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Recycled hardmetal-based powders for thermal spray

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Abstract. The paper focuses on low-cost tungsten carbide based spray powders with particle size of 15–50 μm, produced from recycled hardmetal. Their properties are comparable with commercially produced (Tafa Inc., Sulzer Metco Inc., etc.) powders. Different methods of WC-Co hardmetal powder preparation (plating, milling and mixing) were used to produce spray powders. The composition and structure of recycled hardmetal-based spray powders, produced by the disintegrator, attritor and ball milling, were investigated. Powders were chemically and mechanically plated with Co or agglomerated, using different plating techniques and heat treatment. Chemical composition of powder particles was studied by energy-dispersive X-ray microanalysis and element distribution inside powder particles was investigated on particle cross-sections with the X-ray mapping technology. Best results were obtained using monomodal initial WC-Co and Co powders with the mixing, agglomeration, sintering and crushing techniques.

Key words: recycling, disintegration, milling and mixing, agglomeration and sintering, double-cemented hardmetal powder, particle composition.

1. INTRODUCTION

Considering product lifetime of engineering materials and parts, the surface is of prime concern. This involves both corrosion behaviour and mechanical properties, such as material wear. Traditional tungsten carbide-cobalt (WC-Co) based hardmetals are widely used to increase the wear resistance. A wide range of commercial powders is used for these purposes. A new grade of analogous hardmetal powders from recycled hardmetals suitable for thermal spray is proposed in [1]. A potential application area of these powders is thermal spray

(flame spray and fusion, detonation and HVOF spray). In this case, particle size and morphology (shape parameters) determine the main technological properties of the powders (bulk density, flowability, surface area, etc.) as well as the properties of the coatings and of the final product. For thermal spray, the preferable particle form is spherical to have a high flowability of powders and optimal conditions of particle melting and spraying. Powder granularity must be in a narrow range to have minimal oxidation of particles during spraying and high porosity of the coating.

Earlier studies have shown that the coarser fraction of the recycled hardmetal powder is suitable as the reinforcing phase for spray and fusion in the self-fluxing alloy based powder, and fine fraction – for spray [1]. Finer powder of 30–80 μm has been used for the detonation spray. From the point of view of the efficiency of the detonation spray and lower porosity coatings, finer (30–40 μm) powder is preferred. However, the abrasive-erosive resistance of detonation-sprayed recycled hardmetal coatings is low due to the peculiarities of the powders produced by mechanical milling [2]. In addition to the studies of the particle size, experiments, conducted to determine the influence of the shape of the hardmetal particles (angularity) on the erosion rate of different metallic materials, show that this parameter is essential in powder shape characterization [3]. In [4] the influence of the shape of the powder particles (spherical, angular) on the erosion rate and on the wear mechanism of different metallic materials was studied. The influence of the shape of the reinforcement powder particles in composite spray fusion coatings on the erosion wear resistance was established.

Using commercially produced powders and high-velocity spray methods in thermal spray for wear-resistant coatings, high density (porosity less than 1–2 %) can be achieved. Earlier studies have shown [2,5] that the use of the recycled hard-metal powder in the formation of detonation coatings leads to many problems. Hardmetal powder particles in the range of 32–40 μm, used for detonation spray, produce very porous (4–5 %) and non-uniform coatings. According to our pre-liminary experiments, to improve the properties of sprayed coatings, in addition to the use of powders with different particle size and shape, application of such technological means as metallizing the powder particles with ductile metal, agglomerating the fine powder fraction, etc., are promising.

2. EXPERIMENTAL

A WC-Co hardmetal powder, produced from used hardmetal by disintegrator milling [6], was used as the basic component of the sprayed coatings. The studies were conducted with experimental disintegrators DSL-158 and DSL-160. Granularity and chemical composition of the used initial powders are given in Table 1.

