The Comparison of the Effect of Powder Morphology on the Microstructure and Mechanical Properties of WC-Co-Cr Coatings HVOF-Sprayed on Substrates Made of Alloy AZ31

Abstract: The paper presents results of comparative tests concerning the effect of the morphology and particle size of the WC-Co-Cr coating material on the microstructure and mechanical properties of coatings sprayed (using the high velocity oxy-fuel method (HVOF)) on substrates made of magnesium alloy AZ₃₁. The tests involved the use of two types of commercial powders, i.e. agglomerated and sintered powder (AS) (Höganäs, Amperit 558.074) and sintered powder (S) (Höganäs, Amperit 554.071). The microstructures of the coatings were observed using digital light microscopy and scanning electron microscopy. The tests also involved the determination of porosity and roughness as well as measurements of instrumental hardness ($H_{\rm IT}$) and Young's modulus ($E_{\rm IT}$). The microscopic observations revealed that the coatings were characterized by the relatively compact, dense and uniform structure as well as good adhesion to the substrate. The porosity of the S-type coating was approximately 1.5 times higher than that of the AS-type coating. In addition, the S-type coating was visibly thinner (than the AS-type coating), which could be ascribed to a lower powder feed rate applied during the spraying process. The surface of the AS-type coating was characterized by lower roughness ($R_a = 4.5 \pm 0.1 \,\mu\text{m}$) than that of the S-type coating ($R_a = 5.8 \pm 0.3 \,\mu\text{m}$). The differences in terms of instrumental hardness (H_{IT}) and instrumental Young's modulus ($E_{\rm IT}$) were also small. However, it could be noticed that the more compact structure and lower porosity of the AS-type coating resulted in the obtainment of slightly higher values of both $H_{\rm IT}$ and $E_{\rm IT}$.

Keywords: WC-Co-Cr coating, HVOF spraying, magnesium alloy AZ₃₁, powder morphology, microstructure, mechanical properties

DOI: <u>10.17729/ebis.2022.6/1</u>

No. 6/2022 -

mgr inż. Monika Górnik, dr hab. inż., prof. PWr Leszek Łatka – Politechnika Wrocławska, Wydział Mechaniczny, Katedra Przeróbki Plastycznej, Spawalnictwa i Metrologii (Wrocław University of Technology, Faculty of Mechanical Engineering, Department of Plastic Processing, Welding and Metrology); dr inż. Ewa Jonda – Politechnika Śląska, Wydział Mechaniczny Technologiczny, Katedra Materiałów Inżynierskich i Biomedycznych (Silesian University of Technology, Faculty of Mechanical Engineering, Department of Engineering Materials and Biomaterials)

Introduction

Magnesium alloys belong to a group of materials, which enjoy increasingly high popularity with researchers. Some of the most favourable properties of the aforesaid materials include low specific gravity (1.74 g/cm³) and high specific strength [1–3]. Because of their properties, magnesium alloys are applicable in the automotive, aviation, chemical, shipbuilding, electronic and many other industries [4]. However, the use of magnesium alloys is also limited by their low resistance to corrosion, erosion and abrasion as well as low hardness [5-7]. The above-presented problems could be solved by the deposition of protecting coatings on surfaces of materials made of magnesium alloys. Regrettably, also the applicability of the aforesaid solution is restricted by the high flammability and plasticity of magnesium alloys [8, 9]. For this reason, among many thermal spraying methods it is necessary to select a technique enabling the deposition of a dense and well adhesive coating under conditions of relatively low temperature affecting the substrate [10-12]. The above-named conditions are satisfied by the HVOF spraying method (High Velocity Oxy-Fuel). In addition, the HVOF method can be successfully used to deposit coatings made of hard materials resistant to intense abrasion and corrosion. The aforesaid coatings are also characterised by favourable adhesion and low porosity [13–17]. Taking into account the plastic nature of substrate and the hard nature of the coating as well as the significant improvement of primary mechanical and functional properties of the coating, materials selected for the research-related tests were cermets based on tungsten carbide [18-21]. It should be noted that the HVOF technique is the primary method used to obtain cerametallic coatings [22, 23]. In addition to process parameters, key technological factors include the condition and size of powder particles [24, 25].

