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Novel Synthesized and Milled Carbide-based Composite Powders for HVOF Spray

HEIKKI SARJAS

TUT PRESS

TALLINN UNIVERSITY OF TECHNOLOGY
Faculty of Mechanical Engineering
Department of Materials Engineering

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Supervisor: Priit Kulu, Faculty of Mechanical Engineering, Department of Materials Engineering, Tallinn University of Technology. Prof. Emer.

Opponents: Alexander Ryabchikov, Estonian University of Life Sciences, Assoc. Prof.
Michal Besterci, Institute of Materials Research of Slovak Academy of Sciences, Prof. Emer.

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Lecture hall: U05 216
Tallinn University of Technology
Ehitajate tee 5, Tallinn

Declaration:
Hereby I declare that this doctoral thesis, my original investigation and achievement submitted for the doctoral degree at Tallinn University of Technology, has not been submitted for any academic degree.

/Heikki Sarjas/

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HEIKKI SARJAS

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LIST OF PUBLICATIONS

The present dissertation is based on following papers which are referred in the text by Roman numerals as [Paper I–Paper IV].

Paper I — Sarjas, H., Kulu, P., Juhani, K., Viljus, M, Matikainen, V., Vuoristo, P. (2016) Wear resistance of HVOF sprayed coatings from mechanically activated thermal synthesised Cr_3C_2-Ni spray powder. *Proc. Estonian Acad. Sci.*, 65(2), 101–106.
DOI: 10.3176/proc.2016.2.10

Paper II — Goljandin, D., Sarjas, H., Kulu, P., Käerdi, H., Mikli, V. (2012). Metal-matrix hardmetal/cermet reinforced composite powders for thermal spray. *Material Science (Medžiagotyra)* 18(1), 84–89.
DOI: http://dx.doi.org/10.5755/j01.ms.18.1.1348

Paper III — Sarjas, H., Goljandin, D., Kulu, P., Mikli, V., Surženkov, A., Vuoristo, P. (2012). Wear resistant thermal sprayed composite coatings based on iron self-fluxing alloy and recycled cermet powders. *Materials Science (Medžiagotyra)*, 18(1), 34 – 39.
DOI: http://dx.doi.org/10.5755/j01.ms.18.1.1338.

Paper IV — Sarjas, H., Kulu P., Juhani, K., Vuoristo, P. (2014) Novel WC-Co spray powders and HVOF sprayed coatings on their bases. *Proceedings of the 28th International Conference on Surface Modification Technologies* XXVIII (Ed-s T.S Sudarsan, P.Vuoristo, H. Koivuluoto), 35–42.

Author's contribution

Paper I — Characterization of Cr_3C_2-20Ni powders and HVOF sprayed coatings properties produced by mechanical thermal synthesis.

Paper II — Performance of experimental part – production of mechanical disintegrator milled WC-Co and Cr_3C_2-Ni powders properties.

Paper III — Experiments with HVOF spray of coatings. Study and evaluation of Fe- and Ni- matrix based WC-Co and Cr_3C_2-Ni mechanical disintegrator milled powders hard phase composite HVOF sprayed coatings properties.
All above mentioned papers were prepared and written by the author of thesis.

Paper IV — Characterization of WC-Co powders and HVOF sprayed coatings properties produced by mechanical thermal synthesis.

INTRODUCTION

Wear is the loss of material from a component due to mechanical interaction with another object. Capital equipment and its cost are a constant consideration. Whether expenditure is for replacement, efficiency improvements or compliance with new Health & Safety or environmental legislation (HardChrome), best practice demands must be designed in from the onset for operational reliability. Therefore, it is important to plan equipment so that the need for unproductive repairs and the wider effects of material discharge and contamination are eliminated [Kingfisher Industries, 2015].

Wear damage from abrasion, erosion, corrosion-erosion, and impact wear affects businesses with machine downtime, lost productivity, and maintenance costs. Wear solutions are not such that one size fits all. Every company, every industry, every application, every machine is different [Kennametal, 2015]. In addition, wear resistant materials (ceramics, hardmetals or alloyed steels) are expensive compared to ordinary mass production used steels (for example, S235). Thermal spray contributes to the functionality of hardmetals for large parts, which cannot be produced for technical or economical reasons [Berger, 2014].

As a new area of interest, mainly WC-Co or Cr_2C_3 based powders are used for wear resistant applications. Co and Ni are mostly employed as a binder material in hardmetal/cermet compositions. The properties of thermally sprayed coatings depend heavily on feedstock materials, their characteristics and process(es) used for spraying. High velocity oxy-fuel (HVOF) spray has proved to be the best technique for spraying wear resistant coatings due to high velocity and low spraying temperature, which ensure high density and low porosity of coatings, characterized with good adhesion with the substrate material.

Most commonly, hardmetal thermal spray powders for HVOF are produced at agglomeration [Zimmermann, 2009]. However, in these powders, high temperature and nonequilibrium phases have been observed with defects from spray drying like porosity. Moreover, agglomerated powders tend to be quite expensive. As feedstock material represents a considerable amount of the running costs of the thermal spray process [Sartwell, 2006], it is definitely topical from the economic point of view. Sintered or fused thermal spray powders are blocky and irregular in terms of morphology and they tend to have brittle W_2C or ŋ-phases in feedstock materials.

Cost saving and environmental protection by law has been a driving force in the last decades for more frequent hardmetal recycling. Equally important is the fact that the prices of natural resources are growing. Milling recycled hardmetals by collision has proven to be more energy efficient than the traditional methods [Tamm, 1996]. Therefore, utilizing recycled hardmetal powder with a low cost iron alloy based binder could be an interesting alternative.

Based on these shortcomings, the main aim of this thesis is to offer lower cost feedstock powders using alternative methods for HVOF spray coatings, which have competitive wear performance against the coatings produced from analogous commercial powders.

In this study two alternative methods: a) mechanically activated thermal synthesis and b) the mechanical method of disintegrator milling of hardmetals and cermets to produce spray powders has been used. In terms of wear properties, main attention was paid to abrasive wear resistance.

Results of the doctoral thesis have been published in the form of scientific papers: 8 – in international journals and 2 – in international conference proceedings. Results of the study have been presented at international conferences and at different research seminars.

ABBREVIATIONS AND SYMBOLS

AEW – Abrasive Erosive Wear
APS – Atmospheric Plasma Spray
ARWW – Abrasive Rubber Wheel Wear
ASTM – American Standards for Materials Testing
AWS – American Welding Society
DGS – Detonation Gun Spray
EDS – Energy-dispersive X-ray spectroscopy
EMI – Electro-Magnetic Impulse
HVOFS – High Velocity Oxy-Fuel Spray
MAS – Mechanically Activated Synthesis
MATS – Mechanical Activated Thermal Synthesis
MDM – Mechanical Disintegrator Milling
OEM – Original Equipment Manufacturer
PTAW – Plasma Transferred Arc Welding
PVA – Polyvinyl Alcohol
RFI – Radio Frequency Interference
RTS – Reactive Thermal Spray
SEM – Scanning Electron Microscopy
TSS – Thermal Spray Society
vol% – volume percent
VPS – Vacuum Plasma Spray
wt% – weight percent
XRD – X-ray diffraction

SYMBOLS

E – modulus of elasticity, GPa
ε_v – relative volumetric wear resistance
F – normal load, N
FR – Failed Area Ratio (%)
H – nanohardness of coating, GPa
HU – universal hardness
HV1 – low force Vickers hardness (at 9,8 N)
HV30 – Vickers macro hardness (at 294 N)
Iv – volumetric wear rate, mm^3/kg
k – wear coefficient, $mm^3/N*m$
Q – quantity of the abrasive, kg

1 CARBIDE BASED SPRAY POWDERS AND WEAR RESISTANT HVOF SPRAYED COATINGS ON THEIR BASES

1.1 Conventional powder production methods for wear resistant coating applications

In general, thermal spray powder production methods have evolved from powder metallurgy processes [Gan, 2015]. In the wear resistant applications of the HVOF spray, hardmetals/cermets (mainly different variation of WC-Co or Cr_3C_2-Ni powders) are most common. The properties of powders depend on the production method and can vary considerably. Selected powder production methods are shown in Fig. 1.1. Important powder characteristics for thermal spray that need to be controlled are: a) particle size, b) particle size distribution, c) particle shape, d) particle density [Davis, 2004].

Commonly, different mechanical methods, such as crushing, milling, blending and several other complex processes, like sintering and crushing, agglomerating and sintering, are used to produce brittle carbide powders.

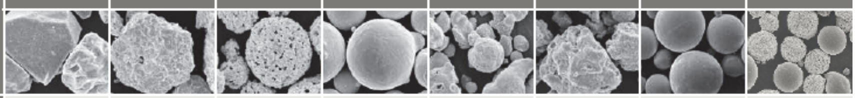
POWDER TYPE	Fused and crushed	Sintered and crushed	Agglomerated and sintered	Gas atomized	Water atomized	Dense coated	Spheroidized	Blended
								
PROCESS	Fusing in arc furnaces, followed by cooling and crushing	Sintering of raw materials, crushing	Spray drying of a suspension consisting of fine powders and organic binder and subsequent sintering	Atomizing molten metal or alloy with high pressure gas (Ar, N_2) stream into a chamber	Atomizing with water into a chamber and subsequent drying	Reduction of a metal salt solution	Feeding of agglomerates using a plasma flame to produce spherical shaped particles	Mixing of 2 or more powders
CHARACTE-RISTICS	Blocky, irregular, dense	Blocky, irregular, relatively dense	Spherical, porous, constituents homogenously distributed	Spherical, dense, high purity, low oxygen content	Irregular, dense, increased oxygen content compared to gas atomized	Blocky or irregular composite	Spherical, porous or hollow, partly open (shells)	Different morphologies, segregation possible
EXAMPLES	Al_2O_3; Cr_2O_3; ZrO_2-Y_2O_3	WC-Co; WC-CoCr	WC-Co Cr; Cr_3C_2-NiCr; ZrO_2-Y_2O_3	MCrAlY; Ni-, Co-base alloys; NiAl	NiCr; NiAl	Ni-Graphite	ZrO_2-Y_2O_3	NiSF + WC-Co; Mo + NiSF; Cr_3C_2-NiCr

Figure 1.1 Methods of thermal spray powder production [H.C.Starck, 2015]

The blended raw materials are pressed into bricks or cylinders, followed by sintering at 1100 to 1400 °C and subsequent crushing. The crushing stage is performed using a steel jaw or hammer crushers. A problem faced in this process is powder contamination with abraded iron dust from the crushers. The iron dust can settle down on the surfaces of the powder particles, non- alloyed in the metallic binder phase. The result obtained from sintered and crushed powders may be a coating that has lower resistance to corrosion than the coatings from agglomerated and sintered powders [TWI Ltd., 2015].

In the agglomeration and sintering process, the homogenized starting materials are dispersed in water along with a suitable polymer (PVA) binder. This dispersion is atomized into a powder by a technique known as spray drying. In this technique, a nozzle or a centrifugal atomizer is used to produce droplets of the dispersion inside a heated chamber. The water is rapidly removed and solid particles or pellets are formed, held together by the organic binder. These powder particles or pellets are collected as they fall to the bottom of the chamber.

Sintering is conducted similar to the 'sintering and crushing' process but with an initial lower temperature step to remove the organic binder prior to sintering. Spray dried powders may or may not be subsequently crushed. If crushing is required, this can be done with ease because the sintered material is more porous and loosely held together. Use of heavy crushing equipment is therefore unnecessary, and iron contamination is avoided. In many cases, the as-spray dried powder has a suitable powder particle size after sintering and needs no crushing. These powders can have the advantage of being spherical in shape.

1.1.1 Mechanically activated synthesis in powder production

Many techniques are used for powder milling. Milling systems come in a large variety; they are capable of high energy milling [Benjamin, 1970; Suryanarayana, 2001]. Ball mill is a system the main advantages of which are its simplicity and relatively inexpensive equipment [Wank, 2003; Schubert, 1995]. It is mainly used to prepare nanocrystalline materials with heavy cyclic deformation of the powders. There are two types of milling processes: dry and wet. The purpose of adding liquid is to avoid sticking powder particles to equipment and more importantly, it increases the milling speed since the liquid penetrates to particle pores and eases the cracking of the particles [El-Shall, 1984]. Therefore, the efficiency of wet milling is higher.

The high-energy ball milled nanocrystalline powders are heavily workhardened with a high density of lattice defects and an excess stored enthalpy [El-Eskandarany, 2000]. Particle size of the high-energy milled powders is at nanoscale (< 100 nm) with an internal crystallite size approximately a few nanometers [Koch, 1993]. After mechanical activation, the powder mixture has higher free energy and chemical reactivity than the powder mixture without activation. Recent studies have shown that during high-energy milling, nanocrystalline WC-Co [Joost, 2008], Cr_2C_3-Ni [Juhani, 2009] and TiC [Koch, 1997] powders can be produced from respective metals and carbon powders. As there is negative free enthalphy between metals and carbon powders, elemental respective feedstock powders are required for high-energy milling [Barin, 1977]. First, carbon atoms segregate the crystal interfaces of a metal, then diffuse and finally react with the metal to form carbide completely.

Reactive milling alone cannot be applied for carbide formation due to too low negative energy at room temperature. However, reaction temperature of carbide formation (metal and carbon) is reduced significantly by high-energy ball milling [Joost, 2010a; Juhani, 2010]. In this technique, called mechanically activated synthesis (MAS), high-energy milling of the metal-carbon mixture as the first stage is combined with subsequent heating to complete the synthesis reaction [Ban, 2001]. (See Fig. 1.2 as an example).

