EFFECT OF POWDER PARTICLE SIZE ON THE STRUCTURE OF HVOF WC-Co SPRAYED COATINGS

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Abstract
Tungsten carbide coatings were deposited on steel substrate using a high velocity oxy-fuel (HVOF) spraying method. WC-Co coatings were prepared from commercially available WC-12% Co powders with different powder particle size distribution. Three different nominal powder particle size distributions were used: -45+20 μm, -45+11 μm and -20+5 μm. The microstructures of the coatings were analyzed by light microscopy, scanning electron microscopy and phase composition by X-ray diffraction. Powder particle size distribution was found to be an important parameter, strongly affecting the coating quality. Powder particle size influences porosity and morphology of the splats, as well as phase composition. The smallest porosity and visible lamellar microstructure was achieved using the smallest powder particles. The coating sprayed from powder with the coarsest particle had a higher amount of retained WC. In coating sprayed from powder with the smallest particles, a considerable amount of WC probably has been transformed on $W_2C$ and $W$ and part of WC has reacted with cobalt forming amorphous complex phases of $Co_xW_yC_z$.

Keywords: thermal spraying, tungsten carbide, coatings, HVOF, X-ray diffraction, structure

INTRODUCTION
WC-Co cermets are used extensively for numerous wear-resistant applications in a variety of industrial environments. Thermally sprayed WC-Co coatings of a thickness of 200-400 μm are widely used to protect the components from sliding, abrasion, fretting and erosive wear. The hard WC particles in the coating lead to high coating hardness and high wear resistance, while the metal binder (Co, Ni, or CoCr) supplies the necessary coating toughness. Many thermal spraying techniques such as air plasma spraying and high velocity oxy fuel spraying can be applied to deposit the WC-Co coatings. The properties of coatings strongly depend on the spraying technique. High-velocity oxy-fuel (HVOF) spraying has shown itself to be one of the best methods among thermally sprayed techniques for depositing WC-Co coatings. Oxygen and a fuel gas are combusted and through nozzle design and torch design are accelerated to very high velocities. Such high velocity flame consequently results in the formation of a spray particle stream with high velocity
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Comparison to conventional flame and plasma spraying. The very high kinetic energy of particles striking the substrate surface does not require the particles to be fully molten to form high quality HVOF coatings. This is certainly an advantage for the carbide cermet type coatings. HVOF coatings are used in applications requiring the highest density and strength not found in most other thermal spray processes. Several factors such as carbide grain size, cobalt and carbon content play an important role in determining the wear performance of the coatings. In general, an alloy with a high retention of tungsten monocarbide and metal cobalt in WC-Co cermets is desirable. However, during HVOF spraying, the decomposition and decarburization cannot be totally eliminated. During HVOF process the hot particles undergo a phase change in-flight such as: \( WC + O_2 \rightarrow W_2C + CO_2 \). Accordingly, WC may decompose to hemicarbide \( W_2C \), even to metallic tungsten and the decomposition products may dissolve into metallic cobalt to form an amorphous or nano-structured Co-W-C phase or complex carbides such as \( Co_3W_3C \), \( Co_2W_4C \), \( Co_6W_6C \) and \( Co_3W_9C_4 \) [1-6].

The possibility to eliminate the degradation of the phase using cold (gas dynamic) spraying was demonstrated in [7].

In the present investigation, the effects of powder particle size on the microstructure and phase composition of HVOF-sprayed WC-Co coatings are studied.