Available reference publications contain little information concerning the deposition of protective coatings thermally sprayed on base materials made of magnesium alloys [26, 27]. The authors' individual studies constitute an attempt to fill this gap in research publications [28–30].

The tests discussed in the article aimed to compare the effect of the size of powder particles and powder morphology on the microstructure and primary mechanical properties of WC-Co-Cr cerametallic coatings deposited (using the HVOF method) on the substrate made of magnesium alloy AZ₃₁.

Test materials and methods

The coatings were deposited using a JP-5000 HVOF spray gun (TAFA). The substrate was made of 5 mm thick magnesium alloy AZ31. The surface of specimens was previously subjected to abrasive blasting. The aforesaid surface processing method aimed at surface cleaning and expansion. The coating material was cerametallic powder based on tungsten carbide, on the matrix of cobalt with an addition of chromium WC-10C0-4Cr (% by weight). The tests involved two types of commercial powders, i.e. agglomerated and sintered powder (AS) (Höganäs, Amperit 558.074) and sintered powder (S) (Höganäs, Amperit 554.071). The size and the average size of powder particles are presented in Table 1. The powder particles are presented in Figure 1.

powder particles				
Powder	Size range,	Average particle		

Table 1. Comparison of the size and average size of test

Powder type	Size range, µm	Average particle size, µm	
AS	15 - 45	$d_{50} = 32$	
S	5 – 25	$d_{50} = 17$	

The primary process parameters are presented in Table 2. Differences in coating deposition process parameters resulted from various sizes of powder particles (selected on the basis of individual preliminary tests) [32, 33].

The roughness of the surfaces formed during the spraying of the coatings was measured in

CC BY-NC

Specimen designation	Fuel flow rate l/h	Oxygen flow rate l/min	Powder feed rate g/min	Spraying distance mm
AS	26	800	70	360
S	16	600	30	280

Table 2. Designation of specimens and spraying process parameters



Fig. 1. Coating materials in the as-received state: a) powder AS and b) powder S [31]

accordance with the ISO 4288 standard, by identifying parameter R_a (arithmetic average of absolute values of ordinates in the roughness sampling cut-off). The measurements (involving 10 repetitions) were performed using a Mahr Surf PS 10 contact profilometer. To observe the microstructure of the coatings, the specimens were cut across to sample specimens which were subsequently included in resin and subjected to metallographic preparation using SiC paper and diamond slurry having a grain size of 3 µm. The subsequent stage involved observation performed using a VHX6000 digital light microscope (Kyence) and a scanning electron microscope. The porosity of the coatings was determined in accordance with the ASTM E2109-01 standard. The computer-aided image analysis was performed using the ImageJ software programme. The values of porosity were calculated on the basis of 20 photographs obtained using a magnification of 500x. Hardness instrumented indentation was determined in accordance with the ISO 14577-4 standard using an NHT³ hardness tester (Anton Paar). The

indenter used in the tests was characterised by Berkovich geometry; the maximum force amounted to 500 mN. The measurements were performed in accordance with methodology described by Oliver and Pharr [34]. In turn, the value of Young's elastic modulus by instrumented indentation was identified in accordance with the methodology described in publication [35]. To determine the value of the aforesaid modulus, the value of maximum force changed within the range of 50 mN to 500 mN (at a step of 50 mN). The value of the parameter describing brittle crack resistance $K_{\rm C}$ was identified using the Vickers indenter and measurements of lengths of cracks formed in the corners of the indentation (Fig. 2) [36].

