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Metal-Matrix Hardmetal/Cermet Reinforced Composite Powders for Thermal Spray

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Recycling of materials is becoming increasingly important as industry response to public demands, that resources must be preserved and environment protected. To produce materials competitive in cost with primary product, secondary producers have to pursue new technologies and other innovations. For these purposes different recycling technologies for composite materials (oxidation, milling, remelting etc) are widely used. The current paper studies hardmetal/cermet powders produced by mechanical milling technology. The following composite materials were studied: Cr_3C_2-Ni cermets and WC-Co hardmetal. Different disintegrator milling systems for production of powders with determined size and shape were used. Chemical composition of produced powders was analysed. To estimate the properties of recycled hardmetal/cermet powders, sieving analysis, laser granulometry and angularity study were conducted. To describe the angularity of milled powders, spike parameter–quadric fit (SPQ) was used and experiments for determination of SPQ sensitivity and precision to characterize particles angularity were performed. Images used for calculating SPQ were taken by SEM processed with Omnimet Image Analyser 22. The graphs of grindability and angularity were composed. Composite powders based on Fe- and Ni-self-fluxing alloys for thermal spray (plasma and HVOF) were produced. Technological properties of powders and properties of thermal sprayed coatings from studied powders were investigated. The properties of spray powders reinforced with recycled hardmetal and cermet particles as alternatives for cost-sensitive applications were demonstrated.
Keywords: grindability, angularity, recycling, hardmetal/cermet powders, morphology.

1. INTRODUCTION

Product lifetime is the main concern in the field of material engineering. High Velocity Oxygen Fuel (HVOF) spray coatings show significant reliablity even in harsh conditions [1]. Recently, attention has been focused on reduced consumptions of existing resources and materials recycling due to increasing cost of primary materials during the last decade [2, 3].

From that point of view, recycling of materials is becoming more important in order to preserve natural resources, on the other hand industrial needs have to be considered. Thermal spray powders may involve considerable amount of all spraying process expenses.

However, utilization of industrial hardmetal scrap in metallurgical processes is often irrational [4]. One of the effective methods for producing those materials is grinding by collision [5]. Disintegrator technology allows to produce different hard and brittle materials.

One of the main limitations of using thermal spray coatings is the high cost of feedstock materials. Today use of iron based self-fluxing alloys is relatively limited compared with more expensive nickel, chromium or tungsten alloys. Hence, utilizing cheap iron based alloys reinforced with recycled hardmetal particles could be a rational alternative.

For producing high-quality powders and coatings, the shape and size of particles in production process must be well controlled. Usually, spherical and homogenous powders with high flowability are preferred. The size of powder articles can be determined by image or sieving analyses. Another important parameter is morphology [6, 7] that can be characterized by description or quasi-quantitatively.

In this paper Disintegrator milling of Cr_3C_2-Ni, WC-Co hardmetals was conducted with grindability, granulometry and angularity analysis. Composite powders based on iron and nickel based alloy reinforced with hardmetal/cermet particles were studied, powder granularity and technological properties were estimated before and after mixing.

2. EXPERIMENTAL

For material grinding by collision the disintegrators were used [8]. Refining of materials occurs as a result of fracture in a treated material. By particle collision to a wall (target, grinding body) from the point of contact, an intensive wave of pressure begins to propagate. Values of stresses are higher than material strength. The material processing parameters in a disintegrator differ essentially from traditional milling methods and equipment (jaw crusher, mortar, hand-mill, quern, vibro-, and ballmill). Recycled Cr_3C_2-Ni and WC-Co powders were produced by experimental multi-functional disintegrators. Principal schemes of milling equipment – centrifugal-type disintegrator mill DSL-350 (a) and laboratory disintegrator milling system DSL-175 (b) are shown in Fig. 1.