EXPERIMENTAL

Sheets from structural micro-alloyed steels with a fine-grained structure of steel KODUR E 700 were used for preparing substrate samples. The samples with dimensions of 50x50x10 mm were heat treated to stress relaxation. Substrates were thermally sprayed by HVOF technique in the firm TS-tech, Ltd. Hodonín, Czech Republic. Propane was used as fuel gas and nitrogen was used as powder carrier gas. In the current study WC-12% Co powders composed of 12 wt.% Co and 88 wt.% WC were used as the feed-stock. Powders with various powder particle sizes were sprayed. Three different nominal powder particle size distributions according to a statement by the supplier, were used: -45+20 \( \mu m \), -45+11 \( \mu m \) and -20+5 \( \mu m \). Particle size distribution of powders was determined by SYMPATEC HELOS analyzer based on the physical principles of laser diffraction. Particle size distributions of -45+20 \( \mu m \) and -20+5 \( \mu m \) powders respectively are presented in fig.1 a, b. Measured value \( d_{50} \) is 40.42 \( \mu m \) (for -45+20 \( \mu m \)), respectively 18.45 \( \mu m \) (for -20+5 \( \mu m \)). Spray distance at all granulometric classes was kept at 180 mm. A bigger distance (200 mm) was also applied in one trial using -45+20 \( \mu m \) powders. Just before spraying, the substrates were degreased with acetone and grit blasted. During spraying the samples were rotated. Coating cross-sections were cut from the bulk using a spark wire cutter. Observations of the cross-section morphology of the coatings were conducted in light and scanning electron microscope JEOL JSM-7000F. Coating microstructures were characterized besides making secondary electron mode images (SE) by making backscatter electron images (BSE) in a scanning electron microscope. BSE images give contrast between phases depending on atomic numbers. Phases with high atomic numbers appear bright. The presence of various phases in some of the coatings was analyzed by X-ray diffraction with CrK\( \alpha \) radiation in the range \( 2\theta = 5–165^\circ \). Phase composition of the coatings was determined from measured diffraction profiles using the PDF 2 database (Powder Diffraction File).

RESULTS AND DISCUSSION

There are easily distinguishable changes in character of the coating depending on powder particle size by eye view. Shade of gray were the most bright in coating sprayed from
the smallest particles, vice-versa the darkest gray was observed in coating sprayed from the coarsest particles. From the particle size distribution curves displayed in Figs.1a,b it can be seen that a significant fraction of the powder has particle size outside the nominal size range.

SE and BSE images of the coatings sprayed with -45+20 μm (at a longer spray distance), -45+11 μm and -20+5 μm powders (the same spray distance) are displayed in Figs.2-4. The microstructure of the coatings is characterized by the existence of various pores and splats. Powder particle size influences porosity and morphology of the splats. The smallest porosity and visible lamellar microstructure was achieved using the smallest powder particles -20+5 μm, by contrast the highest porosity and incomplete formation of splats was observed in coating deposited by -45+20 μm particles sprayed from a longer distance. This relates with molten state and velocity of powder particles. Particles of different sizes may have different the molten states and velocities. Shorter spray distance results in higher particle velocity. Particle velocity and melting ratio drop as the powder size increases. A good melting condition helps to decrease coating porosity and to improve deposition efficiency. Ideal lamellar microstructure of a coating formed by fully melted particles [4,8].

![Particle size distribution](image)

Fig.1. Particle size distribution of powders with nominal particle size distribution according to statement by supplier as a) -45+20 μm, b) -20+5 μm.

The images presented in BSE mode, giving contrast of phases with different average atomic numbers. From BSE images of coatings there are clearly seen carbide particles in the binder phase, mainly in Fig.2. The dark and bright regions in the binder correspond to regions of lower and higher mean atomic number, respectively. These bright and dark binder layers are known to be W-rich and Co-rich regions, respectively [9]. The images reveals that the coating sprayed from the powder with the smallest particles (-20+5
μm) has a higher degree of bright phase indicating that some WC has dissolved into the metallic matrix during spraying due to overheating. Overheating causes WC to decompose into W₂C and W. On the contrary, the structures of corresponding coatings applied from powders with coarser powder grains characterized by less overheating and a higher fraction of retained WC particles. This is demonstrated by the SEM BSE images in Figs.2-4. As it is stated in [4] the inhomogeneous composition of the binder resulted from the dissolution of WC during spraying.

Fig.2. SE and BSE images of coatings sprayed form -45+20 μm powder particles. (Spray distance 200 mm).

Fig.3. SE and BSE images of coatings sprayed from -45+11 μm powder particle. (Spray distance 180 mm).

These results indicate different melting behaviors of powders with different grain size distributions. The particle temperature at the spray gun exit is influenced by the powder particle size [9].
Fig. 4. SE and BSE images of coatings sprayed from -20+5 μm powder particle. (Spray distance 180 mm).

Figures 5 and 6 show XRD patterns of coatings sprayed from powders with particles of different sizes -45+20 and -20+5 μm, respectively.