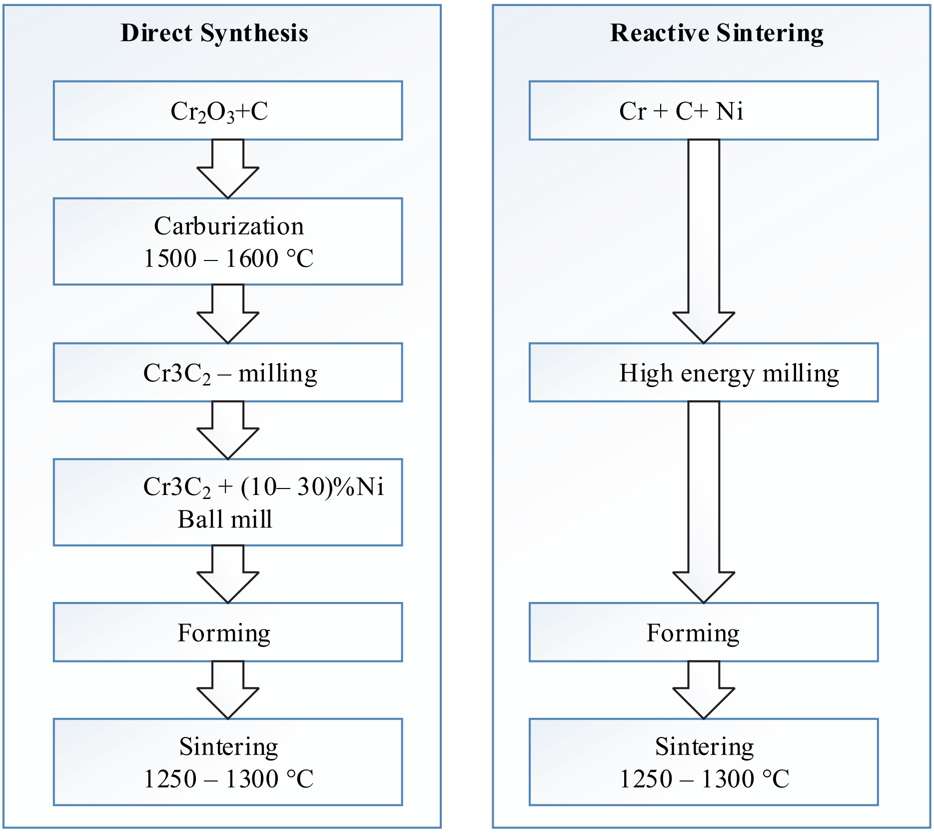


Figure 1.2 Production of chromium cermets based carbides [Pirso, 2006]

The advantages of the procedure are: shorter milling times than it is required for the *in-situ* formation in high-energy reaction milling and, on the other hand, much lower synthesis temperatures than those without the activation [Gao, 1997]. Cermets are typically produced by a liquid phase sintering where carbide grain growth occurs due to Ostwald ripening. Smaller grains have higher solubility in the binder and therefore larger grains grow at the expense of the smaller ones [Viljus, 2012] . However, recent studies have revealed that nearly 90% of densification at sintering takes place at solid state before going to liquid form [Wang, 2008]. In contrast to coarse grained powders, nanosized crystalline powders have increased diffusivity [Arato, 1998]. Therefore, the sintering temperature of nanosized high-energy milled powders is relatively lower than that produced by conventional methods.

Mechanical properties and wear resistance of cermets produced by MAS depend on the chemical composition and microstructure. Hardness and wear resistance are higher when the soft binder content decreases. Mechanical and tribological properties depend on the graphite content in the initial powder [Juhani, 2008a; Joost, 2010b] and are chosen based on the carbide content (W, Cr, Ti) rather than on the binder. Hardness of cermets is significantly reduced if free carbon is found in the structure. Wear resistance of cermets produced by MAS is highest at the stoichiometric point and is reduced drastically if free carbon is found in the structure [Juhani, 2008b].

1.1.2 Disintegrator technology in powder production

Disintegrator technology for grinding soft materials has been known for over a century. In Estonia, it was first introduced [Hint, 1962] for producing silicate bricks. Grinding with collision for brittle materials was first used by Rumpf, [Rumpf, 1965] and Primer [Primer, 1965]. Today, grinding is applied effectively to recycle different materials. The function of first grinding machines was to destruct materials into smaller pieces. However, today homogeneity of the final product is required. Therefore, the grinders have to perform a mixer's function as well [Tamm, 1996]. In some milling systems, particles are broken by colliding against grinding elements by the rotating rotor. These machines are called disintegrators. Various multifunctional DS disintegrators have been developed at Tallinn University of Technology [Kulu, 1996, Goljandin, 1999], depending on the following materials: metal chips [Tymanok, 1999a], diamonds, gold content sand, electronics waste and polymers [Kers, 2008] to be treated on different modes (direct, separative, and selective grinding). These disintegrators can produce fine materials with narrow granulometry. The capacity of materials to be treated varies from a few kg/h to 10 tons/h [Tymanok, 1997].

In disintegrators, grinding is controlled by the velocity of the particles and takes place by collision. The value of the stresses caused by a collision exceeds the strength of the material about ten times [Tamm, 1996, Tymanok, 1999] (Table 1.1). Therefore, the particle or material break-up takes place multiple times in a short period until reaching plastic deformation and heat. This process activates materials mechanically and chemically [Tamm, 1996]. Activation of iron powder at distintegrator milling and its use in the following technological processes was studied [Kulu, 1996]. Particle shape of disintegrator milled powders depends on the material – it is angular for brittle materials [Kulu, 1996]. Fig. 1.3 shows typical disintegrator milled hardmetal powder particle shape [Kulu, 2003].

Table 1.1 Comparison of the traditional method to the collision method [Tamm, 1996]

Parameter, unit	Traditional method	Collision
Velocity of loading, ms^{-1}	0,1–10	30–200
Duration of loading, s	10^{-2}–10^{-1}	10^{-6}–10^{-5}
Duration in active zone, s	1–10	10^{-2}
Ratio of stresses to the strength, σ/[σ]	≥1	>10
Character of stresses	Compressive + shift	Tensile + shift
Shape of the particle	Elongated or lamellar	Isometric

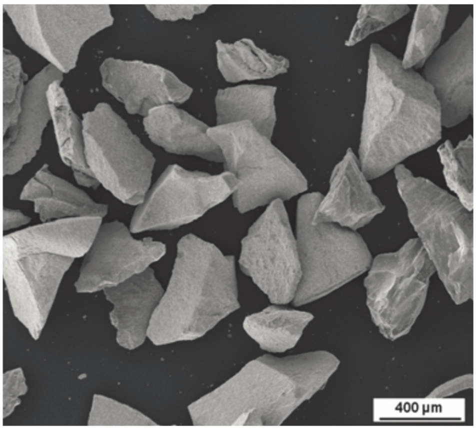


Figure 1.3 Micrograph of WC-15wt%Co hardmetal powder produced by disintegrator milling [Kulu, 2003]

Stresses caused by collision are higher than the strength of the material compared to other mechanical milling equipment like vibro- and ballmill, jaw crushers [Tymanok, 1999c].

In summary, as compared to other conventional grinding machines, disintegrators have a number of advantages: [Goljandin, 2013]

- compactness
- materials grinding with low contamination of media
- lower energy consumption than with other methods (vibration mills, ball mills etc.).
- multiple materials grinding simultaneously
- wide range of productivity (from a few kilograms up to dozens of tons per hour

On the other hand, disintegrators have higher wearing of work surfaces, especially at grinding medium or high hardness materials [Goljandin, 2005].

1.2 Thermal spray of coatings

1.2.1 Thermal spray processes

Thermal spray is a group of coating processes applicable to different materials. Based on heat sources, these processes are divided into two main categories: flame and electrical [Gan, 2015]. Flame spray methods can be divided further on the basis of feedstock materials used, such as powder, wires, rods as well as on the basis of flame formation (conventional flame, detonation based, high velocity) (Fig. 1.4). High velocity methods are classified on the basis of the feed and oxidant used: oxygen fuel, oxygen-air and air kerosene [Majumdar, 2014].

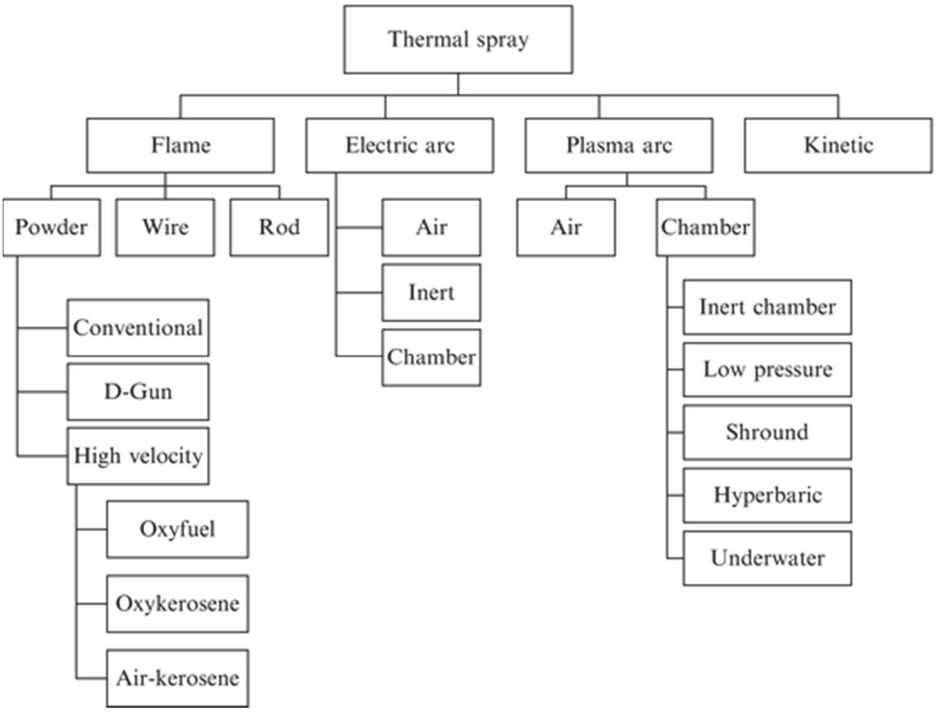


Figure 1.4 Classification of thermal spray processes and subsets [Majumdar, 2014]

The principle is that feedstock materials are heated and accelerated towards the surface of coated materials in a gas stream or atomization jets. At impact, a bond with the surface and subsequent particles causing thickness buildup with a typical lamellar ("splat") structure is formed [England, 2015].

The bond between the substrate and the coating may be mechanical, chemical, metallurgical or a combination all of them [EM 1110-2-3401, 1999]. The properties of thermal spray coatings depend heavily on the spraying process of the feedstock material (fuel, carrier gas flow and mass used etc.), application parameters [Gan, 2015] (Fig. 1.5.), and on the post- treatment of the applied coatings.

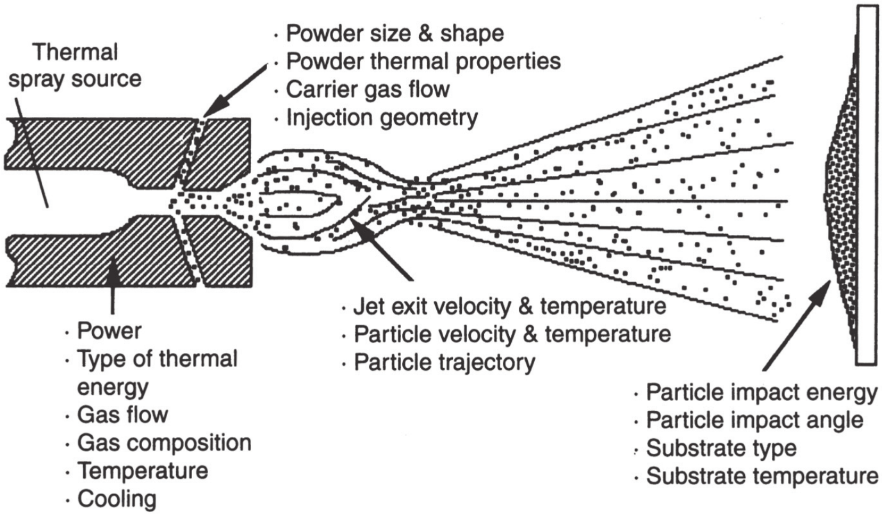


Figure 1.5 Variables and parameters of a typical thermal spray process [Gan, 2015]

A major advantage of the thermal spray process is that nearly all materials that melt without decomposing can be coated [Tucker, 1994]. Another advantage is that coatings can be applied without significant heat input to substrate materials, i.e., properties of coated materials remain unaffected even by use of high melting point materials. Next, in most cases, parts can be stripped and worn or damaged parts recoated without changing dimensions or properties of the coated material. The main limitation of thermal spray is that only areas that the gun can "see" can be coated. There are also size limitations: small deep cavities cannot be coated by thermal spray. From an economic point of view, thermal spray enables the functionality of hardmetals to be realized on the surface of large parts, which cannot be produced by powder metallurgy for technical and economic reasons [Berger, 2007]

In terms of microstructure, thermal spray coatings typically consist of thin lamellar layers, which are conformed and adhered to the substrate surface. The droplets at molten or semi molten condition solidify at very high speed (up to $>10^6$ K/s) after impacting the substrate and forming fine grained polycrytalline coatings or deposits. Sprayed coatings usually consist of some level of porosity, unmelted or partially melted particles, fully melted splats, metastable phases, and some oxidation [EM 1110-2-3401] (Fig. 1.6).

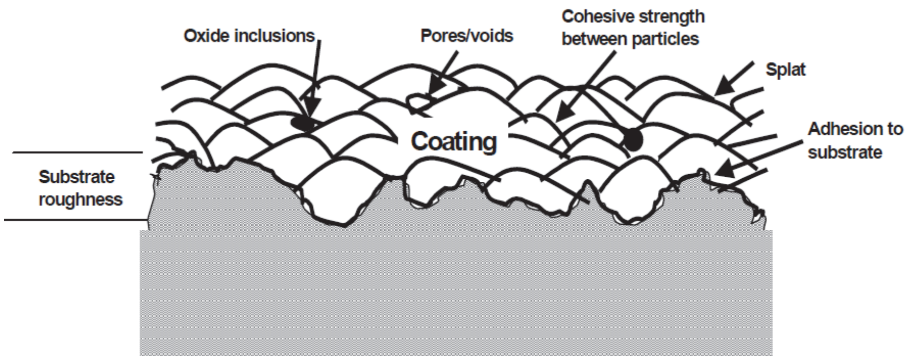


Figure 1.6 Typical cross-section of a thermal sprayed coating [Engineering Manual EM 1110-2-3401, 1999]

Selection of a suitable thermal spray process is determined by a) the desired coating material, b) coating performance requirements, c) economy, d) part size and portability [Davis, 2004] .

A wide range of industries benefit from thermal spraying, serving as an OEM process or a repair technique. Thermal spray can be used on ships, landing gears, in the mining, food machinery, pulp and paper, aerospace industry or virtually for any equipment subjected to wear, erosion, corrosion [Oerlikon, 2015; Kennmetal, 2015]. Moreover, thermal spray is applicable for dielectric, EMI/RFI shielding, biomedical, and solar energy [TST, 2015].

Table 1.2 and Figure 1.7 show a selection of coating processes, process characteristics and applications.

Table 1.2 HVOF spray process characteristics [Metallisation, 2015]

Feature	**Description**
Spray process	HVOFS
Typical spray materials	Metals, carbides
Typical applications	Oil and gas, steel mills, valves, pumps. hard, chrome plate replacement
Key process characteristics	Optimum coating quality, produces excellent carbide coatings, high noise level
Bond strength, MPa	48–80
Coating porosity, %	<1
Capital cost	High
Operating cost	High

Figure 1.7 Examples of thermal spray applications [Metallisation, 2015]

1.2.2 Spray process of hardmetal/cermet coatings

The thermal spray technique was first introduced in the early 1900s and thermal spray coatings have been used in wear resistant applications for a long time [Fauchais, 2014].

However, use of carbide materials was limited before the development of detonation gun spraying (DGS) [Poorman, 1952; Perry, 1952]. Regretfully, the company who owned the patent rights to DGS technology chose to market itself as a coating provider and equipment was not commercialized for sale.