The test involved the making of 15 indentations (involving the cross-section of the specimen), the performance of measurements of characteristic dimensions and the substitution of the latter in the formula proposed by Wilshaw and Evans [37]:

$$K_{\rm C} = 0.079 \left(\frac{p}{a^{3/2}}\right) \log\left(\frac{4.5a}{c}\right) \tag{1}$$

CC BY-NC

where

- P value of maximum force N (amounting to 9.81 N)
- a half of the Vickers indentation diagonal, m
- c crack length from the centre of the indentation, m



Fig. 2. Schematic diagram of Vickers indentation with cracks formed in the test

Test results

The microstructure of the sprayed coatings is presented in Figure 3. As can be seen, the coatings are characterised by the relatively dense, compact and uniform structure as well as good adhesion to the substrate. All substrate surface irregularities were filled by the coating material very well. The area of contact between the coating and the substrate was characterised by the proper mechanical seizure of the particles, which indicated the high adhesion of the coatings. The above-presented structure was consistent with related reference data [18, 38, 39]. Because of the significantly lower feed rate of the powder (Table. 2), the S-type coatings were visibly thinner than the AS-type coatings; the thickness of the coating being 100 μ m and 200 μ m respectively. Both coating types were deposited using the same number of spray pistol runs.

The coating surface was relatively smooth. The slightly lower value of surface roughness identified in specimen AS resulted from the fact that powder particles of spherical morphology tend to form more regular splats and lamellas in comparison with powder particles characterised by irregular shapes [40]. The surface porosity and roughness values are presented in Table 3. The results obtained in the tests were similar to those presented in related reference publications [41, 42].

Table 3. Comparison of the roughness and the porosityof the coating surface

Specimen designation	Surface roughness <i>R</i> _a , µm	Porosity, % by volume
AS	4.5 ± 0.1	2.9 ± 0.7
S	5.8 ± 0.3	4.8 ± 0.9

The average values of hardness instrumented indentation H_{IT} and those of Young's elastic



Fig. 3. Cross-section of the coatings: a) specimen AS and b) specimen S



modulus by instrumented indentation E_{IT} are presented in Figure 4. As can be seen, the differences are only slight, yet the more compact structure and the lower porosity of the AS-type coatings translated into slightly higher values of both H_{IT} and E_{IT} . The hardness values obtained in the tests were very similar to those contained in reference publications [18, 43]. However, the values of E_{IT} were slightly higher than those found in reference publications [44, 45]. The foregoing was probably caused by a different indenter type and the appropriate adjustment of corrective factors [46].

The values of parameter $K_{\rm C}$, representing brittle crack resistance, are presented in Table 4. As can be seen, specimen AS was characterised by higher brittle crack resistance, which resulted from better cohesion between the lamellas and the more compact structure [47]. However, the higher porosity of specimen S could prevent or, at least, slow down the propagation of cracks; an important aspect being the size of pores (usually not exceeding several micrometres) [39]. It should be noted that the results obtained in the tests correlated with related data contained in reference publications [48, 49].

Conclusions

The above-presented tests aimed to identify the effect of the morphology and size of the WC-10Co-4Cr powder particles on the microstructure and mechanical properties of HVOF-sprayed coatings. The analysis of the test results justified the formulation of the following conclusions:

- proper adjustment of process parameters enabled the obtainment of high-quality cerametallic coatings on the substrate made of magnesium alloy AZ₃₁,
- morphology of powder particles significantly affected the structure of the coating and its mechanical properties,
- size of powder particles did not affect mechanical properties; each type of powder was sprayed using a separate set of previously adjusted spraying parameters,
- spherical morphology of the agglomerated and sintered powder translated into higher process efficiency.

References

- Yang X., Liu J., Wang Z., Lin X., Liu F., Huang W., Liang E.: Microstructure and mechanical properties of wire and arc additive manufactured AZ₃₁ magnesium alloy using cold metal transfer process. Materials Science and Engineering: 2020, A, vol. 774, 138942, pp. 1–9.
- [2] Mazaheri Y., Jalilvand M.M., Heidarpour A., Jahani-A.: Tribological behavior of AZ₃₁/ZrO₂ surface nanocomposites

developed by friction stir processing. Tribology International, 2020, vol. 143, 106062, pp. 1–14.

