Proc. Estonian Acad. Sci. Engin., 1996, 2, 1, 49–60
https://doi.org/10.3176/eng.1996.1.06

RECYCLING OF HARD METALS

Priit KULU[a], Aleksei TÜMANOK[a], Daniil ARENSBURGER[a],
Toomas PIHL[b], Valdek MIKLI[c], and Helmo KÄERDI[d]

[a] Tallinna Tehnikaülikooli materjalitehnika instituut (Department of Materials Technology, Tallinn Technical University), Ehitajate tee 5, EE-0026 Tallinn, Eesti (Estonia)
[b] Tallinna Tehnikaülikooli aparaadiehituse instituut (Department of Instrument Engineering, Tallinn Technical University), Ehitajate tee 5, EE-0026 Tallinn, Eesti (Estonia)
[c] Tallinna Tehnikaülikooli materjaliuuringute keskus (Centre for Materials Research, Tallinn Technical University), Ehitajate tee 5, EE-0026 Tallinn, Eesti (Estonia)
[d] Tallinna Tehnikaülikooli matemaatikainstituut (Department of Mathematics, Tallinn Technical University), Ehitajate tee 5, EE-0026 Tallinn, Eesti (Estonia)

Received 4 March 1996, accepted 3 April 1996

Abstract. A substantial amount of industrial hard metal wastes, particularly tungsten carbide-based ones, produced in Estonia, need recycling (retreatment or reuse). Hard metal wastes are produced due to inefficient technologies and low production quality. With the needs growing and prices of tool materials increasing, their recycling is becoming urgent. To retreat hard metal wastes, the parts were preliminarily thermo-cyclically refined and mechanically treated by collision. For mechanical refining, the disintegrators and disintergator milling were used.

This study focused on the grindability of hard metal particles with fraction less than 2.5 mm in disintegrator DSL-160 and on the estimation of the granulometry and morphology of the ground product. Based on the hard metal powder produced and traditional Ni-based self-fluxing alloy powders, new composite powders for wear resistant coatings were elaborated. The research also covered the abrasive erosion wear resistance of different coating compositions.

Key words: hard metals, recycling, disintegrators, milling by collision, composite coatings, wear resistance.

1. INTRODUCTION

Recent developments have concentrated on the sustained utilisation of existing resources and recycling of materials. Among reusable materials, metallic wastes (such as industrial scrap, old scrap, domestic wastes) are significant. Hard metal wastes are part of industrial metal scrap. Hard metals used in oil shale mining and the metal working industry produce large quantities of wastes. The reasons are related to inefficient technologies and low production quality. With the prices of hard metal powders rising, their recycling has become an urgent issue.

Different retreatment methods of tungsten-based hard metals are available, e.g., chemical-metallurgical methods of recovery of tungsten from tungsten carbide, mechanical methods of retreatment of hard metal parts [1, 2]. In the framework of the metallurgical methods, zinc processes and gas phase oxidation/restoration were studied. Quality problems are a concern in tungsten powder production and application.

Furthermore, hard metals can be retreated by the mechanical methods, particularly milling them by the collision method. Disintegrator, a technology of materials treatment by collision, facilitates production of hard metal powders with a typical hard-metal structure (tungsten carbide-based frame structure with cobalt binder), preserving their chemical composition. This hard metal powder can be used as an excellent material for wear resistant detonation sprayed coatings and as a hard component of melted composite coatings. At the same time, specific hard metal powders can be used as a component of composite grinding and polishing tools. Tungsten carbide-based hard metals were chosen because of their wide industrial use as well as for their high mechanical properties. Analogous investigations were carried out with more brittle chromium and titanium carbide-based materials.

2. EXPERIMENTAL METHODS

2.1. Hard metal as an initial material

Our study covered wastes of traditional tungsten carbide-based hard metals with cobalt binder content from 6 to 15%. This paper focuses on tungsten carbide hard metal with 15% cobalt content. Parts from tungsten carbide-based hard metal (WC+15Co), such as tool plates, black oil sprayers, reinforcement elements of mining bores, were used.