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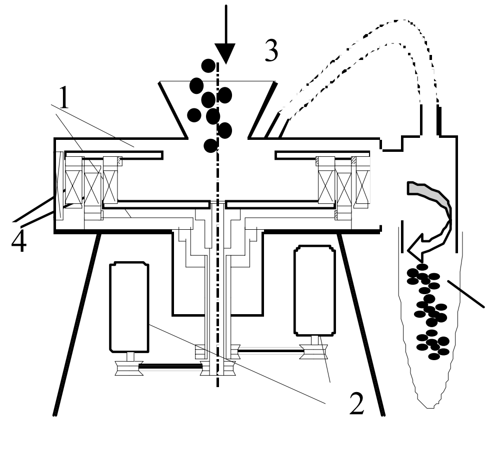


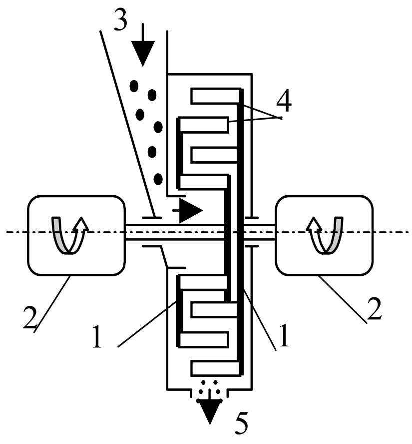


Fig. 1. Schematic representation of preliminary size reduction centrifugal-type mill DSL-350 (a) and vertical laboratory milling disintegrator DSL-175. Equipment (b): 1 – rotors; 2 – electric drives; 3 – material supply; 4 – grinding elements; 5 – output

The main kinetic parameter in materials processing using disintegrator milling systems is the specific energy of treatment regarding the grinding effect and the economic aspect of the process. Grindability, as function of particles size *d* on the specific energy of treatment E_S was studied in [9].

Determination of particle size distribution was carried out on vibratory sieve shaker Analysette 3 PRO for materials with particle size 12.5 mm – 0.025 mm and with a laser diffraction particle sizer Analysette 22 for powders finer than 300 μm was used.

For describing the angularity of milled powders, spike parameter – quadratic fit (SPQ) was described and experiments for determination of SPQ sensitivity and precision to characterise particles angularity were performed. Images used for calculating SPQ were taken by SEM Zeiss EVO MA-15 and processed with Omnimet Image Analyser 22. The parameter SPQ considers only those spikes that are outside the circle with equal particle centred over the particle centroid [10, 11]. The sides of the outside spike are represented by fitting quadratic polynomials. Differentiating the polynomials yields the apex angle Θ and the spike value $SV = \cos(\Theta/2)$. $SPQ = SV_{mean}$ are calculated as the mean SV over the all outside spikes.

Prior to spraying the composite powders were analysed to determine the cumulative particles distribution of composite powders and shape by SEM.

Table 1. Particle size and chemical composition of commercially produced powder

Type of powder	Particle size	Chemical composition. wt %					
		Ni	Fe	B	C	Si	Cr
FeCrSiB	–45+10	6	bal	3.4	2.1	2.7	13.7
iCrSiB	–53+15	bal	2.5	1.6	0.25	3.5	7.5
WC-CoCr	–45+15	WC – 86			Co – 10		4

In the current study composite spray powders consisting of 60 vol% of Fe-based self-fluxing alloy and 40 vol% of recycled hardmetal particles (Cr_3C_2-Ni; WC-Co) were used. The properties of Fe-based self-fluxing alloy and other commercially produced powders used in comparative test are shown in Table 1. The technological properties (flowability and tap density) were determined. FeCrSiB and NiCrSiB powders were produced by Hoganas and had trade marks 6A and 1640-02 respectively. WC-CoCr 86/10/4 is a trademark of Tafa/Paxair.

From technological properties flowability of powders was studied. Hall flowmeter test was performed to determine the flowability of studied composite powders and to compare them with different commercially produced thermal spray powders. Flowability was calculated as time of 50 g of spray powder flowing through 2.5 mm hole in funnel according to standard EVS-EN ISO 4490:2008.

3. RESULTS AND DISCUSSION

Process of production of hard phase materials consisted of three steps:

- Preliminary crushing of the initial plate material (20×10×4) mm under a press-crusher up to particles size less than 5.6 mm;
- Intermediate direct multi-stage milling of the pre-crushed material down to 1.4 mm by the centrifugal-type disintegrator-mill DSL-350;
- Final multi-stage milling with particles size smaller than 50 μm was conducted with laboratory disintegrator system DSL-175.

The parameter of grinding – specific treatment energy E_S was used to estimate grindability. The results of the intermediate direct multi-stage milling of the pre-crushed material parts by the centrifugal-type disintegrator mill DSL-350 are shown in Fig. 2.

