CHARACTERIZATION OF WC-Co THERMAL SPRAY COATINGS BASED ON THE COMPOSITE POWDERS

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Abstract

The article gives an overview of methods suitable for describing WC-Co powder granules and coatings for thermal spray powder development and production. Composite powder particles and microstructure grains vary from a few nanometres to hundreds of micrometers. It is therefore necessary to combine different analysis methods.

In the granule and particle size analysis, laser diffraction, sieve analysis, image analysis and the BET method were used. To describe the microstructure and porosity of the thermal spray coating and composite powder granules, computer analysis was used.

As a result, a good numeric database was obtained that enables us to compare the characteristics of the coating with new experimental coatings and to analyze the resistance of the coating to the abrasive wear.

Keywords: powder granule and coating structure, structure computer analysis, granule size and shape, abrasive wear resistance

INTRODUCTION

Thermal sprayed coatings have a wide range of applications, for instance for repairing damaged details during maintenance or for new details production with high wear resistance. The wear resistance of a coating does not depend only on the used spray system but also on the characteristics of a particular spray powder.

Previous studies have demonstrated [1-3] that the use of recycled hardmetal powders in the formation of thermal spray coatings leads to numerous problems. Hardmetal powder particles sized from 30 to 40 µm in a thermal spray (detonation and high velocity oxygen fuel thermal spray process HVOF) produce very porous (4 to 5%) non-uniform coatings. Therefore, a new technology – mechanically activated synthesis [4] - was used to produce experimental WC-based composite spray powders. The new experimental powder allows the enhancement of coating wear resistance [5].

To guarantee high abrasive wear resistance of a coating, it is necessary to optimise the structure of the coating. Microstructure analysis is a combined characterization of morphology, elemental composition and crystallography of microstructural features by means of a microscope [6]. Composite powder granule structure studies [5] showed that no single universal method exists to acquire all the information needed for material structure characterization. Thus the choice of the method depends on researcher experiences and skills. Inaccurate results typically occur, when computer aided measurements are relied upon with no reflection. In fact, computer aided microstructural analysis can provide highly accurate information in a short time. The article is focused on the analysis of coating structure and the use of obtained data; to improve the abrasive wear resistance of a coating.

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MATERIALS AND METHODS

Materials

Tungsten carbide-cobalt based hardmetal powders were used as coating materials. Additionally, to the commercially produced TAFA 1343 powder (B), two experimental powders were used. Powder (A) is produced from recycled hardmetal. Powder (C) consists of WC obtained from mechanically activated synthesis. The HVOF spraying system TAFA JP 5000 (Praxair Tafa, USA) with kerosene as fuel was used for the deposition of coating. A list of the coatings and their indexing system is shown in Table 1.

Tab.1. Investigated coatings, spray powders, and the indexing system.

Coating index	Type of coating	Powder particle size [μm]
A	(WC-Co)-15Co (experimental, agglomerated)	15-45
B	WC-17Co (TAFA 1343 V) (commercial)	20-50
C	WC-15Co (mechanically activated synthesis)	20-45

Characterization of composite powder granularity and chemical composition

Granule size and distribution in the investigated powders were examined by means of three analysis methods:

- sieve analysis,
- laser diffraction analysis by Laser particle sizer Analysette 22 Compact,
- image analysis based on the Image-Pro Plus 3.0 system (IP) and the corresponding data processing programs.

The chemical composition of powder particles was studied by means of the energy dispersive X-ray microanalysis (EDS) with Link Analytical AN10000 system. The X-ray mapping technique was used for the evaluation of element distribution inside powder particles. According to the results, the resolution of element distribution is 0.5 to 1 μm.

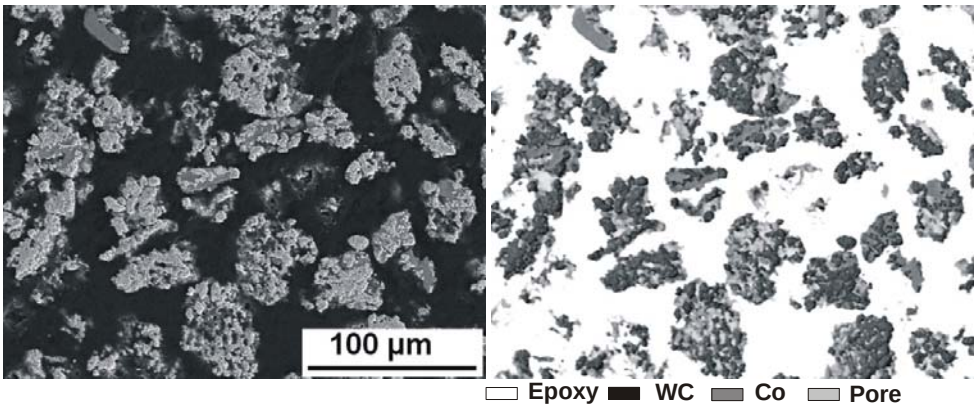
Carbon and oxygen content in the spray powder were measured by the element analysis system Vario EL V2.6 (Elementar Analysen - systeme GmbH).