Granularity values are obtained from the sieve analysis for coarse powders and from the laser diffraction analysis with Analysette-22 analyser for fine powders. Table 1 shows the chemical composition obtained from the energy-

Table 1. Characteristics of initial powders

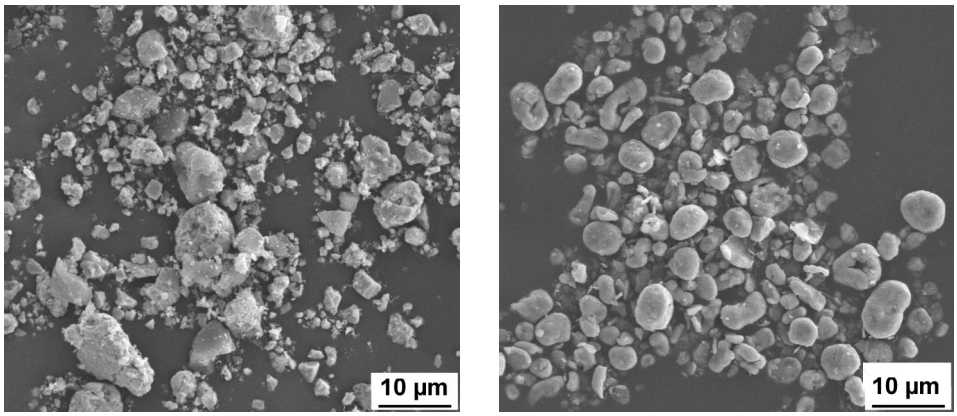
Type of the powder	Granularity, μm	Chemical composition, wt%
WC-Co	250–500 45–90 20–45 2 (mean); 0.5–4 (90%)	WC (74%), Co (10%), Fe (9%), TiC (6%), Cr (0.7%), Ni (0.3%)
Co	19 (mean); 1–50 (90%) >20 3 (mean); 0.5–10 (90%)	Co (99.5 ± 0.5%)

dispersive X-ray microanalysis (EDS). The TiC is introduced into the WC-Co powder composition from the initial material (parts of the recycled material contain TiC). The content of Fe is caused by the disintegrator milling process. The paper [7] deals with this problem in greater detail.

To improve technological properties of spray powders, the following three methods were used:

1) chemical deposition of Co onto WC-Co particles using $CoCl_2$ solution;
2) mechanical plating of WC-Co particles with Co layer by different mechanical plating techniques (ball mill, attritor mill, disintegrator), followed by sintering and crushing;
3) formation of WC-Co + Co powder particles from monomodal initial powders using agglomeration, sintering and crushing.

The binder metal (Co) content in WC-Co composites was 10–15 wt%. Figure 1 shows initial powders used in the agglomeration and sintering process.



(a) (b)

Fig. 1. SEM pictures of initial metal powders used in the agglomeration process: (a) disintegrated WC-Co powder; (b) disintegrated Co powder.

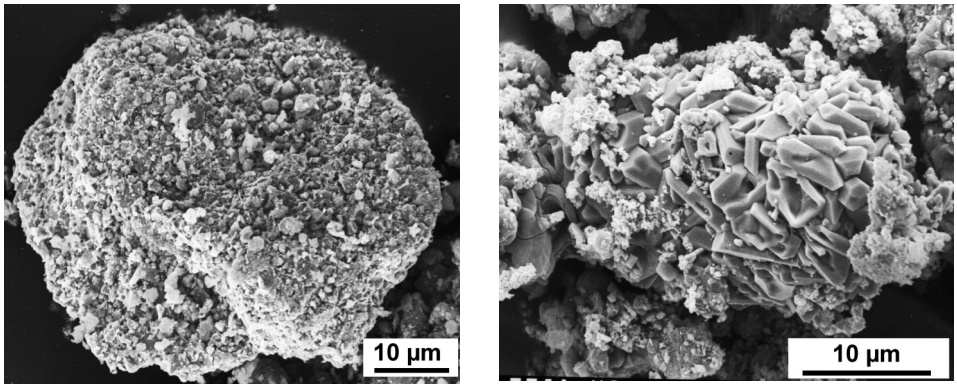
To characterize the produced double-cemented powders, powder particles and their cross-sections were studied with the scanning electron microscope Jeol JSM-840A. Chemical composition of powder particles was studied with the EDS analysis using the LINK ANALYTICAL AN10000 system. To evaluate element distribution inside powder particles, the X-ray mapping technique was used. It gives the resolution of the element distribution approximately 1 μm and is sufficient in the case of 20–100 μm particles.