Fine powder as the final product, with particle size less than 50 μm, suits for thermal spray. Particle size of initial powder for subsequent milling was up to 1.4 mm. The grindability curves, acquired with laboratory disintegrator system DSL-175 of fine-milled powders are shown in Fig. 3. Due to higher brittleness of Cr_3C_2-Ni based cermet

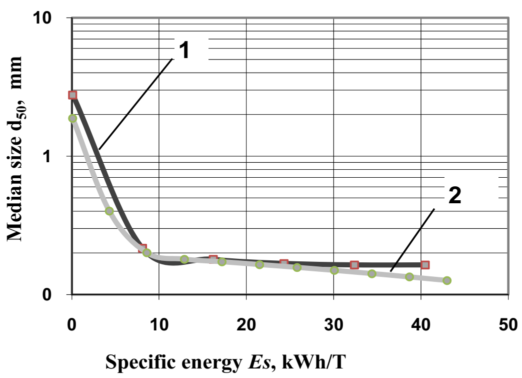


Fig. 2. Dependence of the hardmetal powder particle median size$_{d50}$ on the specific energy of intermediate direct multi-stage milling. Grindability curves of materials: 1 – (Cr_3C_2-Ni); 2 – (WC-Co)

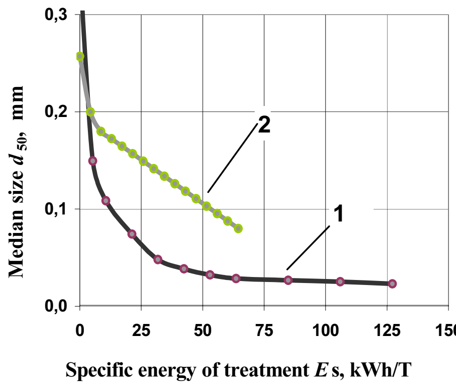


Fig. 3. Dependence of the median particle size$_{d50}$ on the specific energy of final multi-stage milling. Grindability curves of materials: 1 – (Cr_3C_2-Ni); 2 – (WC-Co)

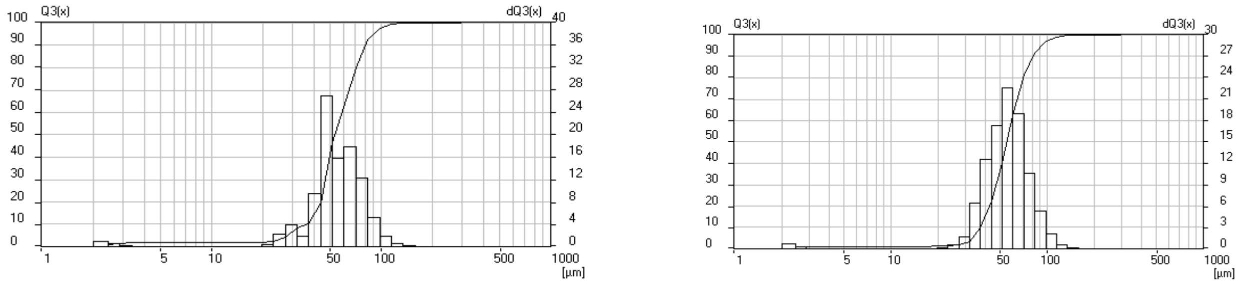
main size reduction takes place during the first 3 – 4 millings.

Particle shape depends on the duration of milling with increase in time. With longer milling time particles sphericity also increases (Fig. 4, a and b). At the same time, the angularity of fine particles, mainly the product of direct fracture, does not always decrease essentially.

Particles of Cr_3C_2-Ni are more spherical and similar to each other than WC-Co. This can be explained by higher brittleness of WC-Co. Fig. 5, a and b, shows the particle size distribution of a ground product.