2.2. Pretreatment of hard metal wastes

As the maximum particle size of treated materials in a laboratory disintegrator is 3–5 mm, hard metal wastes were subjected to preliminary treatment:

1) thermo-cyclical treatment (heating at 400 °C in liquid lead, followed by cooling in liquid nitrogen);

2) mechanical refining.

As a result of thermo-cyclical-mechanical treatment, the fineness of initial material was less than 2.5 mm. Figure 1 shows the particles of pretreated hard metal.

2.3. Grindability study

The pretreated hard metal parts were ground in a laboratory disintegrator DSL-160 at the rotation velocity of rotors 10000/10000 rpm. Table 1 illustrates specific energies of grinding in a multiple process.

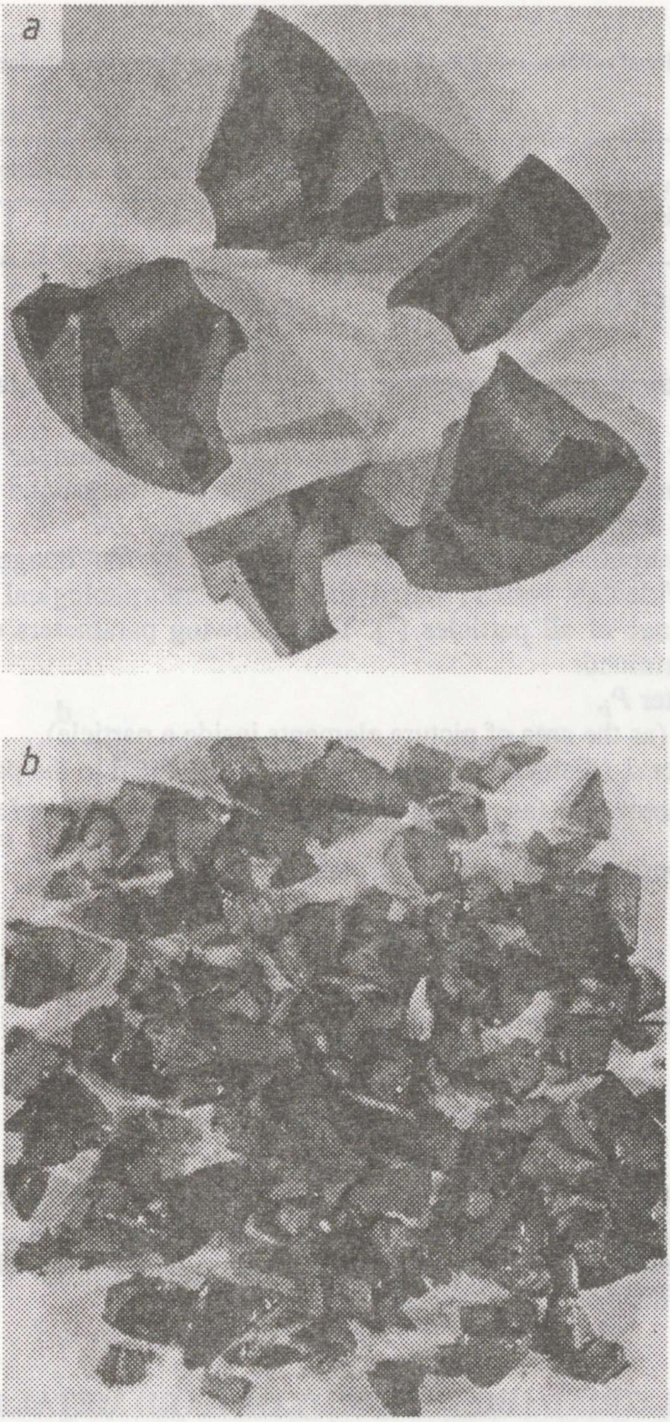


Fig. 1. Initial hard metal parts. Magnification 65×: *a* – thermo-cyclically treated; *b* – mechanically refined.