3. RESULTS AND DISCUSSION

3.1. Chemical plating of WC-Co powder particles with Co

To improve the technological properties of the powder and the cohesion between the particles in the sprayed coatings, chemical plating of WC-Co with Co was used. The recycled hardmetal powder was covered chemically by the $CoCl_2$ layer, followed by thermal treatment (reduced in H_2 environment at 550 °C). Figure 2 shows chemically plated WC-Co powder particles in 0.5 % $CoCl_2$ solution before (Fig. 2, a) and after (Fig. 2, b) annealing in H_2 environment. During the chemical plating process, WC-Co particles are uniformly covered with a $CoCl_2$ layer, but after removing chlorine from the surface of hardmetal particles in H_2 environment, Co layer also appears. Table 2 presents the main characteristics of the chemically plated WC-Co hardmetal powder.

The X-ray microanalysis revealed that the Co layer on the WC-Co powder particles was practically removed as a result of reducing $CoCl_2$, and the technological properties of the powder (flowability, surface area) were practically not improved. The efficiency of the detonation spray and porosity of the coating were low.



(a) (b)

Fig. 2. SEM pictures of chemically plated powders: (a) WC-Co powder coated in 0.5% Co solution; (b) the same annealed in H_2.

Table 2. Main characteristics of the chemically plated WC-Co hardmetal powder

Type of the powder	Mean diameter, μm	Specific surface area, m^2/g
WC-Co powder coated in 0.5% Co solution	18.1	2.301
The same, annealed in H_2	19.7	1.500
WC-Co powder coated in 1.0% Co solution	18.6	–
The same, annealed in H_2	18.3	1.401

3.2. Mechanical plating of WC-Co powder particles with Co

The following mechanical plating techniques for milling and alloying of the WC-Co powder particles with Co were used:

– milling with alloying in the disintegrator mill;
– milling with alloying in the attrition mill;
– milling with alloying in the ball mill.

The main aim of this study was to produce double-cemented WC-Co + Co powders with the three above-mentioned methods. The characteristics of experiments and results are given in Tables 3–5. The tables show the composition and size of the initial powder particles and processing parameters: sintering temperature (*T*), velocity of rotation (*n*) and milling time (*t*). Results and main observations in connection with the production of double-cemented structures are described. Figure 3 describes the disintegrator-plated WC-Co hard-metal powder particles.

Table 3. Milling and mixing in the disintegrator mill

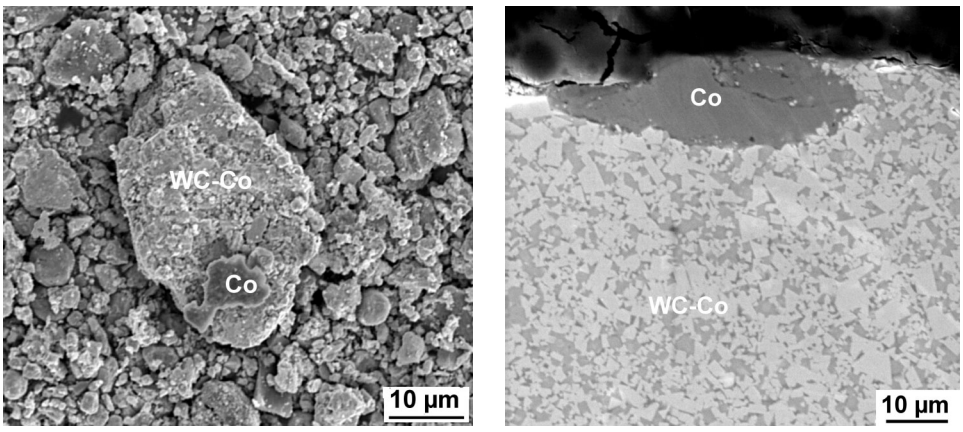
Composition, wt%	Size of initial particles, μm	Processing parameters	Characterization of results
90 (WC-Co) + 10 Co	WC-Co 250–500 Co: 1–50	n_1 = 6000 rpm n_2 = 8000 rpm	Due to the high impact energy, Co fills the surface cavities of hard-metal particles only.
90 (WC-Co) + 10 Co	WC-Co: 45–90 Co < 20	$n_1 = n_2$ = 7200 rpm	Due to the high impact energy only intensive size reduction of WC-Co particles was observed. Co did not stick on the hardmetal particles.