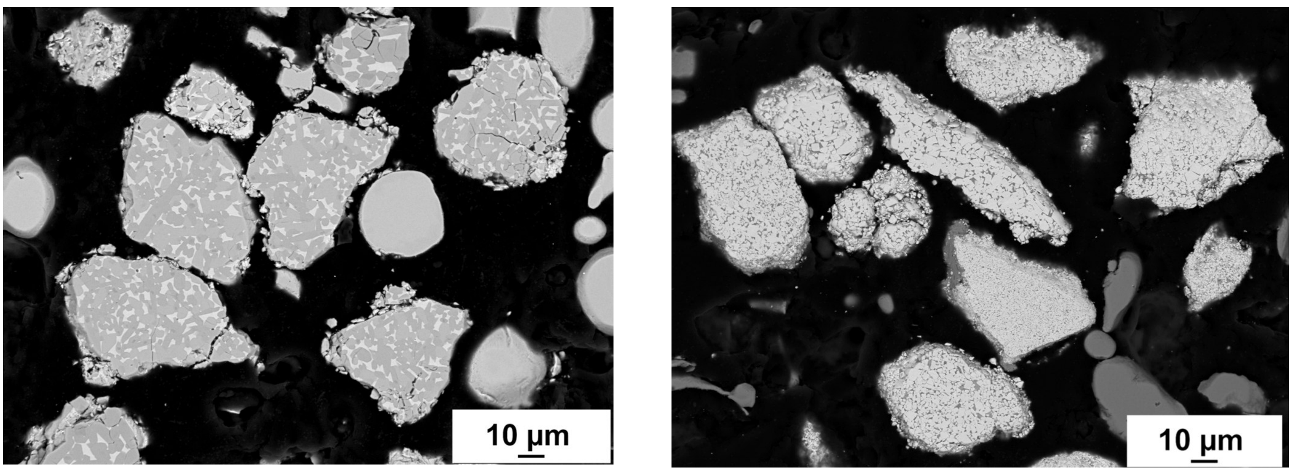
Chemical analysis of the recycled hardmetal powders for thermal spray by EDS showed that about 75 % of powders are carbides (WC-Co; Cr_3C_2-Ni;) (Table 2). Relatively high amount of iron in WC-Co powder has came from milling process (Table 2).

Powder particles in structure are typical of hardmetals: Co and Ni-based metal matrix (Fig. 5, a and b). Carbides grain size is mainly in range of 20 μm – 50 μm.



a b

Fig. 4. Particle size distribution histograms and cumulative distribution functions a – (Cr_3C_2-Ni) , b – (WC-Co)



a b

Fig. 5. Morphology of ground product after final milling by laboratory disintegrator system DSL-17: a – (Cr_3C_2-Ni); b – (WC-Co)

Table 2. Chemical composition and particle size of recycled hardmetal/cermet powders

Type of Powder	Composition, wt %					Screen size, µm
	carbide	Co	Ni	Fe	W	
WC-Co	WC- 75.6	11,5		12,9		+20–50
Cr_3C_2-Ni	Cr_3C_2-78		14	3.1	2.5	+20–50

In Fig. 6 (a and b), the data of angularity studies are shown, where n is number of particles, ε expanded uncertainty of measurement [12] with confidence level 0.95 and s standard deviation of SPQ. Values of SPQ = SV_{mean} and SV_{median} are approximately the same.

The proximity of arithmetic mean and median shows relatively stable behaviour of measurements. The results (Fig. 6) show that angularity of recycled materials acts differently with decrease of particle size: SPQ of WC-Co is stable, while the SPQ of Cr3C2-Ni increases. For WC-Co the standard deviation of SPQ is practically the same in all particle sizes. For Cr_3C_2-Ni powders, the standard deviation of SPQ differs twice when particle size varies. However, the divergence of measurements is not significantly different. The confidence of measurements, which is described by expanded uncertainty ε and is on the order of 5 percent of the SPQ and can be considered at least satisfactory.

Flowability was tested on iron based self-fluxing alloy powders containing 40 vol% of recycled WC-Co and Cr_3C_2-Ni as reinforcement (Table 3).