To achieve the determined granulometry, particles were ground by multiple direct grinding.

Table 1

Velocity of collision and specific energy of processing E_o by the rotation velocity 10000/10000 rpm

Maximum velocity of collision, m/s	Specific energy of processing, kJ/kg, by multiplicity of treatment			
	1×	2×	3×	4×
164	17.2	34.3	51.6	68.8

2.4. Study of granulometry and morphology of hard metal powders

In our study, we used the modified Rosin–Rammler distribution function and the method [3]. The granulometry of the ground product was described in the logarithmic size of particles $\mathrm{Log}_2 X_o/X$.

The morphology of powders was studied by the Image Processing System Videolab ver.2.1, based on the full morphological analysis of binary image of all particles [4]. The following parameters of a particle were determined:

1) perimeter P_i,
2) area A_i (as the area of picture elements inside a particle),
3) diameter d_i (diameter of a circle with an area equal to the particle area),
4) form factor K_{F_i} (as ratio of a particle area A_i to an area of a circle with an equal perimeter of the particle perimeter P_i)

$$K_F = \frac{4\pi \cdot A_i}{P_i^2} \tag{1}$$

medium form factor

$$K_{F_m} = \frac{4\pi}{N} \sum_{i=1}^{N} \frac{A_i}{P_i^2}. \tag{2}$$

Next, the quantity of particles, their total and relative area, total perimeter, and the corresponding average parameters (average area, average perimeter, and average size) will be calculated and shown on the size/form distribution diagrams.

3. GRINDABILITY STUDY OF HARD METAL BY DISINTEGRATOR

Hard metal particles with particle size less than 2.5 mm (which depended on disintegrator construction) were ground by a disintegrator device DSL-160 by direct milling at the rotation velocities of rotors 10000/10000 rpm. The hard metal powder with the determined fraction was obtained by sieving the ground product.