As the DSG process was commercially unavailable, atmospheric plasma spraying (APS) was the main process for hardmetal coating production from the 1960s. The drawback of APS for hardmetal coating production was oxidation and decomposition of feedstock powders, which resulted in poor coating characteristics compared to DSG. Therefore, focus of technical developments shifted to the protection of feedstock powder against oxidation. Use of vacuum plasma spraying (VPS) was also studied. Still, the quality of the coatings was not comparable with DSG due to the high temperature of the process.

In the early 1980s, high velocity oxy-fuel (HVOF) spraying was introduced [Browning, 1980] by using rocket engine technologies to spray metal powders. HVOF spray is popular for wear applications, characterized by dense coatings produced and superior bond strength compared to other thermal spray processes [Thorpe, 1993]. Up to date, HVOF spray is mainly used for carbides and has taken over many applications where previously hard chrome plating was used [Sartwell, 2006; Evans, 2009; Picas, 2006]. Popularity of HVOF spray has grown rapidly, which can be illustrated by the increase of thermal spray systems in the last decades.

Latest studies are focused on improved combinations of particle velocity and process temperature, simultaneously taking into account the economical side of the process. One of these developments is high velocity air-fuel spraying, where air is used instead of oxygen for combustion [Berger, 2013].

In the development of spraying processes, much attention has been paid to supporting equipment of thermal spray hardwere, which has contributed significantly to the quality and reliability of the coatings. Today, manipulating systems, robots, computer controlled systems are used.

1.2.3 HVOF spray process

Prior to spraying, parts to be coated are grit blasted for activating the surface to achive maximum bond strength between the coating and the substrate. In the HVOF spray, molten or semi-molten particles are lead to the surface at high temperature (2300 °C) and high velocity gas stream (particle speed higher than 1000 m/s) produces a dense spray coating, which can be machined later to achieve desired characteristics for specific applications [AWS, 2015], as shown in Fig. 1.8. Wielage found that [Wielage, 2006] high particle velocities lead to short interaction time between hot gas jet and spray particles. Therefore, heat transfer is moderate and particle temperatures are relatively low. Thereby, thermal influence of the feedstock material is low and coatings with small phase changes compared to initial powder can be produced with excellent abrasion resistance. Due to high velocity, the coatings with low thermal input dense wear and corrosion resistant coatings can be produced.

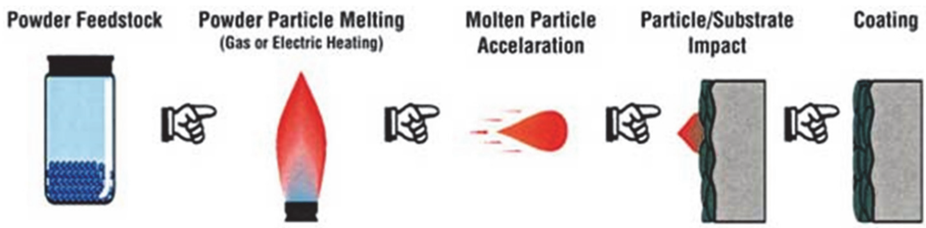


Figure 1.8 Flowchart of HVOF spray process [AWS, 2015]

As was mentioned earlier, HVOF systems are developed for producing extremely high velocities. Although there are several methods to achieve ultrasonic speed, the systems in general can be divided into two, based on the gun's cooling system: air and water cooled. In air cooled systems, high pressure combustion nozzle and an air cap are used. Fuel gas and oxygen are supplied at high pressure within the air cap supplied with compressed air, which acts like a coolant. Powder is fed to the system axially from the centre of the nozzle. Water cooled systems are more complicated: fuel and oxygen are lead axially to the water cooled combustion chamber where hot high pressure flame is produced and forced down from a long nozzle, increasing its velocity. Powder is fed to the system axially under high pressure or through the side of the level type nozzle where the pressure is lower.

1.2.4 Characteristics and applications of HVOF sprayed coatings

HVOF coatings can be characterized as follows:

- high density (porosity of typical coatings is under 2% (some coatings - under 0.5 %) [Picas, 2009]
- high bond strength (for typical carbide coatings an excess of 70 MPa) [Wang, 2006]
- optimum hardness (microhardness of typical tungsten or chromium based coatings are around 1 100 to 1 350 HV0,3 [TST, 2016]
- improved toughness [David, 2008] (depending on chemistry and other factors, the short dwell time and lower temperatures of HVOF can produce wear resistant coatings with excellent impact resistance)
- higher coating thickness (due to a 'shot-peening' effect produced by the high velocity particles impacting upon the previous layers of coating, the thickness of HVOF coating can be higher than that of plasma sprayed coatings; tungsten carbide coatings thickness up to 500 µm, some alloy coatings much higher) [Legg, 2006]
- beneficial residual stress (compressive residual stresses in a coating improve the fatigue life of a coated component, reduce the susceptibility of cracking and permit greater coating thickness limits) [McGrann, 1998]
- excellent wear resistance (HVOF sprayed coatings can exhibit superior resistance to abrasive [Houdkova, 2011], sliding/adhesive wear, fretting, erosion or cavitation, depending on the material and the process parameters chosen)
- superb corrosion resistance due to high density and with a suitable material, HVOF sprayed coatings provide enhanced resistance to the effects of corrosion, including hot corrosion, oxidation and to corrosive media, such as acidic and alkaline atmospheres and liquids) [Chatha, 2012]
- fine surface finishes [Kennametal, 2015]

1.3 Abrasive wear resistance of HVOF sprayed coatings

Abrasive wear is defined as the wear due to hard particles or hard protuberances forced against and moving along a solid surface. Main categories of wear, including abrasive wear, are shown in Fig. 1.9 [Veinthal, 2011]. Table 1.3 shows the characteristics of HVOF and DGS sprayed typical hardmetal coatings.

HVOF spray is most commonly used for wear resistant applications (at room and elevated temperatures). As HVOF sprayed coatings are dense and their porosity is low, they can be used for corrosion resistant applications. For dielectric applications, oxide ceramics and polymers are used [TST, 2015].

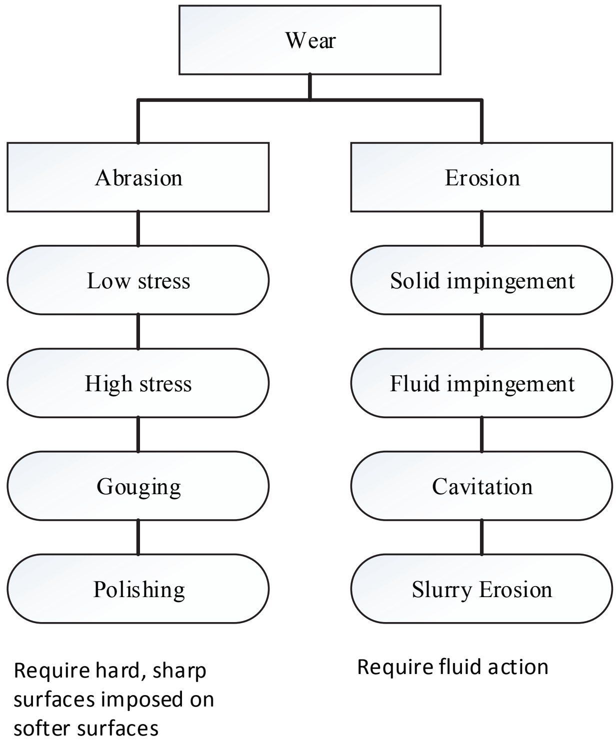


Figure 1.9 Major categories of wear based on abrasion and erosion [Veinthal, 2011]

Table 1.3 Hardness and relative erosive wear resistance of HVOF and DG sprayed coatings from commercial hardmetal powders (v=80 m/s, abrasives particle size 0.1-0.3 µm) [Kleis, 2008]

Deposition technique	**Composition and type of spray powder**	**Porosity, %**	**Hardness HV0.2**	**Relative erosive wear resistance ε**	
				α=30°	α=90°
DGS	WC-Co12 (Amdry 927)	2,1	680/1155	3,1	1,1
HVOFS	WC-Co17 (Tafa 1343V)	2,9	1300	11,2	2,6
HVOFS	Wc-Co10Cr4 (Tafa 1350VM)	0,7	1230	3,1	2,0
DGS	BK9c/WC-9Co (agglomerated/sintered)	–	1310^2	3,1	1,1
DGS	BK9m/WC-9Co (mechanical mixture)	–	1220^2	1,8	0,2
DGS	BK20m/WC-20Co (mechanical mixture)	–	810^2	1,4	0,4

[1] Hardness of metal matrix/hardphase, [2]HV0,05

HVOF sprayed coatings are usable wherever it is required to save materials while maintaining high performance of surface properties, improve component service life, repair existing components to new-like or better condition than original, provide high performance bond coat in a coating system.

1.4 Objectives of the study

The main objective of the study was to produce lower cost hardmetal/cermet based spray powders for HVOFS by use of alternative methods, ensuring their effectiveness in abrasive wear application conditions.

To achieve the main objective, the following activities were planned:

1. Production of hardmetal/cermet based spray powders using mechanically activated thermal synthesis (MATS) and mechanical disintegrator milling (MDM) of hardmetal/cermet powders as a reinforcement for composite spray powders
2. Development of HVOF spray coatings from MATS and composite powders based on commercial spray powders, consisting of recycled hardmetal/cermets hard phase
3. Characterization of sprayed coatings (structure, porosity, hardness) and study of wear properties in abrasion and erosion conditions

Hypothesis of the study:

- Using lower cost thermal spray powders from alternative production technologies enables to produce thermal spray coatings with comparable properties with coatings produced from industrial thermal spray powders.
- By use of MDM WC-Co hardmetal powder instead of WC/W_2C in thermal spray coatings, an improved complex of hardness-toughness properties for their application at impact loading conditions is ensured.

2 PRODUCTION OF SPRAY POWDERS AND THEIR CHARACTERIZATION

2.1 Spray powder production

2.1.1 Mechanically activated thermal synthesis of WC-Co and Cr_3C_2-Ni powders

The production of WC-Co hardmetal and Cr_3C_2-Ni cermet spray powders by mechanically activated thermal synthesis (MATS) is shown in Fig. 2.1, described in [Paper I and Paper IV]. The initial materials were tungsten, cobalt, carbon black for WC-Co hardmetal and chromium, nickel, carbon black for Cr_3C_2-Ni powder production. Carbon content and process characteristics were selected to avoid free carbon in powders after thermal activation. Table 2.1 shows the chemical composition of initial materials and Table 2.2 the process parameters.

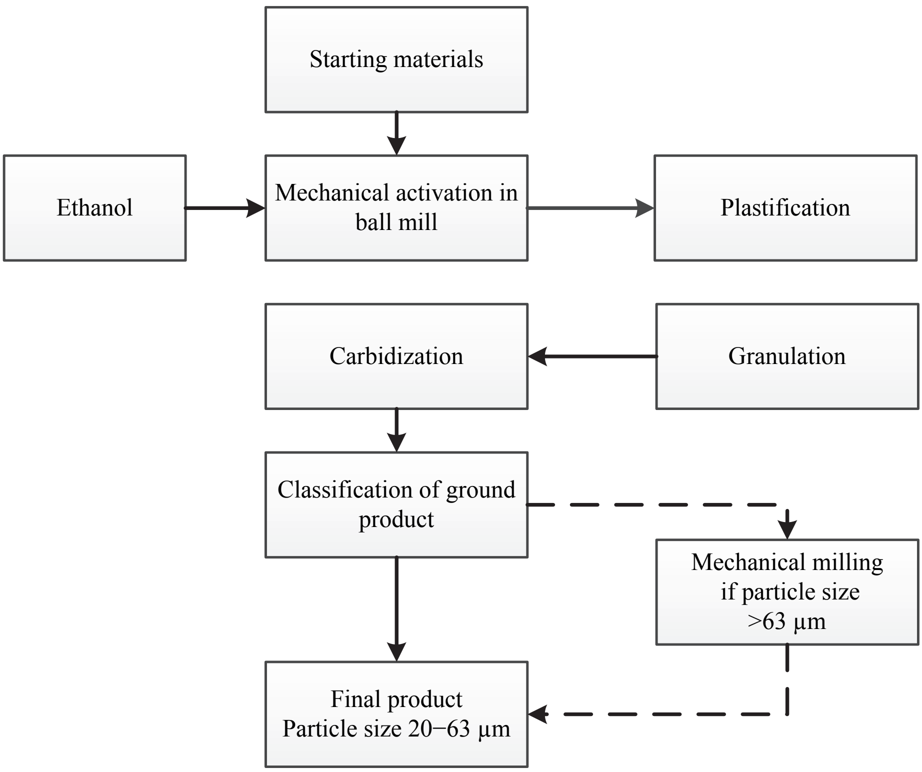


Figure 2.1 Principal scheme of the mechanically activated thermal synthesis [Paper I and Paper IV]

It was necessary to classify the produced powders as after carbidization, the particle size was too coarse for HVOF spray. Therefore, additional treatment in a disintegrator was required in order to achieve a desired particle size from 20 to 63 μm.

Table 2.1 Initial composition mixtures for MATS spray powders

Type of powder	**Chemical composition, wt%**				
	W	C	Co	Cr	Ni
W6,2C- 17Co (Z5)	76,8	6,2	17	–	–
W6,7C- 17Co (Z6)	76,3	6,7	17	–	–
Cr10C-23Ni (P19)	–	10,1	–	67	22,9

Table 2.2 MATS process parameters

Parameter	**WC-Co**	**Cr_3C_2-Ni**
Mechanical activation time, h	72	72
Ball-to-mill (BM) ratio	7/1	15/1
Thermal synthesis temperature, °C	1310	1130

The shape of spray powder particles produced by MATS was from spherical to irregular (Fig. 2.2), characterized by some porosity. However, additional milling had negative effect on the particle size distribution and shape of the WC-Co and Cr_3C_2-Ni powder (Paper I and Paper IV). In addition, flowability tests proved unsuccessful. Lower powder homogeneity and sphericity can lead to lower spraying efficiency and therefore coating quality [Paper IV].

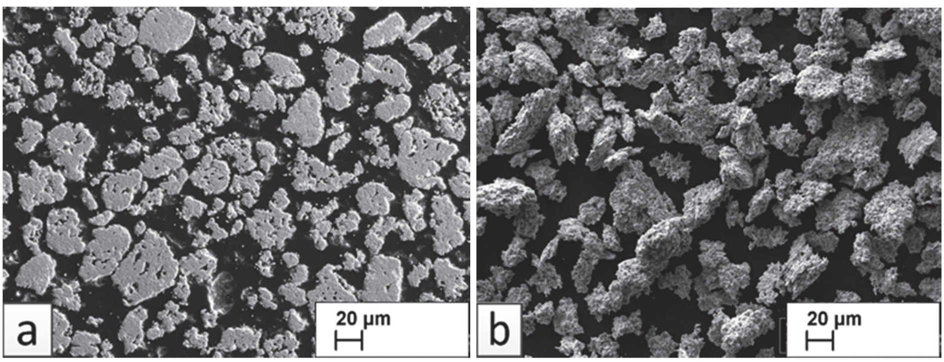


Figure 2.2 SEM images of spray powders: a – WC-Co; b – Cr_3C_2-Ni

In the phase identification of the milled powder, X-ray diffraction (XRD) methods with CuKa radiation (Bruker AXS D5005) were used.

