Figure 1. In both cases, the porosity, as well as cracks of the individual particles (splats), can be observed. The size of the splats is lower in the case of APS coating, resulting from the fine powder compared to the splats originated from the molten wire tips.

Both coatings have a variable microstructure across the cross-sections. Less porosity and inter-splat decohesion was observed in the lower part of the coatings, compared to the upper part. This phenomenon is still unclear, nevertheless, its intensity is dependent on the spraying parameters of each technology, related

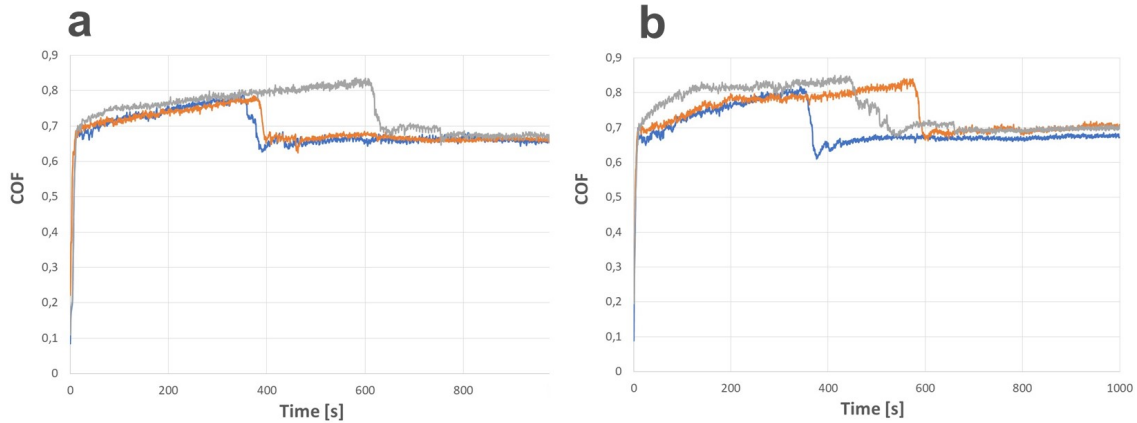


FIGURE 3. Coefficient of friction in dependence on the time of the test for a) APS and b) TWAS sprayed coatings

Mo coating	Hit (GPa) Upper layer	Eit (GPa) Upper layer	Hit (GPa) Lower layer	Eit (GPa) Lower layer
APS	3.76 ± 0.43	138.6 ± 8.6	3.39 ± 0.33	103.7 ± 10.0
TWAS	3.31 ± 0.69	83.3 ± 8.4	2.98 ± 0.46	66.4 ± 8.5

TABLE 1. Results of instrumented indentation.

probably to the temperature and velocity of the particles, as well as to intensity and frequency of cooling during spraying. The amount of energy, transferred to the coated sample can be responsible for coatings densification. Simultaneously, the influence of transferred heat and impact energy can be connected with changes of substrate HV0.1 microhardness (see Fig. 2).

The phase composition was evaluated by XRD. Both coatings composed of Mo, accompanied by a small amount of MoO₂. According to the Rietveld quantitative analyses, its amount reached 0.76 wt.% for APS coating and 2.44 wt.% for TWAS coating.

The thicknesses of the coatings were measured 0.48 ± 0.02 mm and 0.77 ± 0.01 mm for APS and TWAS coating resp. As the number of passes necessary to reach the thickness was 10 and 6, the thickness per pass was 48 μ m and 128 μ m for APS and TWAS coating resp. The consumption of feedstock material was measured during spraying the piston ring spine (\varnothing 120 mm-280 mm long). To spray 1 mm thick coating, the 0.2 kg of powder was consumed during APS spraying, while 1.83 kg of wire was needed for TWAS spraying. The adhesion of the coatings was 37.4 ± 5 MPa for APS and 32 ± 5 MPa for TWAS coating. These values are lower than values, found in Ref [3].

Coating surface roughness was 8.62 ± 0.27 μ m Ra and 56.85 ± 3.80 μ m Rz for APS and 18.89 ± 0.92 μ m Ra and 114.52 ± 4.01 μ m Rz for TWAS coating. While the roughness of APS coating is in agreement with Ref. [3], the Ra of TWAS coating is much higher in [3] (18.89 vs. 9.81 Ra). The surface roughness is connected with the spreading of splats after the droplets impact and can be considered as a parameter of coatings quality.