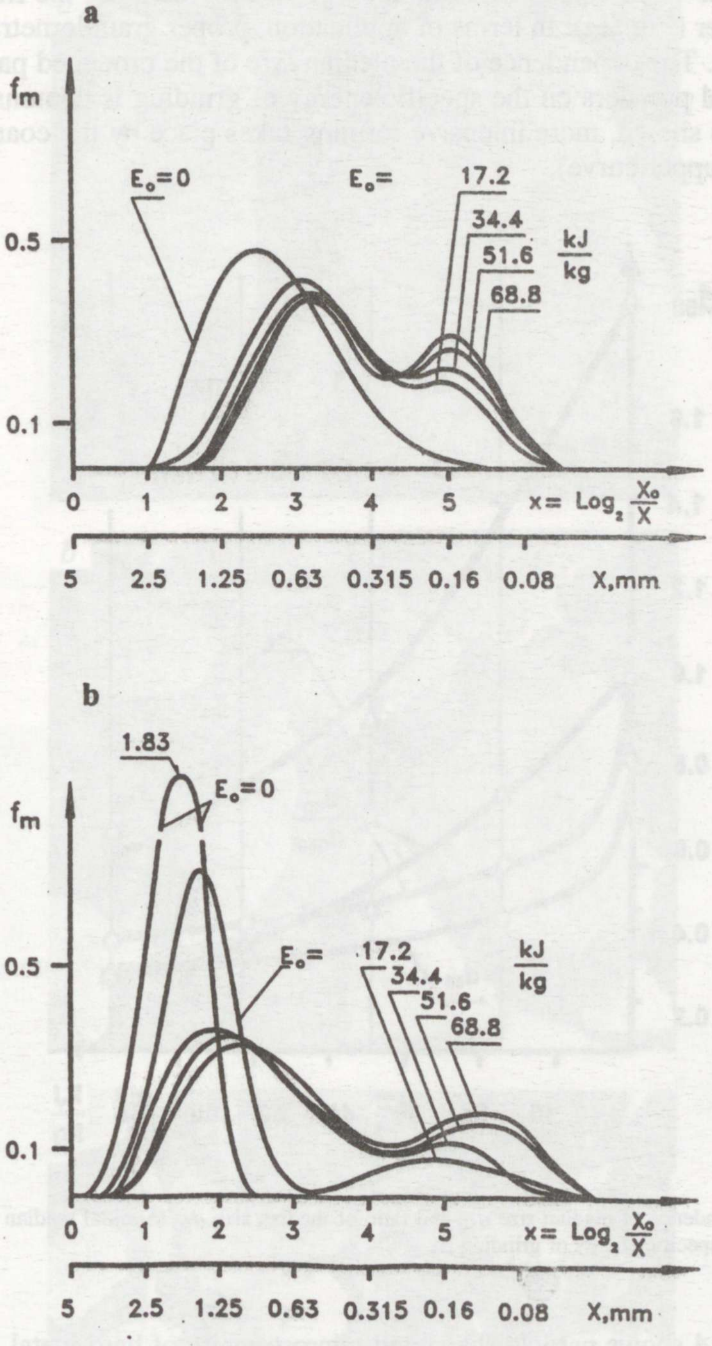


Fig. 2. Dependence of granulometry of hard metal powder on specific energy of grinding E_0: initial material –1.25+0.315 mm (*a*) and –2.5+1.25 mm (*b*).

Figure 2 illustrates the results of the grindability study by direct multi-stage (1, 2, 3, and 4 times) grinding. As shown in Fig. 2*b*, the influence of specific energy of grinding on the granulometry (particle size) is noticeable by the initial material –2.5+1.25 mm. The multiple grinding of hard metal −1.25+0.315 mm did not significantly increase the fineness of the powder (Fig. 2*a*). In terms of application, proper granulometry is most important. The dependence of the median size of the produced particles of hard metal powders on the specific energy of grinding is demonstrated in Fig. 3. As shown, more intensive refining takes place by the coarse initial fraction (upper curve).