Coating and powder granule microstructure characterization

Cross-section polishes were made by a mechanical grinding-polishing procedure for analysis of particle and coating structure (Fig.1a). To analyze coating structure and composition, cross-section polishes were made by hot mounting. The best results for the powder were obtained by a fluid (not viscous) cold mounting with an epoxy-based compound that was mounted using of the Buehler vacuum impregnation system. Due to the high hardness of WC-particles, diamond grinding-polishing was used.

The microstructure of the powder granules and the coating was investigated by means of the optical microscope Axiovert 25 and scanning electron microscope (SEM) Jeol JSM-840A using backscattered electron imaging. Quantitative results of the structure analysis were obtained by the image analysis systems Buehler Omnimet Image Analysis System Version 5.40 (OM) and Image Pro 3.0 (IP) (Fig.1b).

To describe grain and powder granule shape, the following parameters were used: roughness is defined as the ratio of the convex perimeter to the perimeter (if there is no concavity at the edge of the particle, the roughness of this particle is 1.0); sphericity is defined as 4π* area / (perimeter squared) (if the shape of the particle is a perfect circle, the sphericity of this particle is 1); aspect ratio refers to the longest axis of the observed object divided by the shortest axis of the same object [7].



a. **b.**

Fig.1. SEM micrographs of powder C, a – granules' cross-section, b – phase map of the granules.

RESULTS AND DISCUSSION

WC-Co based composite spray powder granules' size and morphology

To produce composite powders with sub-micrometric WC grains, it is necessary to analyze a sub-micrometric powder. Indirect methods like the surface area method by Brunauer-Emmet-Teller (BET) or X-ray Diffraction (XRD) can be used to measure the WC powder particles size (20 to 500 nm). The BET method enables us to find the size of the surface area and then calculate the average particle size. But the BET method does not distinguish WC grains from Co binding material and gives higher results than expected. Thereby the BET is usable to determine the porosity of composite WC-Co granules and can be used for the determination of WC crystal size before composite granules preparation. The XRD method provides an estimation shape of distribution (not precise, though) and an average crystal size. In the case of nano-size powders, the WC grain and crystal size is usually the same. When treating nano-size particles, care should be taken not to oxidize particles during measurements.

For thermal spray, the granule size of the powder should range from 20 to 45 µm to achieve a high productivity of spraying and avoid oxidation processes [8]. It is much easier to determine the particle size and size distribution of composite powder granules than WC nano-particles because of their larger size. To determine the granules size and size distribution, image, sieve and laser particle size analysis can be used.

Sieve and laser analysis may yield different results because of the elongation of the granules (Fig.1). Aspect ratio was used to characterize their elongation. The mean aspect ratio was 1.96, which means that the longest diagonal of the particle is almost twice as long as the smallest one. Because of such elongation, the values for the granule size measured by a laser diffraction analyser were larger than 45 µm (the largest by sieving). By laser analysis, 28% of the granules measured were over 50 µm in size and 5% were less than 20 µm (smallest by sieving). Granules over 45 µm can go through the sieve because of their elongated shape [9]. Granule size distribution is shown in Fig.2.

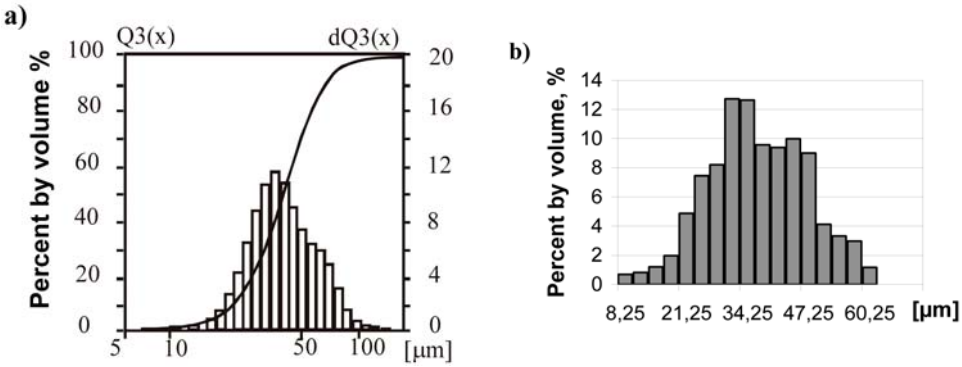


Fig.2. Powder C granules' volume distribution, a) measured by laser particle analyzer, b) by image analysis.