The study showed that in WC-Co powder mixtures all carbon was used at carbidization process However, in powder mixture Z5 4,0 wt% of brittle W_2C

phase was found and none in powder mixture Z6. Therefore it can be concluded that ideal powder mixture from phase composition point of view is powder mixture Z6 as in consist only WC and Co and no brittle phases (Table 2.3). In Cr_3C_2-Ni powder mixture small amount of free chromium (1.3%) was detected, which indicates that initial carbon content needs to be increased by a small margin.

Table 2.3 Composition of MATS spray powders used for HVOF spray

Type of powder	**Chemical composition**		**Particle size, µm**
	Carbide content, %	**Binder content,%**	
W6,2C- 17Co (Z5)	83,5 WC; 4,0 W_2C	12,5 Co	20−63
W6,7C- 17Co (Z6)	89,6% WC	10,4 Co	20−63
Cr10C-23Ni (P19)	75,6 Cr_3C_2	23,1 Ni 1,3 Cr	20−63

As it follows from Table 2.4, experimental spray powders are characterized by low flowability compared to that of commercial ones, which influences the effectiveness of the spray process (powder feed rate). However, it has no influence on the coating structure and hardness, as will be demonstrated later in third paragraph..

Table 2.4 Comparison of experimental MATS and analogous commercial carbide based spray powders

Type of powder		**Particle size, mm**	**Particle shape**	**Density, g/cm³**	**Porosity**	**Flowability**
WC-Co	Exp.	20−63	Near spherical	13,4	Low	Low
	Comm. Amperit 558	15−45	Spherical	13,6	Low	Good
Cr_3C_2-Ni	Exp.	20−63	Irregular	7,0	Low	Low
	Comm. Amperit 588	15−45	Spherical	7,2	Low	Good

2.1.2 Production of hardmetal/cermet powders by mechanical disintegrator milling

WC(12-15)Co hardmetal and Cr_3C_2-Ni cermet scrap were used as initial materials. Two-stage milling of materials by collision was implemented [Paper II]. For preliminary size reduction, disintegrator DS-350 and for final grinding, laboratory disintegrator milling system DSL-175 with an inertial classifier, were applied. Schematics of MDM powder production of hardmetal/cermet powders is shown in Fig. 2.3.

Chemical analyses by the EDS of MDM powders showed that they consist approximately of 75−80 % carbides (WC-Co, Cr_3C_2-Ni). However, in the WC-

Co hardmetal powder, a relatively high amount of iron is obtained from the multi-stage milling process and tungsten in Cr_3C_2-Ni cermet powder from the grinding media. (See [Paper II] and Table 2.5).

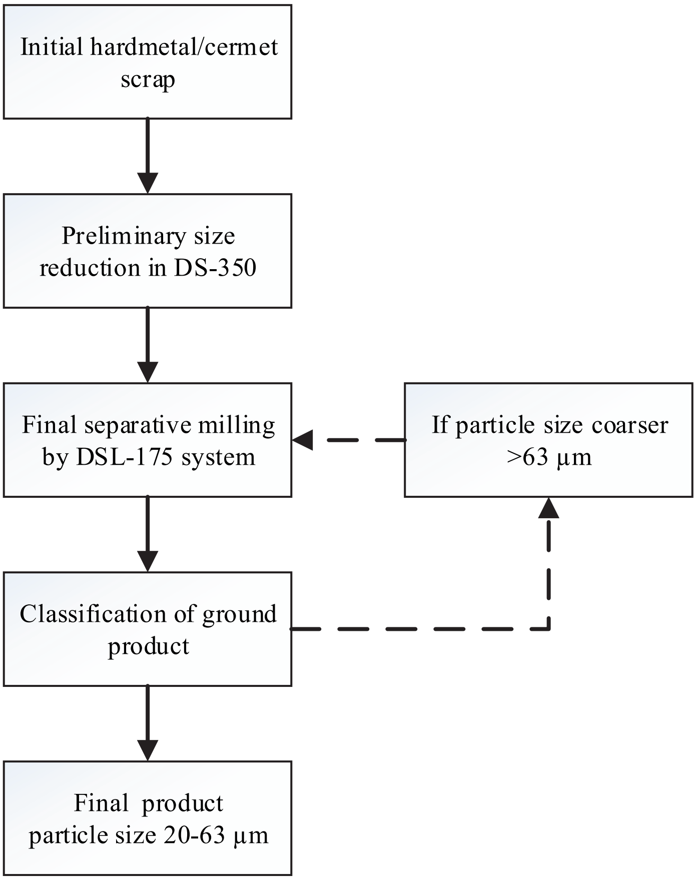


Figure 2.3 Work procedure of retreatment of hardmetal/cermet scrap

Table 2.5 Chemical composition of recycled hardmetals/cermets powders [Paper II]

Type of powder	**Composition, wt %**				
	Carbide	**Fe**	**Ni**	**W**	**Co**
WC-Co	WC-75,6	12,9	–	–	11,5
Cr_3C_2-Ni	Cr_3C_2- 78	3,1	16,4	2,5	

Particle morphology study of MDM hardmetal/cermet powders of fraction 50 µm and less used later in the composite powder for HVOF spray showed that the shape of Cr_3C_2-Ni particles is more spherical and equally distributed compared to that of WC-Co (Fig. 2.4). At the same time, coarser fraction obtained by one-two stage milling was more angular than in the fine fraction produced multi-stage separative milling. (See Fig. 2.4 and [Paper II]).

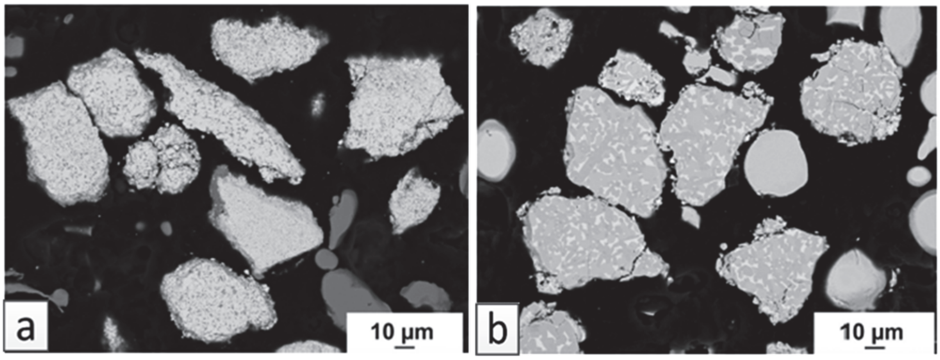


Figure 2.4 Cross-section micropolishes of disintegrator milled hardmetal/cermet powders: a – (WC-Co); b – (Cr_3C_2-Ni) [Paper II]

By morphology studies it was determined that the angularity of recycled materials acts differently at the decrease of particle size: angularity parameter SPQ of WC-Co is stable, while the SPQ of Cr_3C_2-Ni increases [Paper II]. Close look-up of Cr_2C_3-Ni cermet powder particles revealed many more cracks and defects compared to WC-Co hardmetal powder particles [Paper II]. This shows that the ductility of the WC-Co raw material used in the experiment is better and it explains angularity changes when the particle size decreases. Moreover, the possibility of deformation during high velocity spraying later is lower than with Cr_2C_3-Ni due to the absence of internal cracks in the particles. Properties of experimental MDM powders were compared with those of analogous commercial powders. Based on the current study, it can be concluded that experimental powder particles are finer and more spherical but have higher fracture toughness K_{1c} than similar commercial powders [Kulu, 2014] (Table 2.6).

Table 2.6 Comparison of experimental MDM and analogous commercial carbide based powders

Type of powder		Production method	Particle size, µm	Density, g/cm^3	Particle shape	Fracture toughness K_{1c}, MPa·m$^{1/2}$
WC-12Co	Exp.	MDM scrap	20–63	13,4	From angular to rounded	14–15
WC/W_2C-Woka 5005)	Comm.	Fused and crushed	45–90	15,8	Angular	4–5
Cr_3C_2-20Ni	Exp.	MDM from bulk	20–63	7,0	Rounded	10–12
Cr_3C_2-25NiCr Amperit 580.054	Comm.	Sintered and crushed	45–90	6,7	Blocky+ angular	1,5 [Houdkova, 2010]

3 PRODUCTION AND CHARACTERIZATION OF HVOF SPRAYED COATINGS

3.1 Spray powders

Feedstock mechanically activated thermal synthesis (MATS) powders for HVOF spray consisted of synthesized WC-Co or Cr_3C_2-Ni powders (See Table 2.4).

Mechanical disintegrator milled (MDM) hardmetal/cermet powders were used as reinforcement (40 vol%) in the commercial self-fluxing FeCrSiB alloy based powder (Fig. 3.1). See Papers I, II and IV.

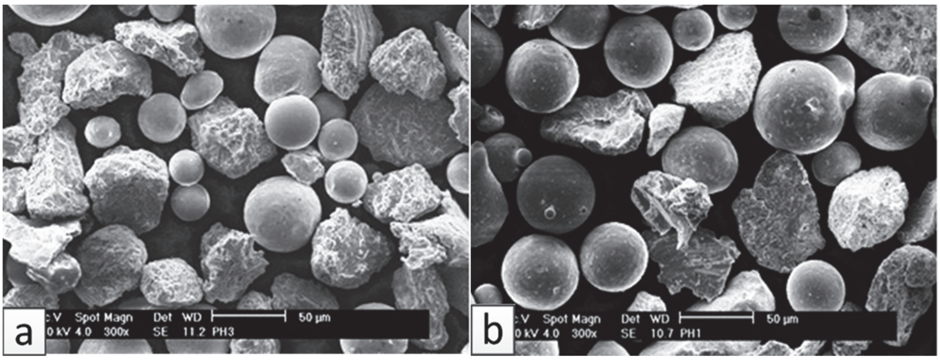


Figure 3.1 Morphology of self-fluxing alloy - MDM hard phase spray powders: a – (Cr_3C_2-Ni)+FeCrSiB; b – (WC-Co)+FeCrSiB [Paper III]

Flowability of powder mixtures, as the main technological property of spray powders, was tested and compared with commercial powders (Paper II).

The lower flowability of experimental powders compared to commercial ones (NiCrSiB and WC-CoCr) is demonstrated in Table 3.1. However, later, during spraying, no negative effects because of lower flowability were noticed.

Table 3.1 Flowability of experimental and commercial spray powders [Paper II]

Composition of powder	Flow rate , g/s
WC-CoCr (Tafa)	138
NiCrSiB (Castolin 16221)	204
FeCrSiB (Hoganas 6A)	N/A
FeCrSiB+40vol% (WC-Co)	84
FeCrSiB+40vol% (Cr_3C_2-Ni)	78

3.2 Spraying technology

HVOFS was performed using Diamond Jet Hybrid 2700 system (propane hybrid gun from Sulzer Metco). Substrate material was steel C45, specimens with dimensions of 100x25x5 mm were used. Substrate materials were blasted before spraying with alumina 36 mesh. HVOF spray parameters are given in Table 3.2.

Table 3.2 HVOF spraying parameters of coatings

Parameter	Value
Propane flow rate, l/min	68
Oxygen flow rate, l/min	240
Air flow rate, l/min	375
Carrier gas flow rate, l/min	12,5
Powder feed rate, g/min	40–60
Spray distance, mm	250

Powder feed rate that depends on the spray powder type was lower with WC-Co (40 g/min) and higher with Cr_3C_2-Ni (60 g/min) based powders.

3.3 Coating characterization

3.3.1 Microstructure

Microstructures of HVOF sprayed coatings from experimental MATS WC-Co and Cr_3C_2-Ni powders are presented in Fig. 3.2 and analogous commercial spray powders in Fig. 3.3.

The thickness of the coatings sprayed from MATS powders determined by SEM analyses with Zeiss EVO MA-15 from the cross-section of investigated images was in the range of 250−400 µm. By X-ray analyses (EDS), it was demonstrated that in general, the coatings were homogeneous, mainly consisting of WC-Co; Cr_3C_2 and Ni phases. Only some pores in the cross section (less than 1%) and a small amount of Al_2O_3 (used for substrate activation before spraying) were found between the substrate and the coating.

It could also be noticed that coatings from WC-Co MATS spray powder (Fig. 3.2a) were rather lamellar compared to coating from Amperit 558 (Fig. 3.3a).

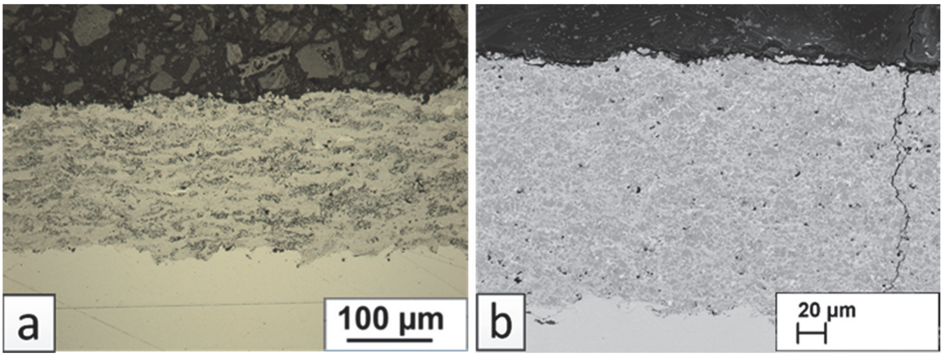


Figure 3.2 Microstructure of HVOF sprayed coatings from experimental MATS powders: a – WC-Co; b – Cr_3C_2-Ni

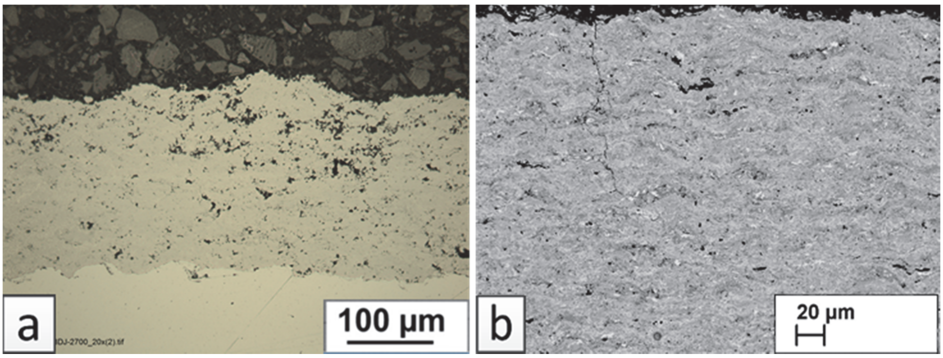


Figure 3.3 Microstructure of HVOF sprayed coatings from commercial spray powders: a – WC-CoCr (Amperit 558); b – Cr_3C_2-NiCr (Amperit 588)

The thickness of coatings from spray powders consisting of the commercial FeCrSiB spray powder and disintegrator milled hardmetal/cermet powders were in the range of 250–400 µm, depending on the composition of the spray powder (cermet or hardmetal). Coatings were homegeneous with some pores and Al_2O_3 and SiO_2 particles between the substrate and the coating (Fig. 3.4). In addition, coating adhesion with the steel substrate was good. In fact, no negative influence of exessive iron in the WC-Co recycled powder could be noticed at the coating structure.