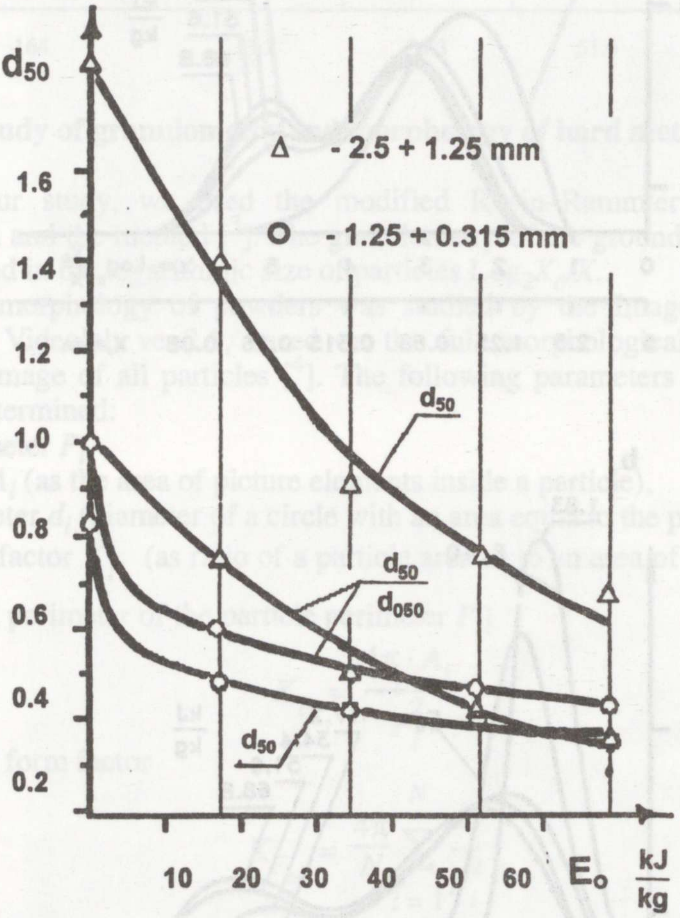
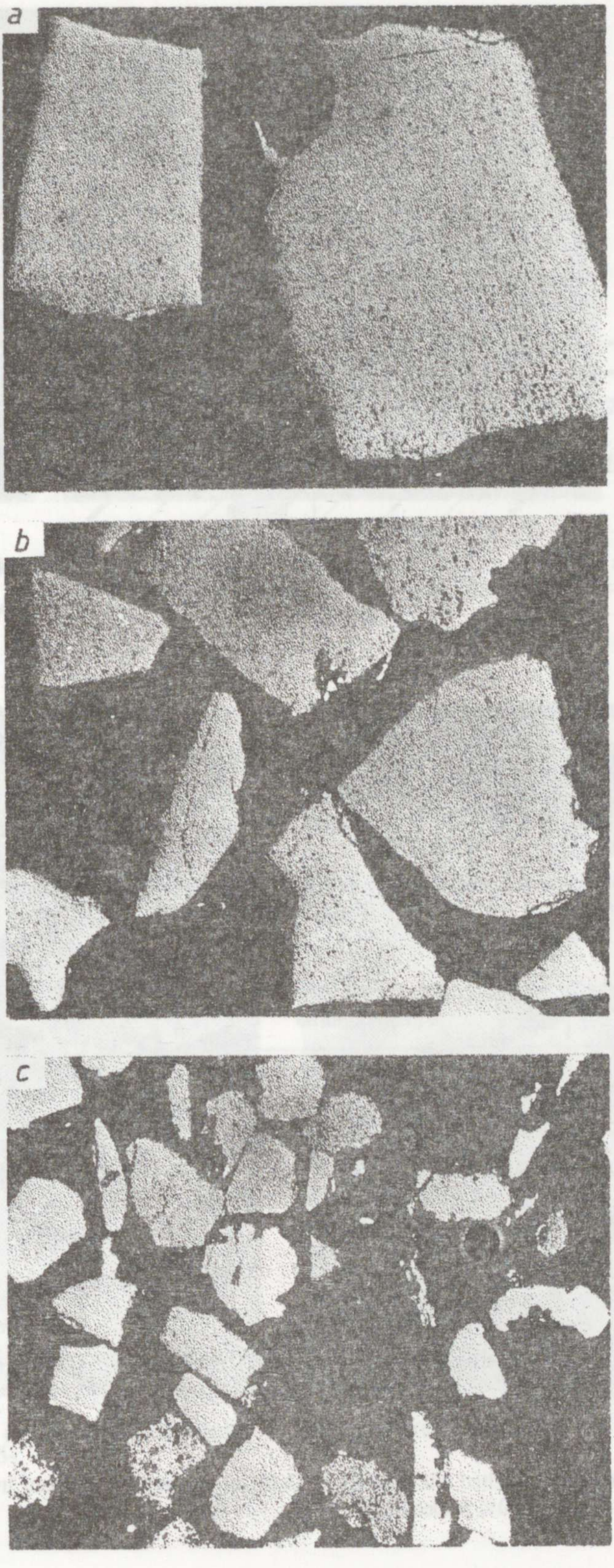


Fig. 3. Dependence of median size d_{50} and ratio of median size d_{50} to initial median size d_{o50} of particles on specific energy of grinding E_o.

Figure 4 shows particle shape and microstructure of hard metal particles. The particles are mainly isometric in form, and the microstructure of particles has a typical hard metal structure, based on tungsten carbide (Fig. 5*b*).