- [3] Pollock T.M.: Weight Loss with Magnesium Alloys. Materials Science, 2010, vol. 328, pp. 986-987.
- Chen D., Pan F.: Research advances in magnesium and magnesium alloys worldwide in 2020. Journal of Magnesium and Alloys, 2021, vol. 9, no. 3, pp. 705-747.
- [5] Fouad Y., El Batanouny M.: Effect of surface treatment on wear behavior of magnesium alloy AZ₃₁. Alexandria Engineering Journal, 2011, vol. 50, no. 1, pp. 19–22.
- [6] Taltavull C., Lopez A.J., Torres B., Atrens A., Rams J.: Optimization of the high velocity oxygen fuel (HVOF) parameters to ings on AZ91 magnesium alloy. Materials and Corrosion, 2015, vol. 66, no. 5, pp. 423-432.
- [7] Song G.-L., Xu ZQ.: The surface, microstructure and corrosion of magnesium alloy AZ31 sheet. Electrochimica Acta, 2010, vol. 55, no. 13, pp. 4148–4161.
- [8] Nie J.-F.: Precipitation and Hardening in Magnesium Alloys. Metallurgical and Materials Transactions A, 2012, vol. 43, pp. 3891-3939.
- [9] Nguyen Q.B., Sim Y.H.M., Gupta M., Lim C.Y.H.: Tribology characteristics of magnesium alloy AZ31B and its composites. Tribology International, 2015, vol. 82 B, pp. 464-471.
- [10] Pawłowski L.: The Science and Engineering of Thermal Spray Coatings. John Wiley & Sons, Ltd., England 2008.
- [11] Fauchais P.L., Heberlein J.V.R., Boulos M.I.: Thermal Spray Fundamentals: From Powder to Part. Springer, New York 2014.
- [12] Łatka L., Pawłowski L., Winnicki M., Sokołowski P., Małachowska A., Kozerski S.: Review of functionally graded

thermal sprayed coatings. Appl. Sci. 2020, vol. 10, no. 15, 5153.

- [13] Berger L.M.: Application of hard metals as thermal spray coatings. International Journal Refractory Metals and Hard Materials, 2015, vol. 49, pp. 350-364.
- [4] Yang Y., Xiong X., Chen J., Peng X., [14] Singh V., Singh I., Bansal A., Omer A., Singla A.K., Rampal A., Goyal D.K.: Cavitation erosion behavior of high velocity oxy fuel (HVOF) sprayed (VC + CuNi-Cr) based novel coatings on SS316 steel. Surface and Coatings Technology, 2022, vol. 432, no. 4–5, 128052, pp. 1–15.
 - [15] Praveen A.S., Arjunan A.: High-temperature oxidation and erosion of HVOF sprayed NiCrSiB/Al₂O₃ and NiCrSiB/WC-Co coatings. Applied Surface Science Advances, 2022, vol. 7, 100191, pp. 1–10.
 - produce effective corrosion control coat- [16] Lima R.S., Marple B.R.: Thermal spray coatings engineered from nanostructured ceramic agglomerated powders for structural, thermal barrier and biomedical applications: A review. Journal of Thermal Spray Technology, 2007, vol. 16, no. 1, pp. 40-63.
 - [17] Picas J.A., Forn A., Matthäus G.: HVOF coatings as an alternative to hard chrome for pistons and valves. Wear, 2006, vol. 261, no. 5-6, pp. 477-484.
 - [18] Qiao L., Wu Y., Hong S., Long W., Cheng J.: Wet abrasive wear behavior of WC-based cermet coatings prepared by HVOF spraying. Ceramics International, 2021, vol. 47, no. 2, pp. 1829-1836.
 - [19] Ma N., Guo L., Cheng Z., Wu H., Ye F., Zhang K.: Improvement on mechanical properties and wear resistance of HVOF sprayed WC-12Co coatings by optimizing feedstock structure. Applied Surface Science, 2014, vol. 320, pp. 364-371.
 - [20] Chen H., Gou G.Q., Tu M.J., Liu Y.: Structure and wear behaviour of nanostructured and ultrafine HVOF spraying WC-17Co coatings. Surface Engineering, 2009, vol. 25, no. 7, pp. 502–506.