The results of image analysis using the IP system for granule size were similar to those of the laser analysis (Figs.2a and 2b). For image analysis, it is necessary to prepare powder metallographic cross-section polishes by cold or hot mounting and pictures. On the image analysis pictures, images of granules' cross-sections have to be cleaned, controlled and WC particles separated from each other in at least 5 images (Fig.1b). Easier and more accurate is to perform laser and sieve analysis, which does not need any special treatment, and the amount of analysed granules is larger. The pictures can be used for verifying of the results, especially in cases where the analysis results does not fit with expected results.

Indirect methods are not suitable for the analysis of composite powder granule sizes. The BET analyses indicated a larger surface area because of open porosity (Fig.1b). XRD can provide the size of WC crystals.

Phase analysis based on SEM images

The most effective and easiest way to analyze powder phases is the XRD analysis. WC-Co granules and coatings have mainly two phases (WC and pure Co), and the phase composition can be studied by XRD, SEM images and by X-ray mapping. According to the XRD analysis, powder granules have the following additional phases: W and Co_3W_3C. The coating has the same phases, except that CoO appeared as a result of oxidation during the spraying process. The XRD analysis does not show the Co-phase because the XRD is not sensitive to cobalt [10]. SEM photographs, X-ray mapping and hardness testing confirm that pure Co is one phase. Co_3W_3C is formed because of the low carbon content (4%) in the powder (less than stoichiometric carbon content of 6.13 mass% for WC) [11].

SEM image phase tones (W and Co have different tones under SEM because of their atom have different masses) can be the basis to obtain the phase content by computer. SEM photos can provide more information for the exact phase analysis because resolution and contrast is higher than for X-ray mapping. The most important step for computer analysis is to recognize the phases and their shape based on tones and pixel combinations. In Figure 3a is shown SEM image of coating (B) structure and in Fig.3b computer recognized phases. The lighter colour is the WC phase, darker is the Co phase and impurities or porosity are black. It can be seen that the SEM picture has less Co phase than computer analysis. This is because for structure analysis it is necessary to separate WC particles by reducing them. To understand the accuracy of the computerized phase, quantitative analysis of SEM pictures the WC phases were separated by hand. The pictures were analysed by the OM and IP system and with OM automatic WC separation. The

results (WC particle size, shape and phase areas) obtained by means of these methods differ approximately 5% and there are no systematic deviations. Computer phase analysis based on SEM pictures can be accurate with automatic WC particles separation.

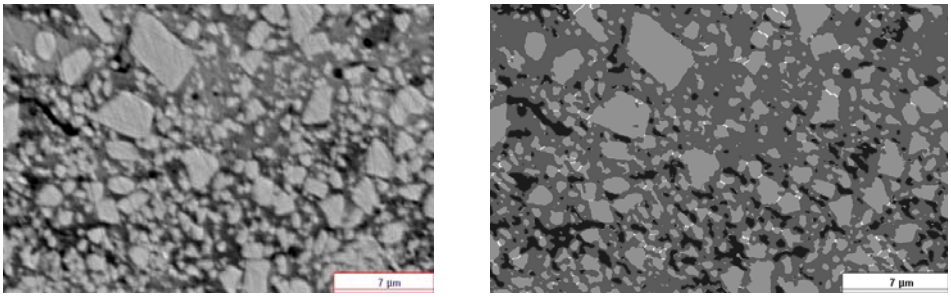


Fig.3. Coating B structure a - SEM picture and b - computer recognized phases.

Microstructure and Porosity of Coating

In order to obtain comparable information of the microstructure and porosity, the same methods should be used. There are several methods for describing the structure. However, even by the same methods, the values can differ and even the results of a computerized analysis depend on the researcher. Therefore, the structure analysis and porosity analysis require a good statistical database.

The database cannot consist of only one metallographic section. The investigated area should be large, depending on the size of the tested sample or samples. In most cases, the area of a sample is rather limited and therefore studies are based on one sample. However, this does not mean that the test area has the same structure as compared to the structure of the rest of material. Figure 4 shows the results of porosity analysis in different fields (polished surface and optical microscope pictures with magnification 500x). The different fields are obtained by grinding a new metallographic plane and porosity analyses were made from it. The coating C porosity can vary from 0.2 to 2.8% in a different area.