Figure 6 shows the size and form distribution of hard metal powder particles ground at the velocity of rotors 10000/10000 rpm four times. Table 2 illustrates the main characteristics of the produced powders. As can be seen, the main fraction of ground powder is 30–70 µm (about 70%) with an average particle area of 2200–2800 µm^2 and form factor of particles between 0.7–0.9.


a
b
c

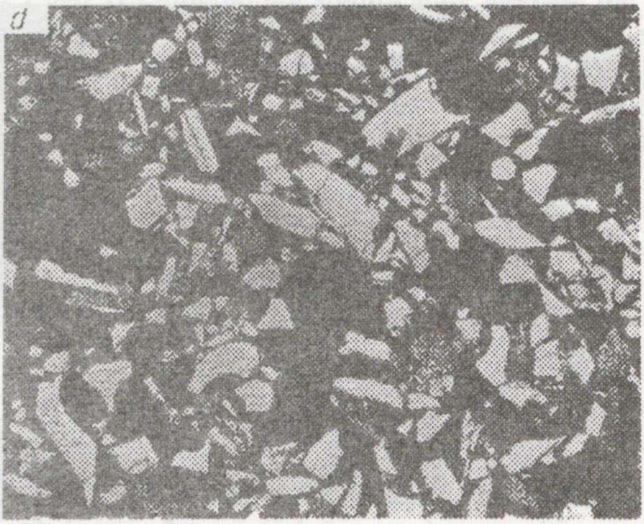


Fig. 4. Particles shape and microstructure of ground hard metal powders. Magnification 65× with granulometry: –1.25+0.315 mm (*a*), –0.63+0.315 mm (*b*), –0.315+0.16 mm (*c*), –0.16 mm (*d*).

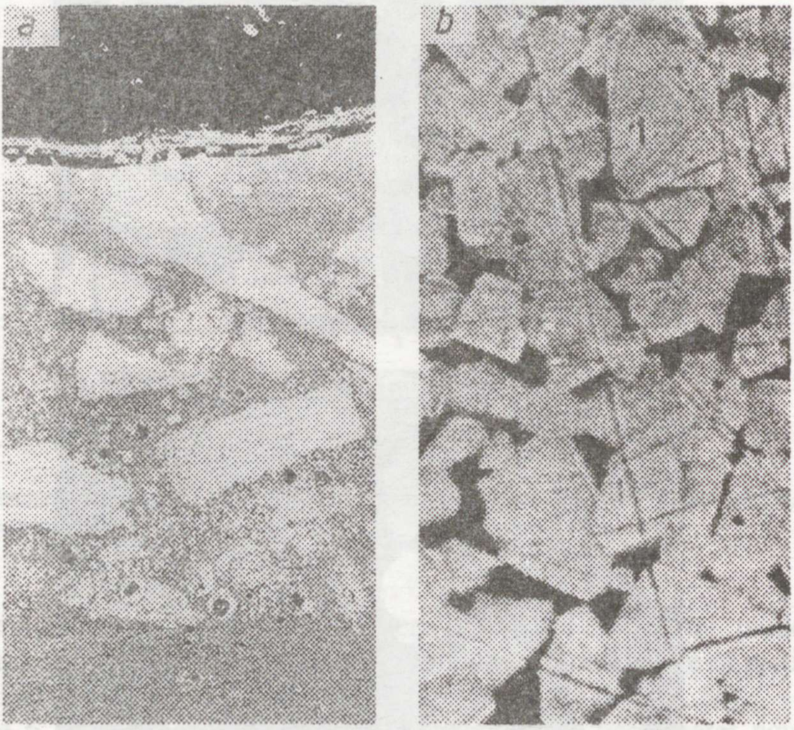


Fig. 5. Microstructure of melted NiCrSiB-25 (WC-15Co) coating (*a*) and hard metal particle (*b*). Magnification 100 and 5000×, respectively.