- [21] Ward L.P., Pilkington A.: The dry sliding wear behavior of HVOF-sprayed WC: Metal composite coatings. Journal of Ma- [29] Jonda E., Łatka L.: Comparative Analysis of terials Engineering and Performance, 2014, vol. 23, no. 9, 106062, pp. 3266-3278.
- Murthy J.K.N., Venkataraman B.: Abra-22 sive wear behaviour of WC-CoCr and Cr3C2-20(NiCr) deposited by HVOF and detonation spray processes. Surface and Coatings Technology, 2006, vol. 200, no. 8, pp. 2642-2652.
- [23] Bang S.S., Park Y.C., Lee J.W., Hyun S.K., Kim T.B., Lee J.K., Han J.W., Jung T.K.: Effect of the spray distance on the properties of high velocity oxygen-fuel (HVOF) sprayed WC12Co coatings. Journal of Nanoscience and Nanotechnology, 2018, vol. 18, no. 3, pp. 1931–1934.
- Berger L.-M., Saaro S., Naumann T., [24] Kašparova M., Zahálka F.: Influence of feedstock powder characteristics and spray processes on microstructure and properties of WC-(W,Cr)₂C-Ni hard metal coatings. Surface and Coatings Technology, 2010, vol. 205, no. 4, pp. 1080-1087.
- [25] Myalska H., Szymański H., Moskal G.: Microstructure and Selected Properties of WC-Co-Cr Coatings Deposited by High Velocity Thermal Spray Processes. Solid State Phenomena, 2016, vol. 246, pp. 117-122.
- [26] García-Rodríguez S., López A.J., Bonache V., Torres B., Rams J.: Fabrication, Wear, and corrosion resistance of HVOF sprayed WC-12Co on ZE41 magnesium Alloy. Coatings, 2020, vol. 10, no. 5, pp. 1-21.
- [27] Aulakh S.S., Kaushal G.: Laser texturing as an alternative to grit blasting for improved coating adhesion on AZ91D magnesium alloy. Transactions of the IMF, 2019, vol. 97, no. 2, pp. 100–108.
- [28] Jonda E., Łatka L., Tomiczek A., Godzierz M., Pakieła W., Nuckowski P.: Microstructure Investigation of WC-Based Coatings

Prepared by HVOF onto AZ₃₁ Substrate. Materials, 2022, vol. 15, no. 1, 40, pp. 1–15.

- Mechanical Properties of WC-Based Cermet Coatings Sprayed by HVOF onto AZ31 Magnesium Alloy Substrates. Advances in Science and Technology Research Journal, 2021, vol. 15, no. 2, pp. 57–64.
- [30] Łatka L., Jonda E., Godzierz M., Górnik M., Tomiczek A.: Comparison of microstructure and residual stress of HVOF double carbides coatings de-posited on magnesium substrate. Proceedings of the International Thermal Spray Conference, ITSC 2022, Vienna, pp. 172–178.
- [31] https://www.hoganas.com/en/powder-technologies/surface-coating/ products/hvof/carbides/. Access date: 13.07.2022r.
- [32] Górnik M., Jonda E., Nowakowska M., Łatka L.: The effect of spray distance on porosity, surface roughness and microhardness of WC-10C0-4Cr coatings deposited by HVOF. Advances in Materials Science, 2021, vol. 21, no. 4, pp. 99-111.
- [33] Górnik M., Jonda E., Łatka L., Nowakowska M., Godzierz M.: Influence of spray distance on mechanical and tribological properties of HVOF sprayed WC-Co-Cr coatings. Materials Science-Poland, 2021, vol. 39, no. 4, pp. 545-554.
- Oliver W.C., Pharr G.M.: An Improved [34] Technique for Determining Hardness and Elastic Modulus Using Load and Displacement Sensing Indentation Experiments. Journal Materials Research, 1992, vol. 7, pp. 1564-1583.
- [35] Łatka L., Chicot D., Cattini A., Pawłowski L., Ambroziak A.: Modeling of elastic modulus and hardness determination by indentation of porous yttria stabilized zirconia coatings. Surface and Coatings Technology, 2013, vol. 220, pp. 131–139.
- [36] Palmqvist S.: Occurrence of crack formation during Vickers indentation as

a measure of the toughness of hard metals. Arch. Eisenhuttenwes, 1962, vol. 33, no. 6, pp. 629-633.