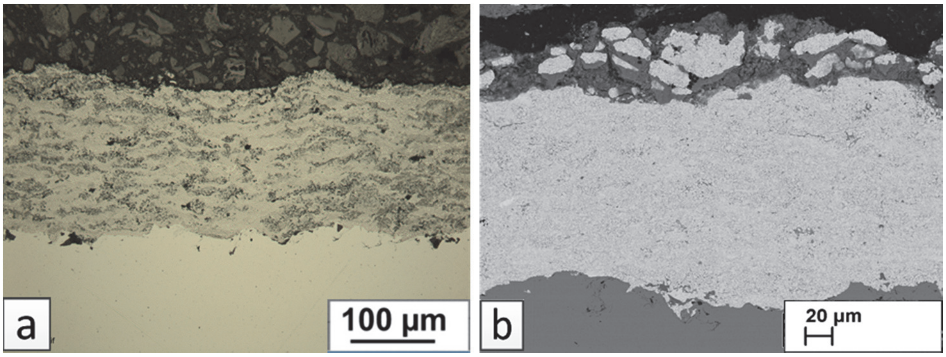


Figure 3.4 Microstructure of HVOF sprayed coatings from commercial self-fluxing alloy and MDM hardmetal/cermet mixtures: a – FeCrSiB+(WC-Co); b – FeCrSiB +(Cr_3C_2-Ni)

3.3.2 Hardness

The macrohardness of the surface and the microhardness in the cross-section were measured. Surface Vickers hardness were performed by Micromet 2001 apparatus at at load 9,8 N (1 kgf). The load was selected to obtain the size of indents comparable with sizes of hard phase in the composite. Microhardness in the cross-section was measured using a Matsuzawa MMT-X device. The applied load was 2,94 N (300 gf).

The macro- and microhardness of experimental and reference coatings are given in Table 3.3.Coatings from MATS and commercial carbide spray powders showed similar results on both hardness tests at different loads. That indicates that from coatings hardness point of view, particle size and equal distribution are not that important as the amount of hard phase. Amperit 588 higher surface hardness can be explained by harder matrix of coating (NiCr compared to Ni or Co matrix). Since as a substrate, soft steel C45 was used then deflection of the coating during higher loading at hardness measurement probably took place, then harder matrix can compensate the deflection during loading.

Surface hardness of coatings from self-fluxing iron alloy based and MDM powders was much lower compared to carbide coatings due to the high amount of softer matrix material. In cross-section, however, at some hardness tests coatings consisting MDM powders were even higher than coatings from MATS or commercial spray powders, but with higher standard deviation due to higher amount of soft matrix material [Table 3.3].

Table 3.3 Thickness and hardness of studied HVOF sprayed coatings

Type of spray powder	Composition of coatings	Coating thickness, µm	Hardness HV	
			HV1 Surface	HV0,3 Cross-section
MATS	W6,2C-17Co	250	690±66	990± 114
	W6,7C-17Co	250	620±59	1050±0,58
	Cr_3C_2-Ni	400	730±80	1010±122
MDM	FeCrSiB+(Cr_3C_2-Ni)	300	390±40	795±35
	NiCrSiB+(Cr_3C_2-Ni)	400	350±40	860±60
	FeCrSiB+(WC-Co)	400	465±35	1050±205
	NiCrSiB+(WC-Co)	400	320±30	1070±190
Commercial	WC-CoCr (Amperit 558)	300	750± 60	1060± 175
	Cr_3C_2-NiCr (Amperit 588)	330	910± 108	1010± 148

3.3.3 Wear resistance

In the abrasive wear tests of the coatings, two different methods were used: a) abrasive rubber-wheel wear (ARWW) and b) abrasive erosive wear (AEW) at impact angles 30° and 90°. Quartz sand with a particle size of 0,1–0,3 µm was used as an abrasive. Hardness of the abrasive was 1000–1200 HV. Abrasive particle velocity was 2.4 m/s at abrasion and 80 m/s at erosion wear tests. The relative wear resistance to steel C45 was calculated at ARWW and AEW. Results of abrasive wear tests are given in Table 3.4.

Table 3.4 Relative volumetric wear resistance of experimental and commercial coatings

Type of spray powder	Composition	Relative wear resistance, ε_v		
		AEW		ARWW
		30°	90°	
MDM	FeCrSiB+Cr_3C_2-Ni	0,8	0,2	2,2
	NiCrSiB+Cr_3C_2-Ni	0,8	0,2	1,6
	FeCrSiB+WC-Co	1,2	0,3	2,7
	NiCrSiB+WC-Co	1,1	0,3	2,0
MATS	W6,2C-17Co	2,1	1,3	5,0
	W6,7C-17Co	1,9	0,7	5,0
	Cr_3C_2-Ni	1,5	0,3	7,7
Commercial	WC-CoCr (Amperit 558)	4,6	3,3	11,7
	Cr_3C_2-NiCr (Amperit 588)	1,6	0,4	8,2

The results of abrasion of the self-fluxing alloy based coatings with MDM hard phase showed that the experimental coatings tested at ARWW have 1,5–2,7 times higher and the coatings from MATS powders have 5,0–7,7 times higher wear resistance than the reference material steel C45. The relative wear resistance of MATS powder based experimental coatings was found comparable with the wear resistance of coatings produced from similar commercial powders (see Table 3.4 and [Paper I and IV]). Fe-based self-fluxing alloy and MDM cermet/hardmetal based coatings were found to have slightly higher wear resistance than that of Ni-based reference coatings.

At low impact angle AEW (α=30°), relative wear resistance of experimental coatings was about the same as that of the reference material steel C45. The only exception was coatings from MATS WC-Co powders, which had approximately two times higher wear resistance.

At normal impact angle AEW (α=90°), HVOF sprayed coatings are generally incompatible (only MATS based WC-Co powder coatings had satisfactory results) (Table 3.4 and [Paper IV]. Compared to commercial reference coatings, Amperit 588 and 558, the experimental coatings showed comparable [Paper I] or two times lower results [Paper IV]. As the particle size of commercial spray powders is finer, more homogeneous and spherical, the wear resistance is higher as well.

The results of wear mechanism studies are shown in Figs. 3.5–3.8. As it follows from the figures, the predominant wear mechanism at ARWW coatings from MTS powders as well as self-fluxing alloy and MDM recycled hardmetal/cermet based coatings is the loss of the softer matrix phase, which often leads to the loss of a hard phase. The dominating wear mechanism at ARWW was removal of hardmetal particles from the coating, leaving pores on the surface (Figs. 3.5 and 3.8).

The low wear resistance of coatings at AEW at 90° angle (Table 3.4) can be explained with brittleness of the hard phase. As a result of the impact load, Cr_3C_2 particles fracture in the high energy spray process, as it follows from the study of coating structure [Paper III]. Wear at high velocity and impact angles is caused by the carbide particle fracture or removal of the metal matrix microparticles due to the low-cycle fatigue process [Veinthal, 2011].

The main advantage is that the higher toughness of recycled hardmetal reinforcement in the HVOF sprayed coatings was not realized due to the typical lamellar structure of coatings from MATS powders (Fig.3.2) as well as mixtures of metal-matrix and hardmetal powder (Fig. 3.4). The microstructures show that hardmetal particles are deformed and partially cracked (high defectiveness of particles), causing direct fracture in the following impact wear process. In addition, residual stresses in the coatings play a certain role, i.e. the level of compressive stresses in HVOF sprayed coatings is high (about 700−800 MPa [Lille, 2002].

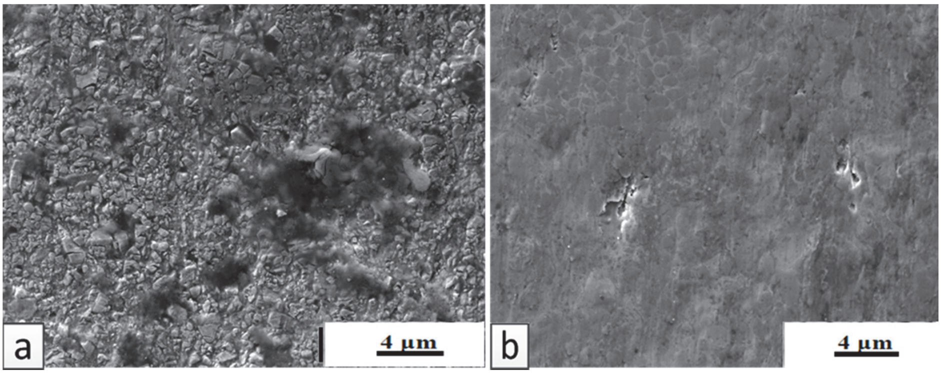


Figure 3.5 Topography of worn surfaces at ARWW of sprayed coatings from MATS hardmetal/cermet powders: a – WC-Co; b – Cr_3C_2-Ni

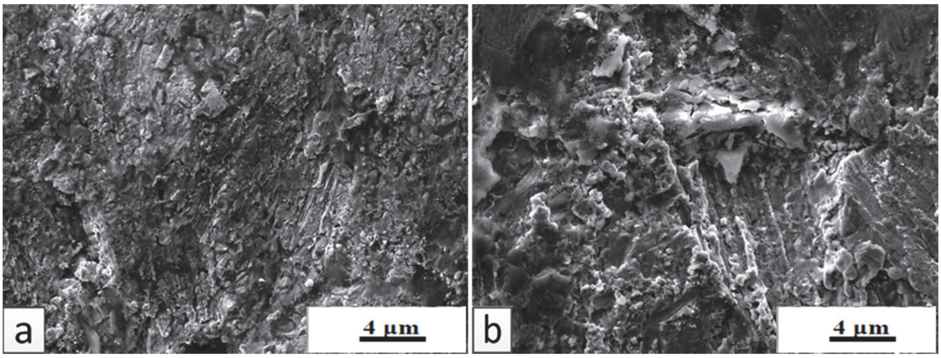


Figure 3.6 Topography of worn surfaces at AEW α=30°) of sprayed coatings from MATS hardmetal/cermet powders: a – WC-Co; b – Cr_3C_2-Ni

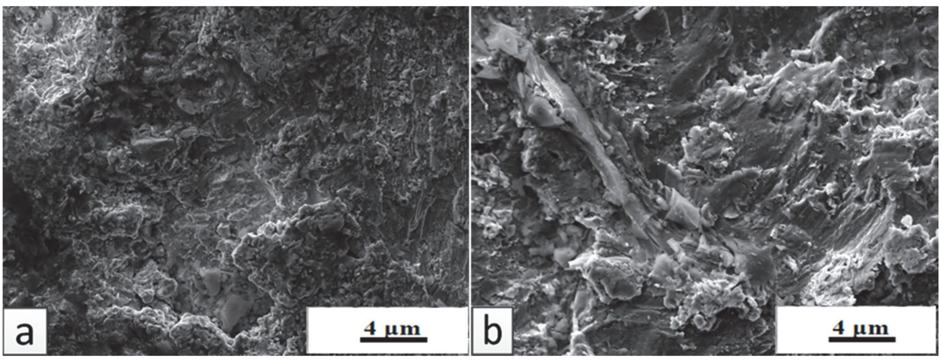


Figure 3.7 Topography of worn surfaces at A AEW α=90°) of sprayed coatings from MATS hardmetal/cermet powders: a – WC-Co; b – Cr_3C_2-Ni

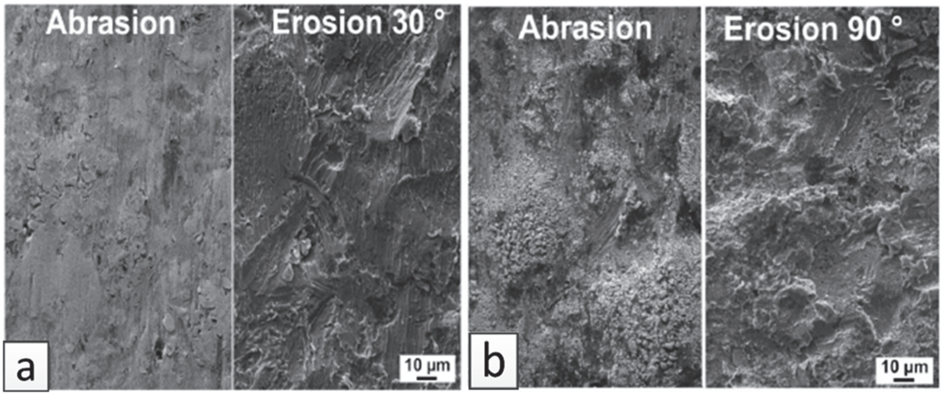


Figure 3.8 Topography of worn surfaces at ARWW and AEW of sprayed coatings based on self-fluxing alloy and consisting of MDM hardmetal/cermet hard phase: a – (Cr_3C_2-Ni)+ FeCrSiB; b – (WC-Co)+ NiCrSiB

3.4 Potential application areas of coatings

The main criteria of coating selection for abrasive wear can be described as follows [Kleis, 2008)]:

- tribological (abrasive hardness, particle size, shape, velocity and trajectory)
- structural (composition, microstructure, hardness, porosity, hardness-toughness, residual stresses)

Based on the above potential areas of application at abrasive media, experimental and commercial HVOF sprayed coatings are applicable at sliding wear (abrasion) or low-impact angle erosion wear; hardmetal-type structures (coatings from MATS powders) are preferable (Fig. 9). Potential areas of applications are summarized in Table 3.5 and Fig. 3.10.

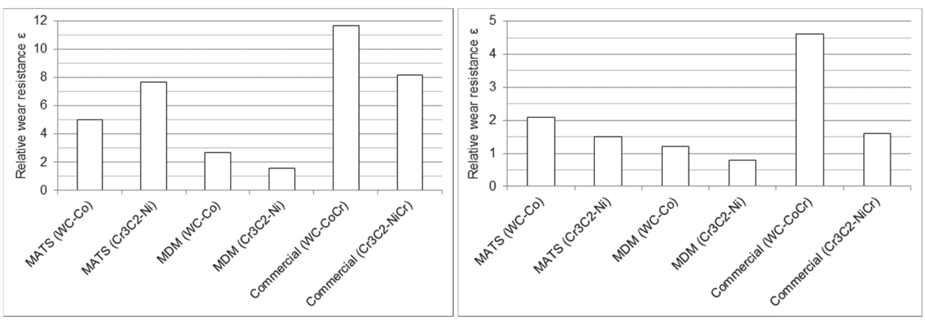


Figure 3.9 Potential application areas of HVOF sprayed coatings based on wear resistance at different applications: a – at ARWW; b – at AEW (30º).