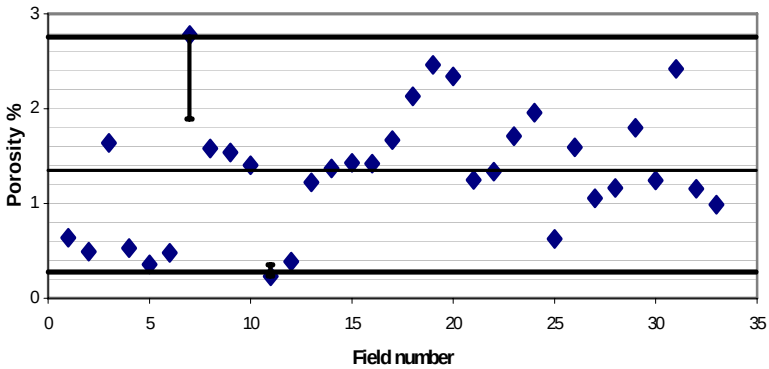


Fig.4. Coating C porosity analysis in different fields.

For porosity measuring with computer it is necessary to adjust the greyscale threshold to the proper level. Threshold makes the greyscale tones understandable to a computer. Figure 5a is an optical microscope picture and Fig.5b is a picture after

adjustment of the threshold level. Greyscale tones on the optical microscope picture can vary and are not always the same. Therefore manually adjusted pictures are more accurate and even then the operator can make a mistake. The uncertainty of the operator is shown in Fig.4 at minimum and maximum coating porosity. The operator adjusts the threshold level several times and the computer calculates the porosity.

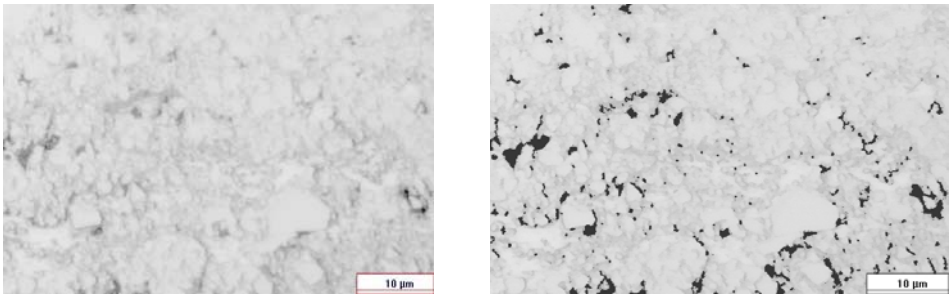


Fig.5. Coating (C) a - light microscope picture and b - computer recognized porosity on it.

In porosity measurements, the type of the microscope used is important because the optical microscope did not detect microporosity and SEM analysis showed black phases that consisted of lighter elements. The results of the optical microscope analysis are more reliable than those based on the SEM pictures. The average results (obtained by optical microscope) of porosity analysis are shown in Tab.2.

Tab.2. Phase area percentages and relative wear resistance

Parameters	A	B	C
Hard phase [%]	38.2	48.5	44.4
Matrix [%]	42.5	49.2	51.9
Porosity [%]	3.7	1.1	1.3
Relative wear resistance	5.3	10.3	23.2

The microstructures of coatings were analyzed by OM and IP systems based on the SEM pictures (2000x). The OM system corrected pictures automatically, only some corrections were made manually. Pictures for the IP system were corrected manually. There was no systematic difference in results because the separation of hundreds and even thousands of WC grains is stochastic. In Figure 3a are shown SEM pictures of coating (B) structure and a computer corrected picture is in Fig.3b. There were WC grains separated by each other and the main problem is that some small grains disappeared because all grains are smaller. The other problem is that the OM system separates some big WC grains to smaller ones. The final average results are comparable with images manually processed and are shown in Tab.3.