- [37] Evans A.G., Wilshaw T.R.: Quasi-static solid particle damage in brittle solids - I. Observations, analysis and implications. Acta Metallurgica, 1976, vol. 24, no. 10, pp. 939-956.
- [38] Luiz L.A., de Andrade J., Pesqueira C.M., esco Sucharski G., de Sousa M.J.: Corrosion Behavior and Galvanic Corrosion Resistance of WC and Cr₃C₂ Cermet Coatings in Madeira River Water. Journal of Thermal Spray Technology, 2021, vol. 30, pp. 205-221.
- [39] Song B., Murray J.W., Wellman R.G., Pala Z., Hussain T.: Dry sliding wear behaviour of HVOF thermal sprayed WC-Co-Cr and WC-CrxCy-Ni coatings. Wear, 2020, vol. 442-443, 203114, pp. 1-10.
- [40] Fauchais P., Montavon G., Bertrand G.: From powders to thermally sprayed coating. Journal of Thermal Spray Technology, 2010, vol. 19, pp. 56–80.
- [41] Agüero A., Camón F., Garcıa de Blas J., del Hoyo J.C., Gamo R.M., Santaballa A., Ulargui S., Valles M.P.: HVOF-Deposited WCCoCr as Replacement for Hard Cr in Landing Gear Actuators. Journal of Thermal Spray Technology, 2011, vol. 20, no. 6, pp. 1292-1309.
- [42] Murugan K., Ragupathy A., Balasubramanian V., Sridhar K.: Optimizing HVOF spray process parameters to attain minimum porosity and maximum hardness in WC-10Co-4Cr coatings. Surface and Coatings Technology, 2014, vol. 247, pp. 90–102.
- [43] Bolelli G., Berger L.-M., Bonetti M., Lusvarghi L.: Comparative study of the dry sliding wear behaviour of HVOF-sprayed WC-(W,Cr)2C-Ni and WC-CoCr hard

metal coatings. Wear, 2014, vol. 309, no. 1-2, pp. 96-111.

- [44] Matikainen V., Peregrina S.R., Ojala N., Koivuluoto H., Schubert J., Houdkova Š., Vuoristo P.: Erosion wear performance of WC-10C04Cr and Cr₃C₂-25NiCr coatings sprayed with high-velocity thermal spray processes. Surface and Coating Technology, 2019, vol. 370, pp. 196–212.
- de Araujo Fernandes Siqueira I.B., Bavar- [45] de la Barbera Y.Y.S., La Barbera-Sosa J.G., Caro J., Puchi-Cabrera E.S., Staia M.H.: Mechanical properties and microstructure of WC-10C0-4Cr and WC-12Co thermal spray coatings deposited by HVOF. Surface Engineering, 2008, vol. 24, pp. 374-382.
 - [46] Chicot D., Roudet F., Zaoui A., Louis G., Lepingle V.: Influence of visco-elastoplastic properties of magnetite on the elastic modulus: Multicyclic indentation and theoretical studies. Materials Chemistry and Physics, 2010, vol. 119, no. 1–2, pp. 75–81.
 - [47] Wang H., Qiu Q., Gee M., Hou C., Liu X., Song X.: Wear resistance enhancement of HVOF-sprayed WC-Co coating by complete densification of starting powder. Materials & Design, 2020, vol. 191, 108586, рр. 1–13.
 - [48] Zhan S.-H., Cho T.-Y., Yoon J.-H., Li M.-X., Shum P.W., Kwon S.-C.: Investigation on microstructure, surface properties and anti-wear performance of HVOF sprayed WC-Cr-Ni coatings modified by laser heat treatment. Materials Science and Engineering B, 2009, vol. 162, no. 2, pp. 127–134.
 - [49] Yao H.-L., Yang C., Yi D.-L., Zhang M.-X., Wang H.-T., Chen Q.-Y., Bai X.-B., Ji G.-Ch.: Microstructure and mechanical property of high velocity oxy-fuel sprayed WC-Cr₃C₂-Ni coatings. Surface and Coatings Technology, 2020, vol. 397, 126010, рр. 1–10.