Surface hardness HR 15N reached comparable values (67.4 ± 1.4 and 67.8 ± 1.5 for APS and TWAS coating resp.). The surface hardness value involved besides the property of the material, also the contribution from present pores, cracks and intersplat boundaries.

The microhardness HV0.3 of the coatings, measured on the coating's cross-sections was slightly lower for APS coating compared to TWAS (327 ± 20 and 387 ± 37 for APS and TWAS coating resp). The presence of a higher amount of hard oxide inclusions can be responsible for higher microhardness of TWAS coating. The overall HV0.3 values are in agreement with the microhardness measured in Ref. [1, 3, 4].

To evaluate the variation of coating properties across the cross-sections, the microhardness depth profile was done. As can be seen from Figure 2, there is not a significant difference between APS and TWAS coating. In both cases, the hardness increases towards the surface. Such observation seems to be in contradiction with the assumption, that the less porous microstructure close to the coating-substrate boundary will be harder than the porous layer in the upper part of the coating.

To confirm the microhardness results, the instrumented indentation measurement was done on both coatings in the upper porous and lower dense layer of each coating. The load of 5 N was used for indentation to include not only the inner splats properties but also the influence of porosity and intersplats cohesive strength. The measured values of Hit and Eit are summarized in the Table 1.

Even though high scatter of the measured values given by heterogeneous microstructures of both coat-