Table 3.5 Potential application areas of novel HVOFS coatings

Type of spray powder	Coating characteristics		Coating cost	Typical applications
	Porosity, %	Hardness/ Toughness		
WC-Co	<1	High HV Moderate K_{1C}	~2x lower compared to analogous commercial ones	Hard chrome replacement in tooling cutting blades
Cr_3C_2-Ni	<1	High HV Low K_{1C}	At the level of commercial coating	Abrasive high temperature and corrosive environments

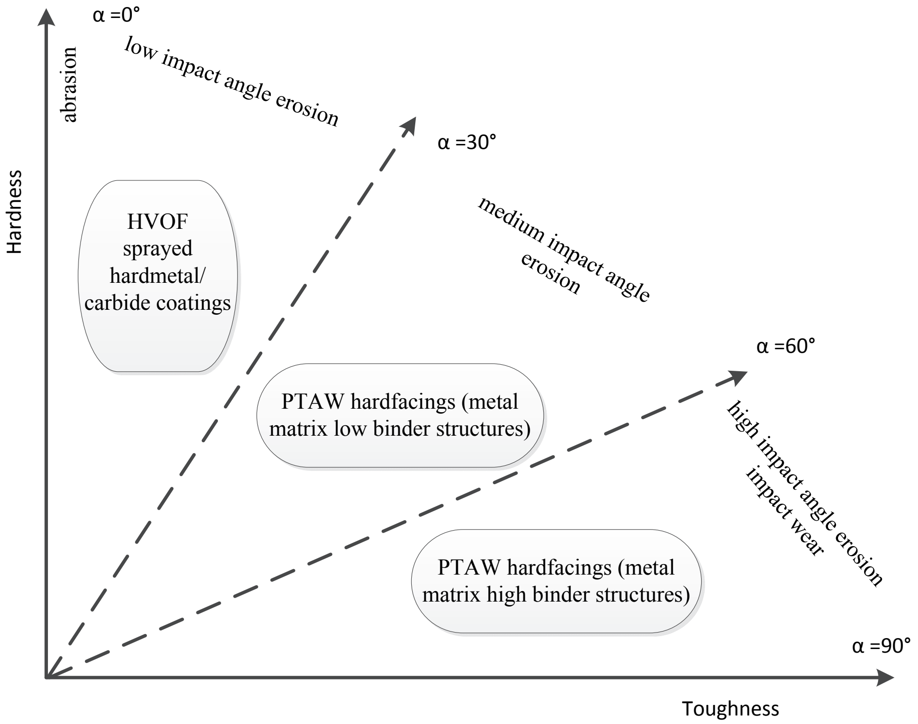


Figure 3.10 Potential application areas of sprayed coatings (for comparison PTA-welded hardfacings)

4 CONCLUSIONS

Alternative methods, *i.e.* mechanically activated thermal synthesis (MATS) and mechanical disintegrator milling (MDM), are proposed for HVOF sprayed coatings in the production of carbide based powders.

- It was demonstrated that WC-Co hardmetal and Cr_3C_2-Ni cermet powders produced by the MATS process are suitable for HVOF spray despite the shortcomings of morphological and technological properties. MDM produced bulk WC-Co hardmetal and Cr_3C_2-Ni cermet powders characterized by angular shape and high density may be used as a hard phase in self-fluxing alloy based spray powders.
- HVOF sprayed coatings from experimental spray powders are characterized by low porosity and high hardness. Coatings produced by WC-Co and Cr_3C_2-Ni powders produced by MATS are comparable with coatings from analogous commercial WC-Co and Cr_3C_2-NiCr powders. In addition, relative wear resistance of these powders is 5–8 times higher than that of reference material steel C45. MDM WC-Co hardmetal (containing a considerable amount of iron) and Cr_3C_2-Ni cermet powders are suitable as a hard phase in iron based matrix HVOF coatings, but no notable increase in the wear resistance at erosion was achieved.
- The abrasive wear resistance determined at abrasion and erosion of HVOF sprayed coatings from spray powders produced by alternative methods is comparable (Cr_3C_2-Ni) or 2 times lower (WC-Co) with the wear resistance of coatings from commercial spray powders. An advantage of bulk hardmetal/cermet (MDM produced) containing HVOF sprayed coatings is its better complex of "hardness-toughness" properties than that of pure brittle WC/W_2C containing composite coatings.
- Elaborated HVOF sprayed coatings may be applied in cost sensitive areas like road construction machines, tooling, high-temperature applications. It was demonstrated that HVOF sprayed coatings from experimental spray powders are prospective first at abrasion wear conditions; at solid particle erosion instead of HVOF sprayed coatings, application of metal-matrix composite coatings (PTA welded hardfacings) is unavoidable, ensuring an optimal complex of hardness-toughness properties.

The novelty of present thesis can be outlined by:

- New WC-Co and Cr_3C_2-Ni powders for HVOF spray produced by mechanically activated synthesis are proposed.
- New composite spray powders on the base of commercial iron self-fluxing alloy powder and reinforcements from WC-Co hardmetal and Cr_3C_2-Ni cermet powders produced by mechanical disintegrator miling HVOF

sprayed coatings with optimal complex of hardness-toughness properties are proposed.

- Lower cost sprayed coatings for cost-sensitive application areas are proposed

Future plans

It is planned to address the following areas:

- Effect of mechanical activation of powders produced by mechanical methods and its use in the following spray process – low temperature cold or dynamic spray;
- Production of carbide based spray coatings using *in-situ* synthesis of carbides in the spray process, so called Reactive Thermal Spray (RTS) process.

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ABSTRACT

Novel Synthesized and Milled Carbide-based Composite Powders for HVOF Spray

Wear damage from abrasion and erosion affects businesses with machine downtime, lost productivity, and maintenance costs. On the other hand, wear resistant materials (ceramics, hardmetals or alloyed steels) are expensive compared to steels used for normal mass production. Thermal spray, specifically High velocity oxy-fuel (HVOF) spray, contributes to the functionality of hardmetals for large parts that cannot be produced for any technical or economical reasons.

WC-Co and Cr_2C_3 based powders, as a new area of interest, are used for wear resistant applications. The properties of thermally sprayed coatings depend heavily on feedstock materials, their characteristics and the process used for spraying. High velocity oxy-fuel (HVOF) spray has proved to be the best technique for spraying wear resistant coatings due to high velocity and low spraying temperature, which ensure dense, low porosity coatings characterized by good adhesion with the substrate material.

As feedstock material contributes a considerable amount of thermal spray running costs, producing spray powders at a lower cost is essential. Most commonly, hardmetal thermal spray powders for HVOF are produced by agglomeration or sintering. However, the drawback of agglomerated powders lies in its price and sintered powders tend to be irregular in shape and contain brittle phases.

The aim was to develop new methods of thermal spray powder production for HVOF spray and to produce coatings for abrasion and erosion wear resistant applications. Focus was on two different methods – mechanically activated thermal synthesis (MATS) for carbide spraying and mechanical disintegrator milling (MDM) of WC-Co and Cr_3C_2-Ni for iron based self-fluxing metal-matrix based composite spray powders. All experimental coatings showed results comparable with similar powders currently used in industry.

Morphology and technological parameters of experimental spray powder particles were studied and their influence on the mechanical properties and wear resistance of produced coatings were evaluated.

Coatings produced from experimental powders were found homogeneous and with low porosity. Mechanical properties of experimental coatings were on same level as coatings from analogous widely used similar commercial powders.

Wear resistance of MATS produced experimental carbide powder coatings at low impact angles was much higher than that of the reference material steel C45. However, at higher impact angle, coating performance was poor. On the other hand, coatings produced from experimental powders were comparable with similar powders widely used in industry.

WC-Co hardmetal scrap and Cr_3C_2 bulk material were successfully treated for usage as a hard phase in iron based matrix HVOF coatings. The main advantage of using hardmetal/cermet hard phase in composite powders over pure carbide powders lies in the improved combination of hardness-toughness properties of the obtained HVOF coatings.

Keywords: tungsten and chromium carbide, mehcanically activated thermal synthesis, mechanical disintegrator milling, high velocity oxy-fuel spray, wear resistance

KOKKUVÕTE

Uudsed sünteesitud ja jahvatatud karbiidide baasil komposiitpulbrid kiirleekpihustuseks

Abrasiivkulumine mõjutab äritegevust negatiivselt kas masinate remondi, vähenenud tootlikkuse või suurenenud hoolduskulude tõttu. Lisaks on kulumiskindlad materjalid (keraamika, kõvasulamid, legeerterased) küllaltki kallid võrreldes tööstuslikult toodetavate tavaterastega. Termopihustus, eriti kiirleekpihustus, võimaldab seevastu kasutada kõvasulameid juhtudel, eriti suurte mõõtmetega detailide puhul, kus see muidu oleks kas tehnilistel või majanduslikel põhjustel mõeldamatu.

Kulumiskindlates rakendustes kasutatakse üldjuhul WC-Co ning viimasel ajal laialdasemalt ka Cr_2C_3-Ni baasil valmistatud pulbreid. Termopinnete omadused sõltuvad suurel määral pihustamisel kasutatavatest pulbritest ning nende omadustest. Kiirleekpihustustehnoloogia on end tõestanud parima moodusena kulumiskindlate pinnete saamiseks tänu suurele osakeste kiirusele ning madalale temperatuurile protsessi ajal, tänu millele saadakse tihedad, madala poorsuse ning aluspinnaga hea nakkega pinded.

Kuna pulbri maksumus moodustab suure osa pindamiskuludest termopinnete korral, on nende hind konkurentsivõime säilitamisel eriti oluline. Enamasti saadakse kõvasulam- ja karbiidpihustuspulbrid aglomeratsiooni ja paagutamise ning sulatamise ja purustamise teel. Aglomeratsiooni ja paagutamise teel saadud pulbrid on suurepäraste tehnoloogiliste omadustega kuid kallid. Sulatamise ja purustamise teel saadud pulbreid iseloomustab pulbriosakeste ebakorrapärane kuju ning üldjuhul ka habraste faaside olemasolu, mis vähendavad pinnete kulumiskindlust.

Antud töö keskendub abrasioon- ning erosioonkulumistingimustes töötavate pinnete saamiseks kasutatavate uudsete pihustuspulbrite tootmismeetodite uurimisele: esiteks mehaaniliselt aktiveeritud termosünteesile (MATS) karbiidpulbrite ning teiseks mehaanilile desintegraatorjahvatusele (MDM) kõvasulampulbri saamiseks.

Uuriti eksperimentaalsete pihustuspulbrite morfoloogiat ja tehnoloogilisi omadusi. Hinnati nende mõju pinnete mikrostruktuurile, kõvadusele ning kulumiskindlusele.

Eksperimentaalsed sünteesitud pihustuspulbritest ja desintegraatorjahvatuse teel saadud kõvasulampulbreid iseräbustuva rauasulampulbrite baasil saadud sisaldavad pinded olid struktuurilt homogeensed ja madala poorsusega. Pinnete kõvadus oli sarnane analoogsete tööstuses kasutatavatest pulbritest pinnate kõvadusega.

Sünteesitud pihustuspulbritest pinnete kulumiskindlus oli märkimisväärselt suurem erosiookulutamisel abrasiivosakestega väikese kohtumisnurga korral. Selgus, et mida suurem oli abrasiivosakeste kohtumisnurk, seda madalam oli kulumiskindlus. Samas, eksperimentaalpinnete kulumiskindlus oli võrreldav sarnastest tööstuslikest pulbritest saadud pinnete kulumiskindlusega.

Kasutatud kõvasulami ümbertöötlemisel saadud kõvasulampulbrist ning kroomkarbiidse kermise jahvatamisel saadud kermispulbrit kasutati edukalt armeeriva materjalina raudmaatriksiga pihustuspinnete saamisel. Raua olemasolu desintegraatorjahvatuse teel saadud pulbrites polnud probleemiks Fe-baasil maatrikspulbri kasutamisel.

Märksõnad: volfram- ja kroomkarbiid, mehaaniliselt aktiveeritud termosüntees, mehaaniline desintegraatorjahvatus, kiirleekpihustus, abrasiivkulumiskindlus

PAPERS

PAPER I

Sarjas, H., Kulu, P., Juhani, K., Viljus, M, Marikainen, V., Vuoristo, P. (2016) Wear resistance of HVOF sprayed coatings from mechanically activated thermal synthesised Cr_3C_2-Ni spray powder. *Proc. Estonian Acad. Sci.*, 65(2), 101–106.

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MATERIALS ENGINEERING

Wear resistance of HVOF sprayed coatings from mechanically activated thermally synthesized Cr_3C_2–Ni spray powder

Heikki Sarjas[a*], Priit Kulu[a], Kristjan Juhani[a], Mart Viljus[b], Ville Matikainen[c], and Petri Vuoristo[c]

[a] Department of Materials Engineering, Tallinn University of Technology, Ehitajate tee 5, 19086 Tallinn, Estonia
[b] Centre for Materials Research, Tallinn University of Technology, Ehitajate tee 5, 19086 Tallinn, Estonia
[c] Department of Materials Science, Tampere University of Technology, FI-33101 Tampere, Finland

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Abstract. In the current study a Cr_3C_2–Ni spray powder was produced by mechanically activated thermal synthesis. The following aspects were studied: (a) production and characteristics of spray powders, (b) spraying and characteristics of coatings by HVOF, and (c) abrasive wear resistance. A HVOF spray system Diamond Jet Hybrid 2700 (propane hybrid gun from Sulzer Metco) was used for deposition. Coating thickness was approximately 350–400 µm. The structure and composition of the coatings were determined by SEM and the phase composition by XRD methods. Coating surface hardness and microhardness in the cross-section were measured. Abrasive rubber-wheel wear (ARWW) and abrasive erosive wear (AEW) were tested. The wear resistance of the coatings produced from an experimental powder was comparable to that of a similar commercial one.

Key words: chromium carbide, spray powder, mechanically activated thermal synthesis, HVOF spray, wear resistance.

1. INTRODUCTION

Application of the thermal spray technology has been increasing rapidly [1]. Thermal spray processes, especially the high velocity oxy fuel (HVOF) spray, provide excellent wear resistant coatings for different industries like aviation, pulp/paper, oil/gas, and metal processing [2–5]. To ensure competitve advantages and to increase the market share, supporting equipment of thermal spray (manipulating systems, robots, computer controlled systems), better combinations of particle velocity and temperature as well as feedstock powders, which contribute significantly to the running costs, are being developed [6,7]. To increase spraying efficiency and produce dense high quality coatings, desired feedstock materials should be spherical and equally distributed in shape and size [8].

Over the last decades Cr_3C_2 coatings produced by the HVOF spray have become increasingly more popular and exceed WC–Co coatings in industrial areas where heat, oxidation, and corrosion resistance are required. On the other hand, the cost of these feedstock materials is relatively high due to their complex composition. Therefore, the price of powder production may be a factor for selecting other powders or technologies.