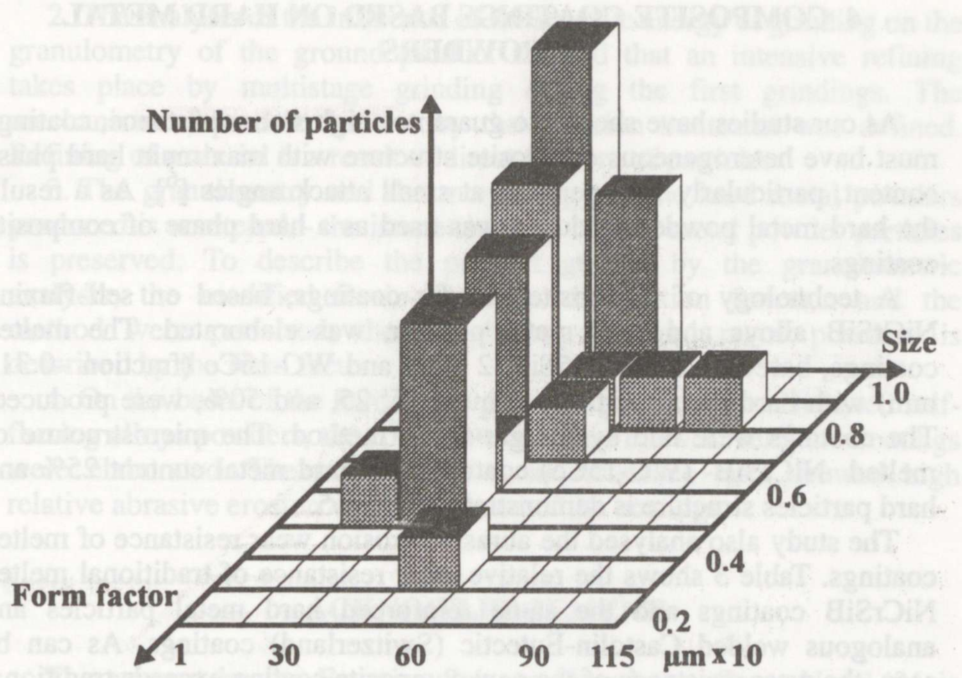


Fig. 6. Size and form distribution of powder −1.25+0.315 mm ground 4× at the velocity of rotation of rotors 10000/10000 rpm.

Table 2

Main characteristics of ground hard metal powders (ground at the velocity of rotors 10000 rpm)

Type of material	Granulometry			Form factor	
	Main fraction, μm and %	Diameter d_m, μm	Area A_m, μm^2	Main fraction	Medium
−0.315 mm, ground 1×	30–70 70	60	2800	0.85	0.72
−1.25+0.315 mm, ground 4×	20–70 73	53	2200	0.9	0.75

On the basis of the study of the fracture mechanism, we can conclude that milling of hard metal particles takes place as a result of direct fracture of particles caused by the intensive stress waves produced by high velocity collisions [5].

4. COMPOSITE COATINGS BASED ON HARD METAL POWDERS

As our studies have shown, to guarantee high wear resistance, coatings must have heterogeneous composite structure with maximum hard phase content, particularly for operating at small attack angles [6]. As a result, the hard metal powder produced was used as a hard phase of composite coatings.

A technology of composite powder coatings, based on self-fluxing NiCrSiB alloys and hard metal powder, was elaborated. The melted coatings, based on Ni80Cr15Si3B2 alloy and WC-15Co (fraction –0.315 mm) with hard metal particles content 15, 25, and 50%, were produced. The coatings were laid by the gas-flame method. The microstructure of melted NiCrSiB- (WC-15Co) coating with hard metal content 25% and hard particles structure is demonstrated in Fig. 5.

The study also analysed the abrasive erosion wear resistance of melted coatings. Table 3 shows the relative wear resistance of traditional melted NiCrSiB coatings and the same reinforced hard metal particles and analogous welded Castolin-Eutectic (Switzerland) coatings. As can be seen, the wear resistance of the new composite coating exceeds traditional NiCrSiB coatings about 1.5 times and is similar to the coatings from the industrially produced welding electrodes.