Tab.3. Results of structure analysis by OM analysis

Parameters	A	B	C
Mean diameter by volume [µm]	1.2	1.8	1.1
Spherical mean diameter* [µm]	0.7	0.8	0.8
Roughness	0.9	0.9	0.9
Sphericity	0.6	0.6	0.6

*Defined as 1.22474 times the circular diameter (square root of (4*area/π))

Microstructure can be of key importance when good abrasive wear resistance of a WC-Co coating is to be achieved. No direct dependence of the wear resistance (Tab.2) on the WC grains shape was found (Tab.3). The main microstructure (WC-Co) characteristics that effect the abrasive wear resistance of the coating are as follows: porosity, grain size and size distribution [12]. Therefore particle size distribution by their volume count (Fig.7) is a better indicator showing differences between the microstructures (Fig.6) [13]. Other grain size distributions and mean sizes have a very low sensitivity to some larger particles, as all coatings have almost the same spherical mean diameter (see Tab.3). Particle size distribution functions by volume are shown in Fig.7 and mean diameters are in Tab.3.

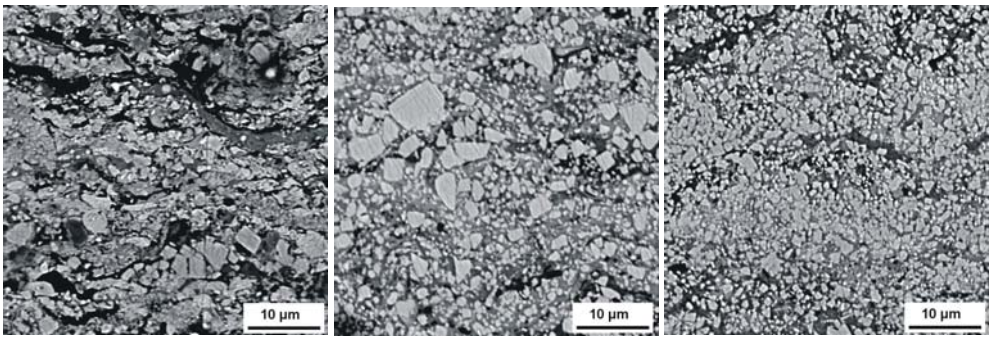
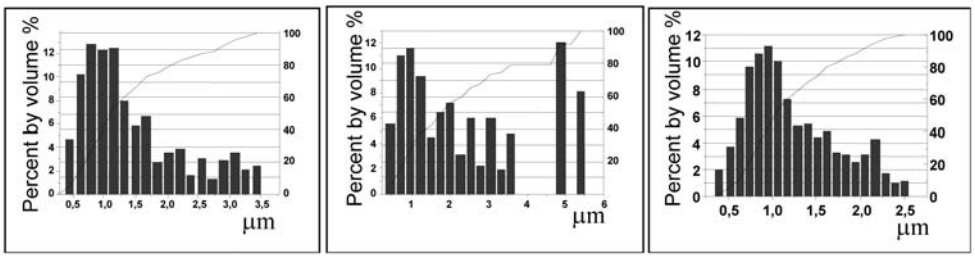


Fig.6. SEM pictures of coating microstructures; a – specimen A, b – B and c – C.



a b c

Fig.7. Hardmetal grain size distribution by particle volume; a - specimen A, b - B and c – C.

Differences in volume distributions are clearly visible. Coating (C) has high wear resistance because of the small and homogeneously distributed grains in the plain. In WC grain size distribution the main mode is at 0.9 µm and the other at 2.2 µm. Despite the smaller porosity of coating (B) (compared to coating (C)), wear resistance is not quite so good because the average size of larger particles is 5 µm, although the average size of small grains is the same. It means that in coating (C), grain size differences between large and small particles are smaller. The structure of coating (A) has approximately the same distribution of small and larger particles as coating (C), but it's porosity is three times higher (Tab.2) and therefore wear resistance is low.

Based on the experiments and microstructural analysis, dry abrasive wear resistance of the WC-Co coatings depend mainly on porosity, carbide content in the coating and volume size distribution. Other investigated parameters had a minor effect on wear resistance.

CONCLUSIONS

1. To characterize the thermal spray composite powder granules, numerical values are needed for purposes of comparison with other experimental results.
2. Computer corrected pictures can be of the same quality as hand corrected, but the correction program and results have to be controlled.
3. To obtain average numerical values of the microstructure and porosity, it is necessary to examine more fields (15 to 20 fields depending on the homogeneity of the coating structure).
4. Grain size distribution of particle size is not sensitive to changes in the microstructure; therefore, in order to obtain useful information, grain size distribution by volume must be used.
5. Microstructural analyses of coatings enable us to show that one particular WC particle volume distribution: uniform distribution of small-size hard particles (about 1 μm) and a certain amount (5 to 10% by volume) of larger hard particles (2 to 3 μm) is one of the main reasons of good dry abrasive wear resistance.
6. High porosity of a coating (about 2 to 3%) can reduce its wear resistance.

Acknowledgments

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