From the XRD patterns in Fig.5 we can determine, that the major component of coating sprayed with the coarsest powder particle (-45+20 μm) is WC phase. Reflections corresponding to expected peaks of hemicarbide W₂C and elemental W are weak. It arrives at this, that if these phases are present in this coating, only in paucity (close to detection limit). In XRD pattern there is evident a broad reflection of low intensity which can correspond to fine, but crystalline Co₆W₇C₂ phases (nanocrystalline phases).

Fig.5. XRD pattern of coatings sprayed from the coarsest powders (-45+20 μm).

Qualitative phase analysis of XRD pattern of coating sprayed from the smallest powder particle (Fig.6) confirms the presence of tungsten carbide WC with hexagonal crystal structure. At the 2θ diffraction angles between 59 – 63° there are two sharp reflections, which respond to 100% intensity reflections of W₂C and W phases. Identification of these phases is however not unambiguous because of overlapping of these reflections with reflections of WC phase on the other diffraction angles. At the 2θ
diffraction angles between 55 – 75° it is possible to observe a considerable diffraction line broadening which is characteristic for an amorphous component. This amorphous part can be created by \( \eta \) phases – Co\(_x\)W\(_y\)C\(_z\). The sharpest reflection lines of all \( \eta \) phases (Co\(_3\)W\(_3\)C, Co\(_6\)W\(_6\)C, Co\(_2\)W\(_4\)C and Co\(_3\)W\(_9\)C\(_4\)) are localized in this range. Formation of intermetallics - \( \eta \) phases result from the elemental diffusion by tungsten carbide and the cobalt binder. The original cobalt binder phase of the powder is also often replaced in the coating by an amorphous or nanocrystalline binder phase. The formation of non-WC carbide phases is generally considered detrimental to the wear performance, although it appears that in some cases the integrity of the microstructure and the intersplat cohesion can be affect the wear rate more than the degree of loss of WC [10]. On the basis of qualitative phase analysis of the coating sprayed from powders with the smallest particles -20+5 \( \mu \)m it could be stated that the major component of the coating is WC though part of WC during spraying has transformed to W\(_2\)C and W and part of WC has dissolved in cobalt forming complex amorphous phases of the Co\(_x\)W\(_y\)C\(_z\) type.

Fig.6. XRD pattern of coatings sprayed from the smallest powders (-20+5 \( \mu \)m).

Comparing the XRD pattern (Fig.5) of the coating sprayed from the powder in range of particle size (-45+20 \( \mu \)m) with the XRD pattern (Fig.6) of coating sprayed from the powder in range of particle size (-20+5 \( \mu \)m) it can be observed that intensities of WC reflections are markedly higher (approximately 2x) in coating sprayed from coarsest powder particles. Less intensity of WC reflection in coating sprayed with the smallest powder particles are likely as a consequence of a decrease of WC content by its transformation to W\(_2\)C and W. Another reason can be fineness of coating microstructure causing a broadening of peaks and decreasing their intensity.

On the basis of the qualitative analyses of the coating sprayed from the smallest powder particles it can be stated that the major phase is WC, but a certain part of WC has been transformed during the spraying process to W\(_2\)C and W and part of WC has reacted with cobalt forming amorphous complex phases of Co\(_x\)W\(_y\)C\(_z\) type. WC is the major phase of the coating sprayed from the coarsest powder particle and phases W\(_2\)C, W and Co\(_x\)W\(_y\)C\(_z\) are in very low quantity, as well as these \( \eta \) phases which are crystalline.
Hence, thermal decomposition more likely occurs with the small powder particles. Optimizing spray conditions is difficult with large particle size distribution. Either the small particles are overheated or cause WC decomposition, or the large particles are not sufficiently heated and cause pores in the coating [9,11].

HVOF coating performance is strongly dependent on its microstructure. Microstructure character is result of particle in-flight behavior influenced by temperature, velocity, melting and oxidation of particles. Operating conditions such as particle size, as well as spray distance, injection velocity and angle affect the in-flight behavior of particles.

CONCLUSION
It was confirmed that particle size of WC-Co powder has a significant effect on microstructure and the phase composition of coating. Powder particle size influences porosity and morphology of the splats, as well as the phase composition of coatings. This relates with the molten state and velocity of powder particles. Particles of different sizes may have different molten states and velocities. The smallest porosity and visible lamellar microstructure was achieved using the smallest powder particles, though on the other hand the smaller powders have larger surface activity and are more liable to react, generating a new phases during spraying process.

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REFERENCES