Table 4. Milling and mixing in the attrition mill

Composition, wt%	Size of initial particles, μm	Processing parameters	Characterization of results
87 (WC-Co) + 13 Co	WC-Co 45–90 Co < 20	*T* = 1300 °C *n* = 800 rpm *t* = 1 h	Powder particles were easily shattered to pieces after sintering.
85 (WC-Co) + 15 Co	WC-Co: 20–45 Co: 3 (mean)	*n* = 168 rpm *t* = 1 h	WC-Co was milled, but particles were easily shattered to pieces.

Table 5. Milling and mixing in the ball mill

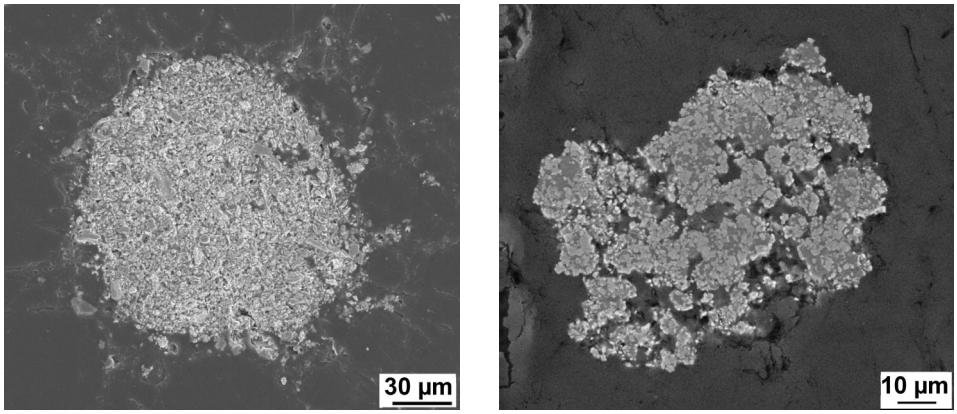
Composition, wt%	Size of initial particles, μm	Processing parameters	Characterization of results
85 (WC-Co) + 15 Co	WC-Co 20–45 Co < 20	n = 81 rpm t = 48 h	No significant granulation and plating of WC-Co particles with Co was observed.
85 (WC-Co) + 15 Co	WC-Co: 20–45 Co: 3 (mean)	n = 65 rpm t = 48 h	No significant granulation and plating of WC-Co particles with Co was observed.
87 (WC-Co) + 13 Co	WC-Co: 20–45 Co: 20	T = 1280 °C n = 81 rpm t = 2 h	WC-Co and Co particles were separate after sintering as the sintering temperature was too low.
85 (WC-Co) + 15 Co	WC-Co: 20–45 Co < 20	T = 1300 °C n = 81 rpm t = 24 h	The WC-Co particles were milled and mixed with Co. Best result with the ball mill technology.
85 (WC-Co) + 15 Co	WC-Co: 20–45 Co < 20	T = 1400 °C n = 81 rpm t = 24 h	Due to the too high sintering temperature it was impossible to crush the sintered substance.



(a) (b)

Fig. 3. SEM pictures of powders 90% (WC-Co) + 10% Co mixed in disintegrator mill: (a) WC-Co 45–90 μm, Co < 20 μm; (b) WC-Co 250–500 μm, Co 1–50 μm.