Table 3

Relative abrasive erosion wear resistance of melted NiCrSiB- (WC-15Co) coatings
(abrasive quartz sand 0.1–0.3 mm, $v = 80$ m/s)

Composition of coatings	Hardness on coating HV	Wear resistance E_v	
		$\alpha = 30°$	$\alpha = 90°$
NiCrSiB	480	1.3	0.8
NiCrSiB-15(WC-Co)	480/1220*	1.5	0.7
NiCrSiB-25(WC-Co)	480/1220*	1.9	0.6
NiCrSiB-50(WC-Co)	480/1220*	2.0	0.6
8811 (Castolin)	560/1460**	2.1	0.7

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* hardness of hard metal,

** microhardness of hard metal particles.

5. CONCLUSIONS

1. Our studies demonstrate the possibility of recycling (retreatment and reuse) of hard metal wastes by the mechanical disintegrator milling method.

2. The analysis of the influence of the specific energy of grinding on the granulometry of the ground product showed that an intensive refining takes place by multistage grinding during the first grindings. The mechanism of particle fracture by the collision treatment was defined. Refining of material is a result of direct fracture of particles.

3. The granulometry and the morphology of the hard metal powders produced is unaltered – the isometric form of hard metal powder particles is preserved. To describe the product ground by the granulometric analysis, the modified Rosin–Rammler distribution function and the method were preferred; the morphology of hard metal powders is described by the form factor.

4. On the basis of the hard metal powders produced and Ni-based self-fluxing alloys powders, the composite powders for wear resistant coatings were elaborated. The comparative wear resistance tests showed high relative abrasive erosion wear resistance of the coatings.

ACKNOWLEDGEMENT

The support by the Estonian Science Foundation Grant No. 1426 is greatly appreciated.

NOMENCLATURE

α – attack angle by abrasive erosion wear, deg

$A(A_m, A_i)$ – area, µm^2

$d(d_m, d_i, d_{50}, d_{o50})$ – size of a particle (diameter), µm

E_o – specific energy of processing, kJ/kg

E_v – relative volume wear resistance

F_m – distribution function (the modified Rosin–Rammler distribution function is used)

$K_F(K_{F_m}, K_{F_i})$ – form factor

$P(P_m, P_i)$ – average perimeter

rpm – rounds per minute, min^{-1}

v – velocity of abrasive particles, m/s

X – natural size of a particle

X_o – upper limit of possible size of a particle

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KÕVASULAMITE KORDUVKASUTUS

Priit KULU, Aleksei TÜMANOK, Daniil ARENSBURGER,
Toomas PIHL, Valdek MIKLI, Helmo KÄERDI

Vajadus kõvasulami, eelkõige volframkarbiidse kõvasulami korduvkasutuseks on tingitud märkimisväärse koguse kõvasulamjäätmete olemasolust Eestis. Jäätmete teke on seotud kasutatavate tootmistehnoloogiate suhteliselt madala taseme ja sellega kaasnevate kvaliteediprobleemidega. Pidades silmas kasvavaid vajadusi tööriistamaterjalide järele ja nende hinnatõusu, on kõvasulami korduvkasutus väga aktuaalne.

Kõvasulami ümbertöötlemisel on kasutatud eelnevat termotsüklilist ja mehaanilist peenendamist ning järgnevat löökjahvatust desintegraatoris. On uuritud eelnevalt peenendatud kõvasulami (osakeste suurus kuni 2,5 mm) jahvatatavust desintegraatorseadmes DSL-160 ning jahvatusprodukti granulomeetriat ja morfoloogiat. Saadud kõvasulampulbrite kasutusvõimalusi on selgitatud iseräbustuva nikkelsulami ja volframkarbiidse kõvasulami abil pulberkomposiitpinnetes. Võrdlevalt on teimitud pulberkomposiitpinnete ja traditsiooniliste kulumiskindlate pulberpinnete vastupidavust.