Reactive sintering (also called mechanically activated synthesis (MAS) or integrated mechanical and thermal activation (IMTA)) is the process that has been developed and used successfully for producing bulk hardmetal/cermet materials from WC–Co, Cr_3C_2–Ni, and TiC–NiMo with promising results [9–11]. In that process the initial powders are first activated mechanically, for example in a ball mill, and then thermally synthesized by sintering. Carbides are formed during the thermal process, although some formation of carbide can be noticed already in the mechanical activation phase. The purpose of mechanical

* Corresponding author, hsarjas@yahoo.co.uk

activation in powder metallurgy is to use lower sintering temperatures [7].

The aim of this study was to produce Cr_3C_2–Ni spray powders for wear resistant applications via mechanically activated thermal synthesis (MATS) and compare the properties of experimental coatings with similar commercial ones.

2. EXPERIMENTAL MATERIALS AND METHODS

2.1. Powder production and characterization

Experimental spray powders were produced from 99.5% pure chromium (Pacific Particulate Material) with an average grain size 7 μm, carbon black KS6, and nickel powders with a particle size 2–3 μm. A mixture consisting of 11.45 wt% C, 20 wt% Ni, and 68.55 wt% Cr was prepared. The selected carbon content and temperature were to help avoid free carbon in the structure after sintering. Powders used for spraying were manufactured according to the procedure shown in Fig. 1. Mechanical activation was conducted in a ball mill in an ethanol environment. The milling time was 72 h, and the ball-to-material ratio was 15 : 1. The mill and the balls were made of WC–Co hardmetal. Thermal synthesis was carried out in a conventional vacuum sintering environment at 1100 °C and holding time of 30 min. It was followed by mechanical milling to obtain feedstock powder with a particle size of 20–63 μm for HVOF deposition.

Powder granularity was determined by a particle size analyser Analysette 3 PRO and the particle shape was determined with a scanning electron microscopy (SEM) apparatus Zeiss EVO MA-15. For X-ray analysis (EDS) an Oxford Instruments INCA Energy system was used. The phase of the synthesized powder was identified using the X-ray diffraction (XRD) method with Cu Kα radiation (Bruker AXS D5005).

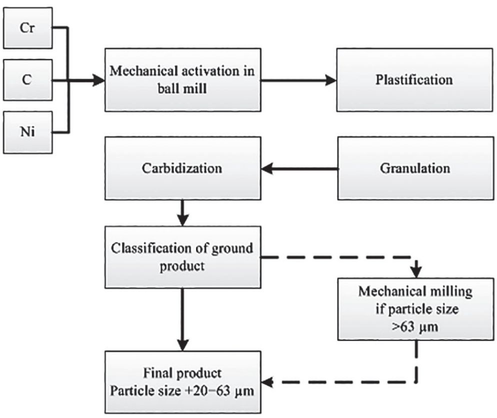

Fig. 1. Powder production via mechanically activated thermal synthesis.

2.2. Spraying of coatings

Carbon steel C45 with dimensions 100 mm × 25 mm × 5 mm was used as the base material for coatings. Coatings were deposited by a HVOF spray system Diamond Jet Hybrid 2700 (propane hybrid gun from Sulzer Metco) from Tampere University of Technology. The commercial powder Cr_3C_2–25NiCr (Amperit 588.074), widely used in industrial wear resistance applications, was selected as a reference. The parameters of the HVOF spray are shown in Table 1. Prior to spraying, the steel substrates were grit blasted by using alumina with mesh 36 to improve coating adhesion. Coatings were deposited layer by layer (about 50 μm per pass) to obtain the final coating thickness of 400 μm.

2.3. Microstructure and hardness of coatings

Polished coating cross-sections were subjected to optical microstructural examination by a light microscope (OM) using an Omnimet image analysis system and SEM Zeiss EVO MA-15. The Oxford Instruments INCA Energy system was used for EDS to estimate the composition of coatings.

Surface Vickers hardness (HV) measurements were performed at a load of 9.8 N (1 kgf). Microhardness in the cross-section was measured using a Matsuzawa MMT-X device at a load of 2.94 N (300 gf). This load was selected to obtain the size of indents comparable with the sizes of the hard phase in the composite. On both occasions, Vickers indentor was used and the standard deviation (STD) of the measurements was calculated.

2.4. Abrasive wear testing

The coatings were tested for abrasion based on the abrasive rubber-wheel wear (ARWW) test. The diameter of the ring was 228.6 mm, the applied force 130 N, the feed rate of the abrasives 330 g/min, and the speed of rotation 200 1/min (linear velocity 2.4 m/s). The testing time was 5 min.

The abrasive erosive wear (AEW) of the coatings was tested at the impact angles 30° and 90°. The velocity

Table 1. Spraying parameters

Parameter	Value
Propane flow, L/min	68
Oxygen flow, L/min	240
Air flow, L/min	383
Carrier gas flow, L/min	12.5
Powder feed rate, g/min	60
Spray distance, mm	230

of abrasive particles was 80 m/s and the feed rate of abrasives was 600 g/min. The testing time was 10 min.

Quartz sand with a particle size of 0.1–0.3 mm was used as the abrasive. The relative volumetric wear resistance to steel C45 (normalized, 200 HV30) was calculated at ARWW and AEW based on the volume wear rates of the reference steel C45 and the studied coatings.

3. RESULTS AND DISCUSSION

3.1. Characterization of spray powder

Powder particles produced by MATS and then mechanically milled were irregular in shape and size (Fig. 2). In addition to particles of 20–63 μm, the powder contained very small particles coming from mechanical milling. The same effect was observed in an earlier study with WC–Co powders [12].

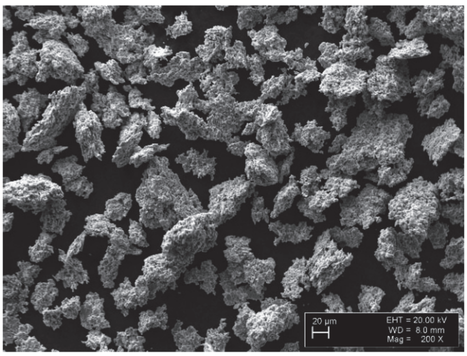

Fig. 2. Shape and size of powder particles produced by MATS.

On the XRD patterns two main phases Ni and Cr_3C_2 were identified (Fig. 3). Some of the spectrum peaks are somewhat broadened, giving evidence of residual stresses and crystal lattice defects. Quantitative composition of the powder was also calculated from the XRD patterns. The results are presented in Table 2.

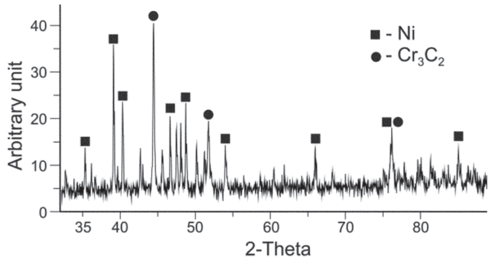

Fig. 3. XRD patterns of Cr_3C_2–20Ni powder produced by MATS.

Table 2. Composition of Cr_3C_2 based spray powders

Type of powder	Chemical composition, %			Particle size, μm
	Cr_3C_2	Ni	Cr	
Experimental Cr_3C_2–20Ni	75.7	22.7	1.5	+20–63
Reference Cr_3C_2–25NiCr (Amperit 588.074)	75	25		+15–45

3.2. Characterization of HVOF coatings

The thickness of the sprayed coatings determined by the SEM analyses of the cross-section of the investigated images was in the range 350–400 μm (Fig. 4). Micro-

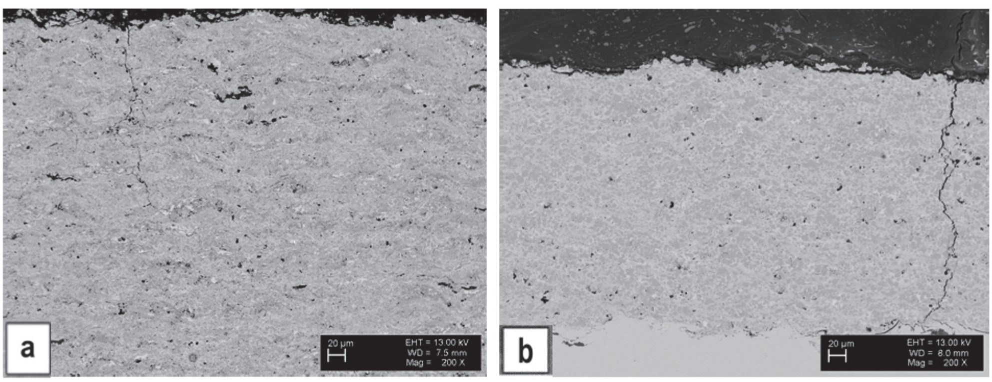

Fig. 4. Coating structures: (a) Cr_3C_2–Ni; (b) Amperit 588.074.

hardness of the sprayed coatings was the same for experimental and reference coatings. However, the surface hardness of the experimental coating was around 1.5 GPa lower than that of the commercial coating (Table 3) due to a softer matrix (Ni vs NiCr, respectively).

3.3. Abrasive wear resistance of coatings

3.3.1. Wear resistance

Table 4 shows the results of abrasive wear tests. At the ARRW test, the experimental coating showed 7.7 times higher wear resistance than the reference steel C45 and its resistance was almost the same as that of the coating produced from the commercial powder (Table 4).

At the low impact angle AEW test ($\alpha = 30°$), the wear resistance of the experimental coating was 1.5 times as high as that of steel C45 and approximately the same as that of the commercial reference coating Amperit 588.074 (Fig. 5). However, in the high impact angle AEW test ($\alpha = 90°$), both the experimental and the commercial coating showed poor results compared to the reference steel C45. This agrees with the results of earlier studies of AEW [13].

3.3.2. Wear mechanism

Due to grinding in the wearing-in stage of the ARWW test, smoothing of the surface takes place. As it follows from the topographical image (Fig. 6), some wear traces can be seen in the area of pores and/or inclusions.

Topographical images of the eroded surfaces of the experimental coating at a low impact angle ($\alpha = 30°$) and at a normal impact angle ($\alpha = 90°$) are shown in Fig. 7a and 7b, respectively. As can be seen, differences in the wear mechanism at the studied impact angles are insignificant. At the low impact angle, the traces of microcutting (Fig. 7a) and at the normal impact angle, some ploughing of the surface and traces of direct removal of hard particles can be seen (Fig. 7b).

Table 3. Thickenss and hardness of HVOF sprayed coatings

Type of coating	Thickness, μm	Vickers hardness HV, GPa	
		Surface	Cross-section
		HV1	HV0.3
Experimental Cr_3C_2–20Ni	400	7.3 ± 0.80	10.1 ± 1.48
Reference Cr_3C_2–25NiCr	350	9.6 ± 1.08	10.1 ± 1.22

Table 4. Wear rates at ARWW and AEW tests of HVOF coatings

Type of coating	Wear rate, mm^3/kg	
	ARWW	AEW 30°/90°
Experimental Cr_3C_2–20Ni	2.1	24.9/93.1
Reference Cr_3C_2–25NiCr	2.0	22.1/64.3
Reference C45	29.4	35.7/27.2

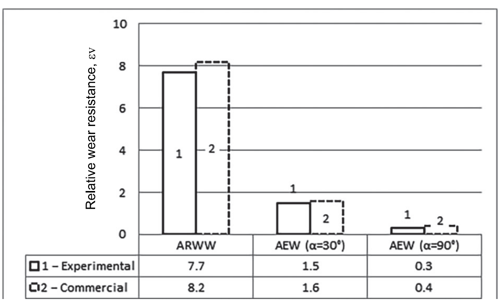

Fig. 5. Relative wear resistance of sprayed coatings to steel C45.

4. CONCLUSIONS

- The results of the study of powder production demonstrated that the mechanically activated thermal synthesis (MATS) technology can be used to produce feedstock materials for the HVOF spray.
- The HVOF sprayed coatings obtained from the experimental powder are competitive with the coatings from analogous commercial powders: the microhardness of the experimental coating was the same as that of a similar commercial powder.
- In the wear tests, the results of the experimental coatings were relatively similar to those of the coatings produced from the commercial powder.

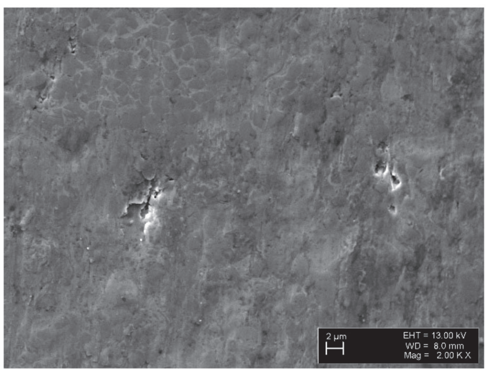

Fig. 6. Topography of the wear surface after ARWW of Cr_3C_2–Ni.

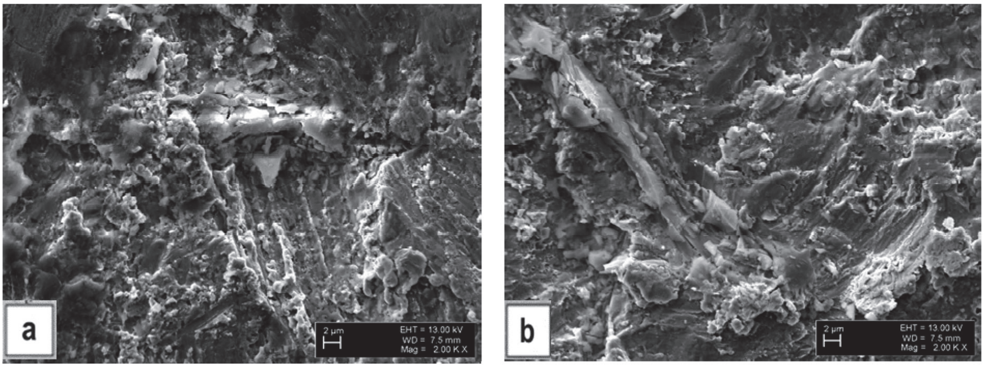

Fig. 7. Topography of eroded experimental Cr_3C_2–20Ni coatings: (a) α = 30°; (b) α = 90°.

- In the wear studies the coatings from the experimental powder showed better results at abrasion than steel C45. At abrasive erosion, the wear resistance of the experimental and commercial coatings was slightly higher at a low impact angle wear as compared to steel C45; at a normal impact angle, the HVOF sprayed coatings studied did not work: their relative wear resistance was about 0.3–0.4.

ACKNOWLEDGEMENTS

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Mehhanoaktiveeritud termosünteesitud kulumiskindlad pinded Cr_3C_2–Ni pihustuspulbritest

Heikki Sarjas, Priit Kulu, Kristjan Juhani, Mart Viljus,
Ville Matikainen ja Petri Vuoristo

Kroomkarbiidi baasil kiirleekpihustuspinded on volframkarbiidsete kõrval leidmas üha laiemat kasutust eelkõige valdkondades, kus kuumus- ja korrosioonikindlus on olulised. Kuid tulenevalt keerulisest koostisest on nimetatud pulbrid kallid.