Disintegrator, attrition and ball milling were used to “glue” the Co particles on the surface of the WC-Co hardmetal particles. Using high-energy milling technologies (disintegrator and attrition milling) in preparation of double-cemented hardmetal particles, no significant alloying or mixing of WC-Co and Co particles was observed. In the case of disintegrator mill the impact energy was too high and the intensive size reduction of WC-Co particles was observed. Only



(a) (b)

Fig. 4. SEM pictures of powders 85% (WC-Co) + 15% Co mixed in different mills: (a) WC-Co 20–45 µm, Co 3 µm milled in attrition mill; (b) WC-Co 20–45 µm, Co < 20 µm milled in ball mill and sintered at 1300 °C.

small surface areas of the hardmetal particles were covered with Co. In the attrition mill, the size reduction of initial powders and the following agglomeration processes took place. But in spite of sintering, the formed agglomerates (Fig. 4, a) were very weak and particles were easily shattered to pieces. Only after high-temperature sintering of the powders milled in ball mill, the fusion of WC-Co and Co particles together was detected. At the sintering temperature of 1280 °C, the hardmetal powder was minimally covered with Co. Better results were obtained by sintering at 1300 °C (Fig. 4, b). A porous double-cemented powder structure was obtained, but the initial WC-Co and Co particles were quite heavily fused to one another. The sintering temperature of 1400 °C was too high. The obtained (WC-Co)-Co substance was heavily fused and it was impossible to separate the partially fused particles.

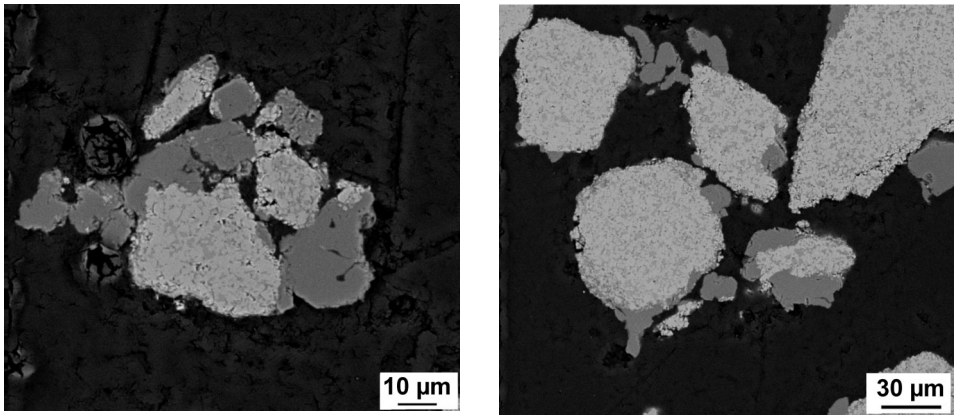
3.3. Formation of the (WC-Co)-Co powder particles by the agglomeration and sintering process

In this study the initial powder particle size, the compacting pressure of the mixed powder and the sintering temperature were varied. Initial powders were mechanically mixed in the laboratory drum mixer. Plating and agglomerating processes were induced by sintering. Table 6 shows the results (p is compacting pressure).

Similarly to the experiments with different milling systems, sintering temperature lower than 1300 °C was not sufficient to achieve the expected results. The end product was similar to the initial powders. No significant fusion of WC-Co hardmetal and Co was observed. Plating and agglomeration proceeded effectively at 1300 °C. Depending on the size of the initial powder particles, the

Table 6. Mechanical mixing and agglomerating of powders

Composition, wt%	Size of initial particles, μm	Processing parameters	Characterization of results
83 (WC-Co) + 17 Co	WC-Co: 20–45 Co < 20	T = 1150 °C	Sintering temperature was not sufficient. WC-Co hardmetal particles were only partially plated with Co.
87 (WC-Co) + 13 Co	WC-Co: 20–45 Co < 20	T = 1300 °C	WC-Co and Co particles were joined into bigger agglomerates. No significant plating took place.
87 (WC-Co) + 13 Co	WC-Co: 45–90 Co < 20	T = 1300 °C	WC-Co particles were partially covered with a Co layer.
85 (WC-Co) + 15 Co	WC-Co: 2 (mean) Co: 3 (mean)	T = 1300 °C	Small hardmetal particles were fused into Co matrix. Agglomeration process had taken place.
85 (WC-Co) + 15 Co	WC-Co: 2 (mean) Co: 3 (mean)	T = 1300 °C, p = 80 N/mm^2	By help of compacting, porosity of agglomerates was reduced.