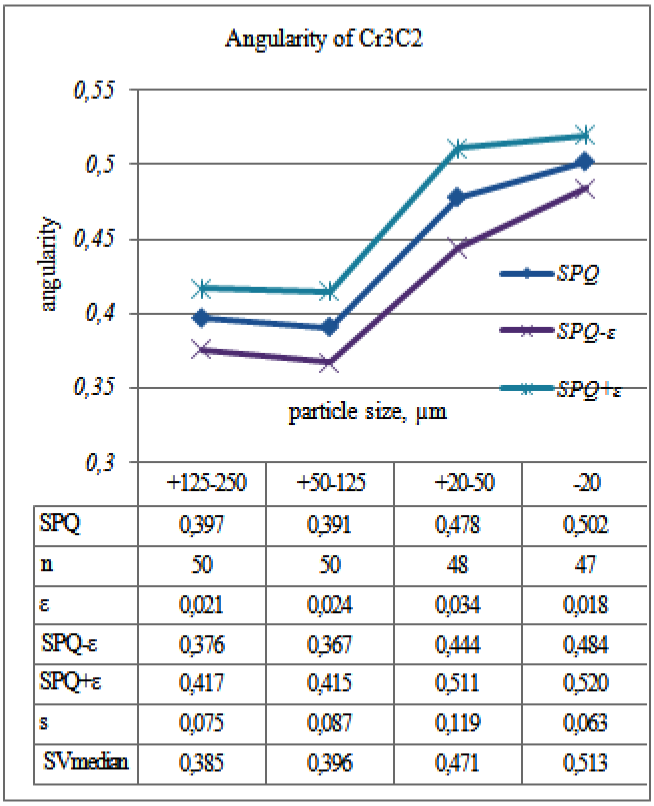
Table 3. Flowability of different spray powders

Composition of powder	Time, s	Flow, g/h
WC-CoCr	22.3	2.3
NiCrSiB	14.8	3.4
FeCrSiB	X	X
FeCrSiB+WC-Co	35.9	1.4
FeCrSiB +Cr_3C_2-Ni	38	1.3

The results show that studied composite powders have significantly lower flowability than commercially produced (NiCrSiB and WC-CoCr) powders while tests with FeCrSiB self fluxing alloy were unsuccessful probably due to high occurrence of high magnetic forces in process.

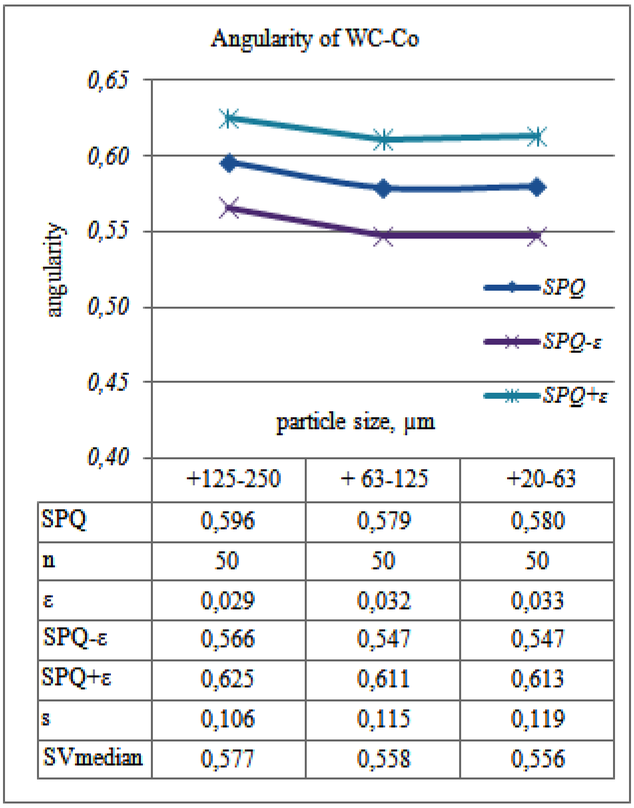
SEM images of composite powders shown in Fig. 7 containing 40 vol% of hardmetal/cermet and 60 vol% of self-fluxing alloys were studied prior to spraying via granulometry and SEM once again to estimate the size and distribution of powders (Fig. 8, a – d). All particle size probability density function charts have one sharp maximum (mode) indicating homogenous distribution of powders size.