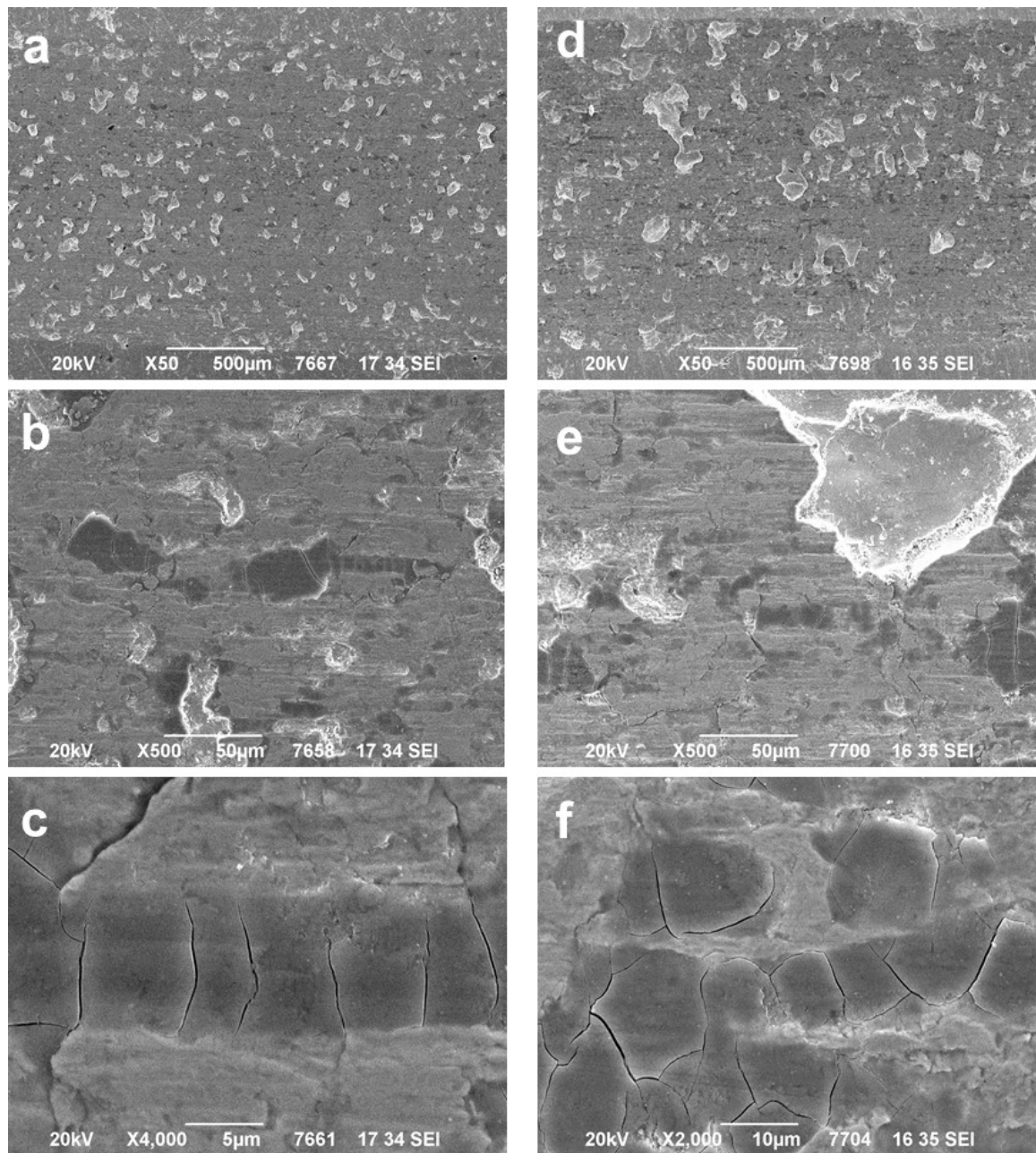


FIGURE 4. Wear mechanism for APS (a,b,c) and TWAS (d,e,f) sprayed coatings

ings, it can be observed that the lower dense close-to-interface layer has a lower hardness and lower modulus of elasticity, compared to a higher, more porous layer close to surface. This observation is in agreement with the HV0.1 depth profile measurement.

During the Ball-on-Flat linear oscillating test, the coefficient of friction (COF) was recorded and can be seen in Figure 3. Similar behavior of both types of coatings can be seen. The continuous slow increase was followed by a sudden drop of COF value in 400-600 s of the test. After, the constant COF value of 0.7 was recorded till the end of the test. The sudden decrease of COF is usually connected with the creation of stable tribolayer in the wear track. Also, the transfer of worn coating material onto the surface of the counterpart can be another reason for COF

decrease, however, it was not analyzed during this study.

The wear resistance of both types of coatings is very similar. For APS sprayed coating, wear coefficient K was $1.91 \cdot 10^{-4} \pm 1.9 \cdot 10^{-5} \text{ mm}^3/\text{Nm}$, while for TWAS coating $2.06 \cdot 10^{-4} \pm 2.8 \cdot 10^{-5} \text{ mm}^3/\text{Nm}$. For comparison, the wear coefficient of AISI 316L steel is 2.74 ± 1.37 . In [2] the reported wear rate was much lower compared to the results of samples evaluated in this study. The differences in wear tests (ASTM G-99 vs ASTM G-133) and particularly in used loads (5N vs 25N) can play a significant role in the wear rate.

The wear mechanism can be seen in Figure 4. For both types of coatings, the delamination of the parts or whole splats was identified (Fig. 4b,e) as the main mechanism responsible for wear. Except of delam-

ination, ploughing takes place. In the wear track, the tribo-layer was locally identified (Fig. 4c,f). The tribo-layer usually consist of deformed coating wear debris, transferred counterpart material and oxides, originated during sliding [13]. The EDX analyses show the presence of Fe (ca. 3-4 wt.%) and Cr (ca. 1-1.5 wt.%) in the wear track, originated from the counterpart, together with 11-14 wt.% of oxygen confirming the assumption of tribo-oxidation. There are no differences in the wear mechanism between APS and TWAS sprayed coating, except the size of delaminated areas. They are bigger in the case of TWAS coating, which is connected with bigger splats dimensions (see Fig. 1). The bigger size of delaminated splats is than responsible for slightly higher wear volume.

4. CONCLUSIONS

Despite of the differences in deposition process principles, the properties of the coatings don't differ with respect to their functional properties. Both coatings reached comparable hardness, microhardness, wear resistance and coefficient of friction. Wear mechanisms also don't differ - splat delamination and ploughing are the main observed mechanism responsible for wear. In the case of TWAS, the size of delaminated areas is bigger in consequence of the bigger size of original splats. Considering the economic aspects, the significantly lower deposition efficiency of TWAS technology and longer time of deposition makes the TWAS 70 % more expensive than APS SimplexPro for spraying of a reference component, despite of more than 2 times higher unit price of Mo powder compared to wire.

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