(a) (b)

Fig. 5. SEM pictures of mechanically mixed 83% (WC-Co) + 17% Co powders sintered at 1300 °C: (a) initial size of particles for WC-Co 20–45 μm and Co < 20 μm; (b) WC-Co 45–90 μm and Co < 20 μm.

plating (Fig. 5, b), agglomeration (Fig. 6, a) or plating-agglomeration (Fig. 5, a) process occurred. The compacting pressure reduces the porosity of powder particles, which are formed during the agglomeration process. With larger initial powder particles, the compacting pressure has no marked influence on the plating process.

The best results were obtained with mechanical mixing of the monomodal micropowders (mean grain size for WC-Co hardmetal was 2 μm and for Co 3 μm) and using the compacting pressure of 70–90 N/mm^2 of mixed powders before

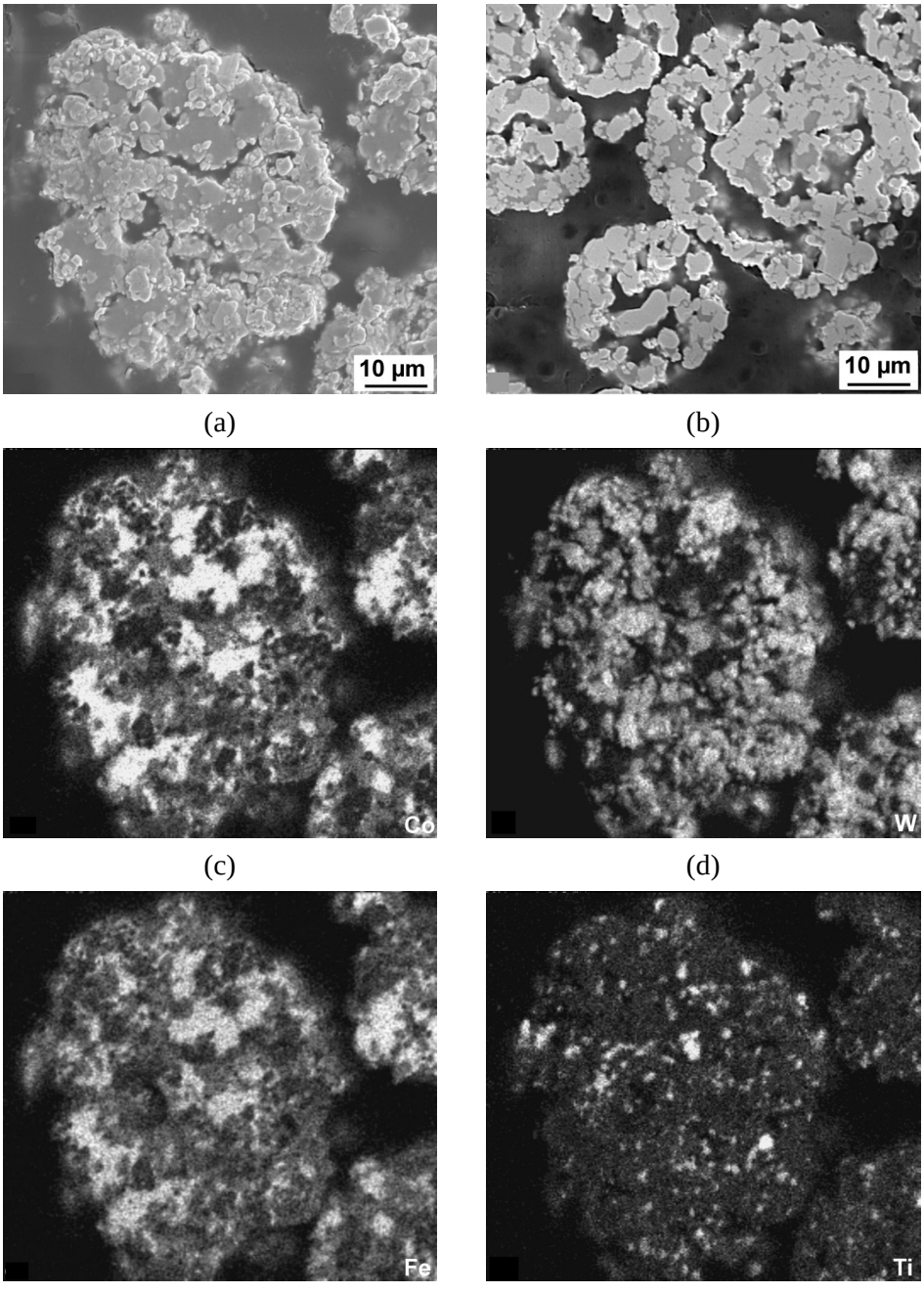


Fig. 6. SEM images and X-ray maps of studied powders: (a) SEM image of the agglomerated experimental powder 85% (WC-Co) + 15% Co by conditions: WC-Co 2 μm, Co 3 μm, p = 80 N/mm^2, T = 1300 °C; (b) SEM image of commercial WC-17Co (Tafa 1343V) powder; X-ray images of experimental powders: (c) Co; (d) W; (e) Fe; (f) Ti.

sintering. Figure 6 shows the structure and composition of the double-cemented powder. To compare the results of the produced powder with similar commercially produced Tafa powder, the SEM micrograph of WC + Co (17%) (Tafa 1343V) powder is presented in Fig. 6, b. The structures of the agglomerated powder and Tafa 1343V powder (Fig. 6, a and b) are similar. Tafa powder contains only WC and Co particles. Experimental powder contains additionally Ti (Fig. 6, f) and Fe (Fig. 6, e). As it was mentioned above, Ti is derived from the initial material (WC-TiC-Co hardmetal was used). Fe is obtained from the hardmetal recycling process due to the interaction between hardmetal particles and disintegrator impact blades (made from steel). After sintering, Co and Fe stay in separate phases (Fig. 6, c and e).

4. CONCLUSIONS