Powders based on Ni self-fluxing show slightly sharper maxima and narrower distribution than expected based on data in Table 1 and Table 2. Morphology study of those powders also demonstrated that there is more dust in iron based self-fluxing alloy based powders than Ni based self-fluxing alloy. SEM analysis also showed and



	+125-250	+50-125	+20-50	-20
SPQ	0,397	0,391	0,478	0,502
n	50	50	48	47
ε	0,021	0,024	0,034	0,018
SPQ-ε	0,376	0,367	0,444	0,484
SPQ+ε	0,417	0,415	0,511	0,520
s	0,075	0,087	0,119	0,063
SVmedian	0,385	0,396	0,471	0,513

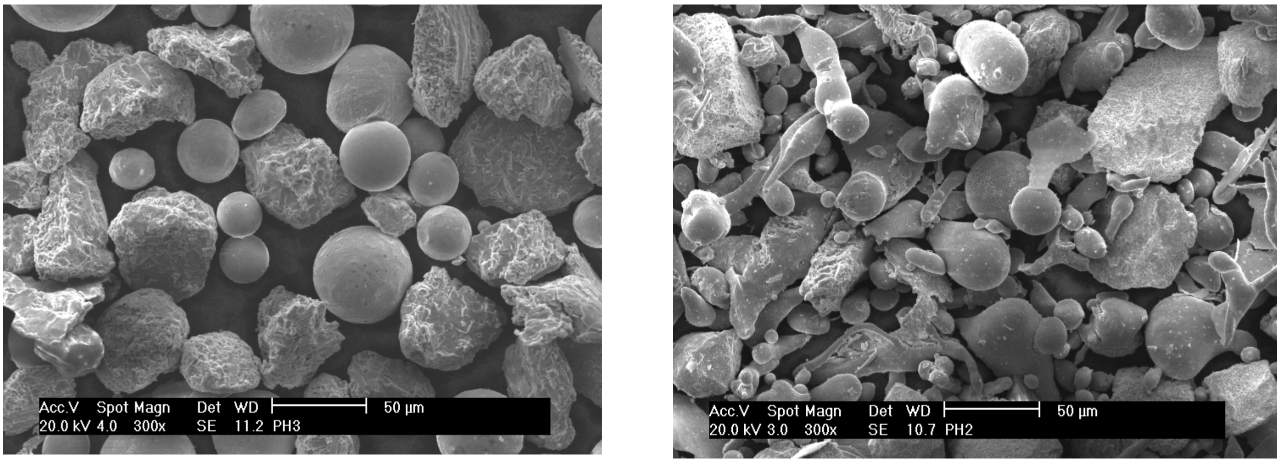
a



	+125-250	+ 63-125	+20-63
SPQ	0,596	0,579	0,580
n	50	50	50
ε	0,029	0,032	0,033
SPQ-ε	0,566	0,547	0,547
SPQ+ε	0,625	0,611	0,613
s	0,106	0,115	0,119
SVmedian	0,577	0,558	0,556

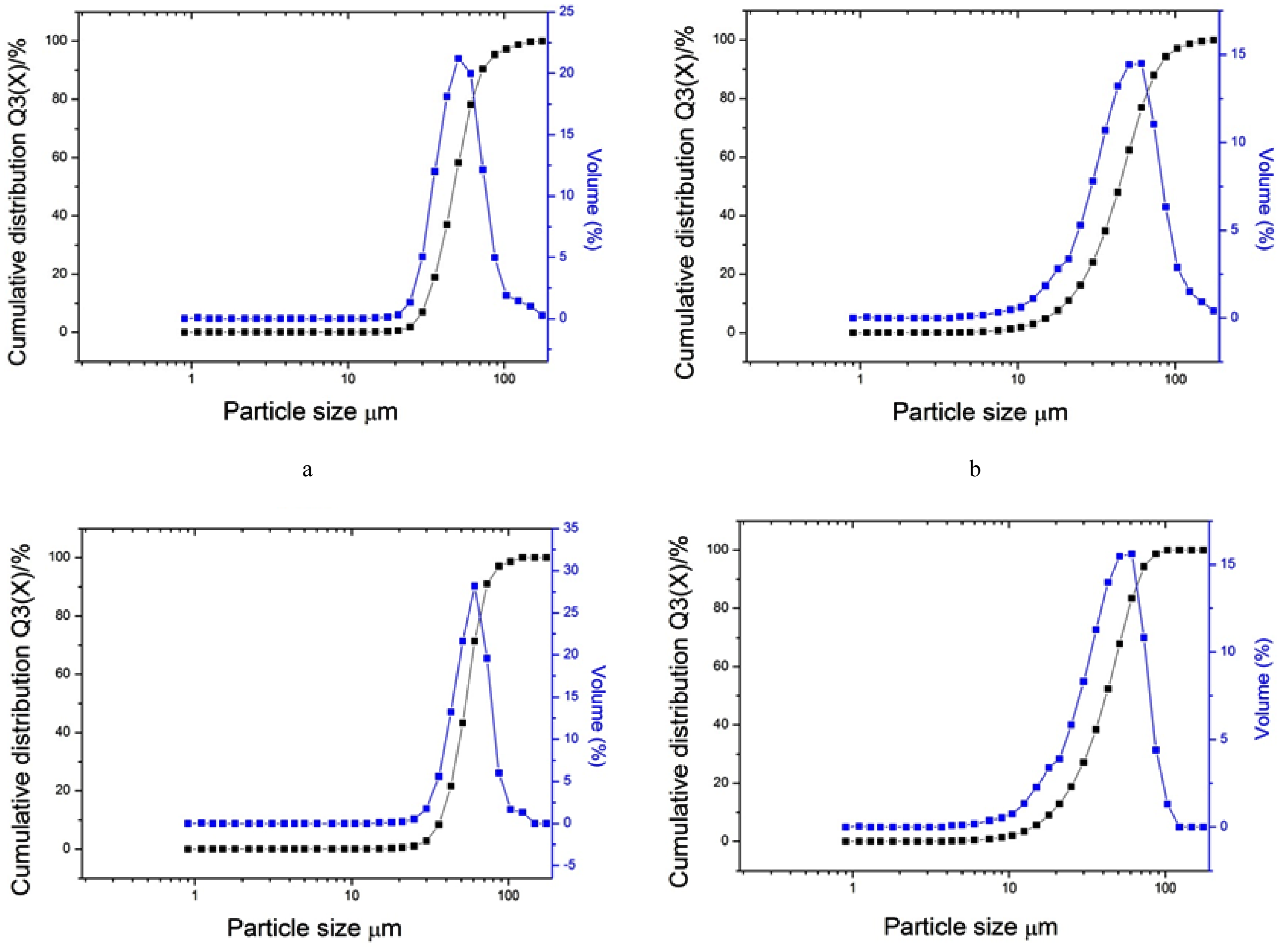
b

Fig. 6. Angularity integrals of milled powders a – (Cr_3C_2-Ni); b – (WC-Co)



a b

Fig. 7. Morphology of spray powders a – (WC-Co)-FeCrSiB, b – (Cr_3C_2-Ni)+NiCr SiB



a b

c d

Fig. 8. Spray powders particle size probability density functions and cumulative distribution functions a – (WC-Co)+NiCrSiB, b– (WC-Co) FeCrSIB, c – (Cr_3C_2-Ni)+NiCrSiB, d – (Cr_3C_2-Ni)+FeCrSiB

confirmed that the angularity of WC-Co particles is higher than the ones of Cr_3C_2-Ni, which can be seen on Fig. 7, a and b.

According to the results of the study composite powders have significantly lower flowability due to more angular shape of hardphase particles than commercially produced (NiCrSiB and WC-CoCr) powders while tests with FeCrSiB self fluxing alloy were unsuccessful probably to due high occurrence of high magnetic forces in process.

4. CONCLUSIONS

1. The grindability of hardmetal/cermet using milling by collision in disintegrator was studied and the influence of particle size reduction on specific energy of treatment was clarified.
2. The technology of producing hardmetal/cermet powders from used (recycled) hardmetal consisted of preliminary crushing and mechanical size reduction of hardmetal parts and final milling of pretreated product by collision in the disintegrator mill. The dependence of grindability (decrease in particle size) on the specific energy of treatment was studied. Hardmetal powders production with a predicted particle size is available.
3. Angularity parameter SPQ of recycled materials acts differently with decrease of particle size: SPQ of WC-Co is stable, while the SPQ of Cr_3C_2-Ni increases. The divergence of measurements is not significantly different and the confidence of measurements, which is on the order of 5 percent of the SPQ, can be considered at least satisfactory.
4. The size probability density functions of composite powders based on self-fluxing alloys reinforced with hardmetal/cermet particles are narrow and showed sharp maximum values that indicate a small variance of particle size.

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