1. To obtain recycled hardmetal powders for thermal spray, different mechanical preparation techniques (disintegrator, attrition and ball milling) were applied. The best results were obtained with the ball and attrition milling.

2. Due to the high impact energy, in a disintegrator mill milling rather than plating is predominant; by the ball and attrition milling, only partial gluing of Co onto the hardmetal particle surface took place.

3. By mechanical mixing of the about micron-size initial monomodal WC-Co hardmetal and Co powder particles, further compression of the mixture at 80 N/mm^2 and sintering it at 1300 °C gives a double-cemented (WC-Co)-Co powder, comparable with a commercial product.

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Korduvkasutatavast kõvasulamist pulbrite valmistamine termiliseks pihustamiseks

Valdek Mikli, Priit Kulu, Riho Tarbe, Priidu Peetsalu ja Sergei Zimakov

Uurimistöö eesmärgiks oli termilisel pihustamisel kasutatavate kõvasulamist pulbrite valmistamine korduvkasutatavast materjalist. Valmistatavate pulbrite osakeste suurus peaks olema vahemikus 15–50 μm ning pulbrite omadused peaksid vastama tööstuslikult toodetud pulbrite (Tafa Inc., Sulzer Metco Inc. jne) omadele. WC-Co-pulbrite valmistamiseks kasutati mitmesuguseid meetodeid (jahvatamine, segamine). Uuriti desintegraatoris, atriitoris ja kuulveskis valmistatud pulbrite struktuuri ja koostist. Kasutades erinevaid pulbrite katmise tehnoloogiaid ja termotöötlust, saavutati WC-Co-pulbrite katmine (keemiliselt või mehaaniliselt) koobaltikihiga. Uuriti WC-Co- ja Co-mikropulbrite (2–5 μm) aglomeratsiooniprotsessi. Koobaltiga kaetud WC-Co-pulbri osakeste keemilist koostist uuriti energiadispersse röntgenmikroanalüüsi meetodil. Elementide jaotust pulbriosakeste sees uuriti pulbritest tehtud ristlihvide röntgenkaardistamise meetodil. Termilise pihustamise jaoks parimate omadustega pulbrid saadi 2–5 μm suurustest algpulbritest (WC-Co ja Co), kasutades pulbrite valmistamiseks mehaanilise segamise, paagutamise ja purustamise tehnoloogiat.