Käesoleva uuringu eesmärgiks on alternatiivmeetoditega saadud pinnete saamine. Need on omadustelt võrreldavad tööstuslikult toodetavatest pulbritest pinnetega.

Lähtekomponentideks Cr_3C_2–Ni kermispulbri saamisel olid Cr, C ja Ni, saamismooduseks mehaaniliselt aktiveeritud termosüntees (*mechanically activated thermal synthesis*, MATS). Töös vaadeldi järgmisi küsimusi: a) pulbri saamine ja iseloomustamine, b) pinnete pihustamine ja omaduste uuring, c) pinnete abrasiivkulumise uurimine.

Pihustamiseks kasutati kiirleekpihustussüsteemi Diamond Jet Hybrid 2700 (Sulzer Metco propaan-hübriidseade). Pinnete paksus oli vahemikus 350–400 µm. Pinnete struktuuri ja koostist uuriti SEM- ning XRD-meetoditega ja määrati pinde pinna kõvadus ning mikrokõvadus ristlõikes. Pindeid uuriti abrasiiv- ja erosioonkulumise tingimustel. Saadud eksperimentaalpinnete kulumiskindlus oli võrreldav tööstuslikest pulbritest pihustatud pinnetega.

PAPER II

Goljandin, D., Sarjas, H., Kulu, P., Käerdi, H., Mikli, V. Metal-matrix hardmetal/cermet reinforced composite powders for thermal spray. *Material Science (Medžiagotyra)* 18(1), 2012, 84–89.
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Metal-Matrix Hardmetal/Cermet Reinforced Composite Powders for Thermal Spray

Dmitri GOLJANDIN [1] *, Heikki SARJAS [1], Priit KULU [1], Helmo KÄERDI [2], Valdek MIKLI [3]

[1] Department of Materials Engineering, Tallinn University of Technology, Ehitajate tee 5, 19086 Tallinn, Estonia
[2] Chair of Engineering and Mathematics, Estonian Academy of Security Sciences, Kase 61, 12012 Tallinn, Estonia
[3] Centre for Materials Research, Tallinn University of Technology, Ehitajate tee 5, 19086 Tallinn, Estonia

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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.

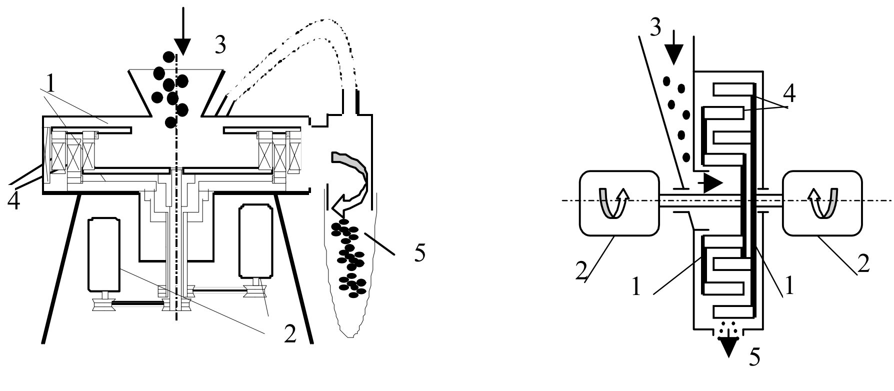
For producing high-quality powders and coatings, the shape and size of particles in production process must be well controlled. Usually, spherical and homogenous powders with high flowability are preferred. The size of powder articles can be determined by image or sieving analyses. Another important 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.

*Corresponding author. Tel.: + 372-6203357; fax.: + 372-6203196.
E-mail address: *goljandin@email.ee* (D. Goljandin)



a b

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

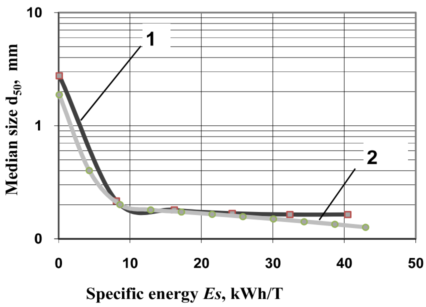


Fig. 2. Dependence of the hardmetal powder particle median size$_{d50}$ on the specific energy of intermediate direct multi-stage milling. Grindability curves of materials: 1 – (Cr_3C_2-Ni); 2 – (WC-Co)

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

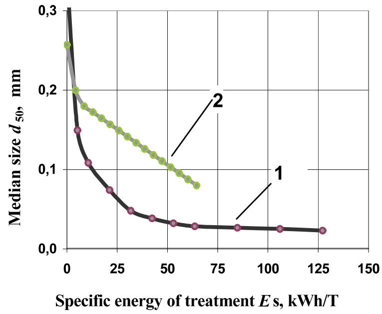
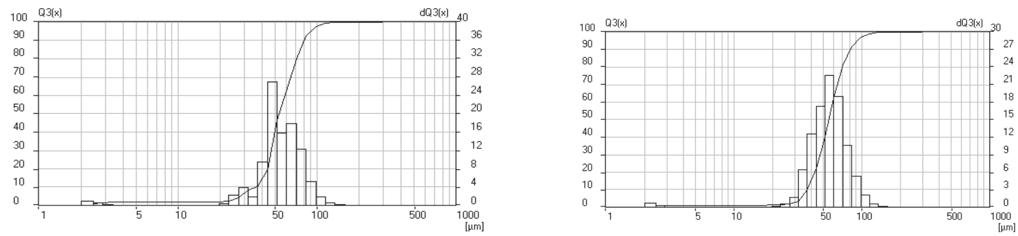


Fig. 3. Dependence of the median particle size$_{d50}$ on the specific energy of final multi-stage milling. Grindability curves of materials: 1 – (Cr_3C_2-Ni); 2 – (WC-Co)

brittleness of WC-Co. Fig. 5, a and b, shows the particle size distribution of a ground product.

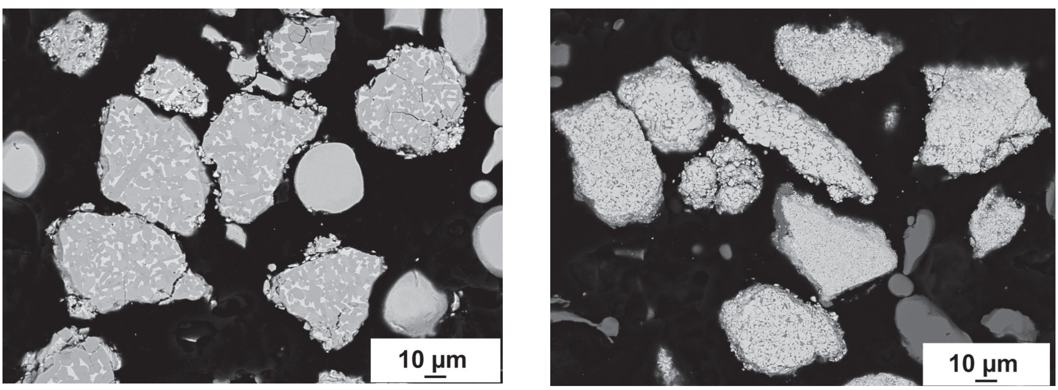
Chemical analysis of the recycled hardmetal powders for thermal spray by EDS showed that about 75 % of powders are carbides (WC-Co; Cr_3C_2-Ni;) (Table 2). Relatively high amount of iron in WC-Co powder has came from milling process (Table 2).

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).

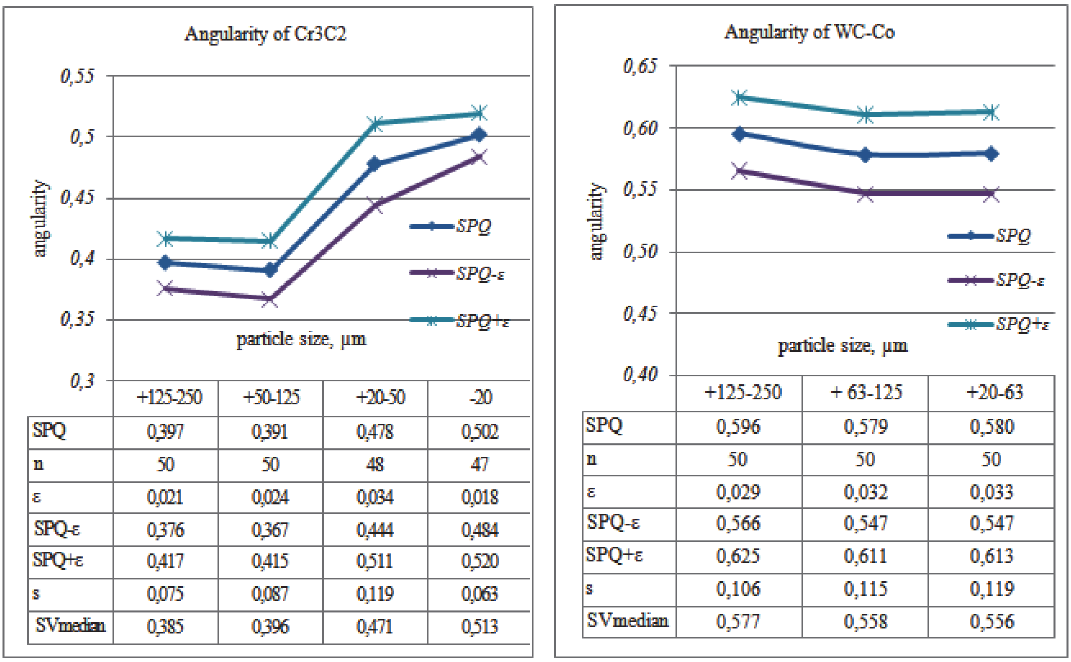
Table 3. Flowability of different spray powders

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



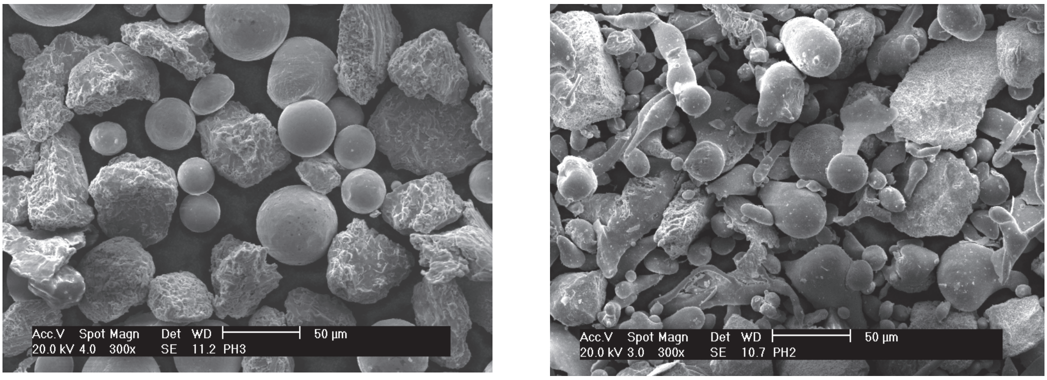
	+125-250	+50-125	+20-50	-20
SPQ	0,397	0,391	0,478	0,502
n	50	50	48	47
ε	0,021	0,024	0,034	0,018
SPQ-ε	0,376	0,367	0,444	0,484
SPQ+ε	0,417	0,415	0,511	0,520
s	0,075	0,087	0,119	0,063
SVmedian	0,385	0,396	0,471	0,513

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

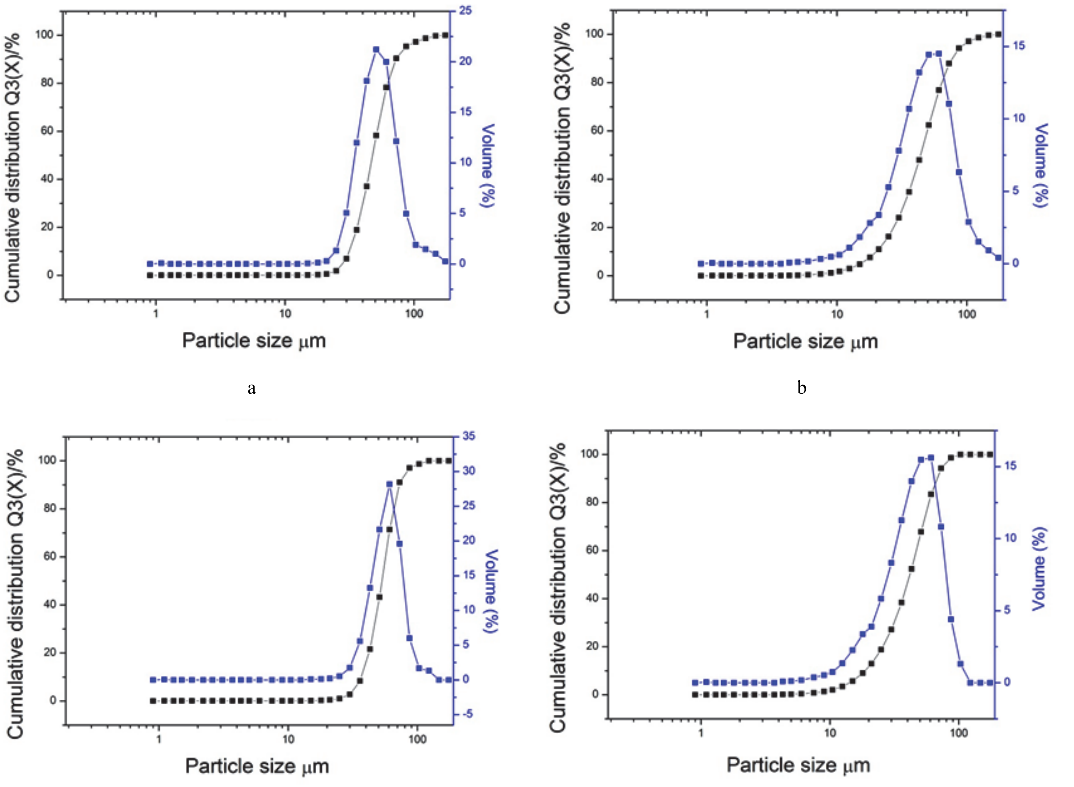
b

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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PAPER III

Sarjas, H., Goljandin, D., Kulu, P., Mikli, V., Surženkov, A., Vuoristo, P. (2012). Wear resistant thermal sprayed composite coatings based on iron self-fluxing alloy and recycled cermet powders. *Materials Science (Medžiagotyra)*, 18(1), 34 – 39.
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Wear Resistant Thermal Sprayed Composite Coatings Based on Iron Self-Fluxing Alloy and Recycled Cermet Powders

Heikki SARJAS [1] *, Dmitri GOLJANDIN [1], Priit KULU [1], Valdek MIKLI [2], Andrei SURŽENKOV [1], Petri VUORISTO [3]

[1] *Department of Materials Engineering, Tallinn University of Technology, Ehitajate tee5, 19086 Tallinn, Estonia*
[2] *Centre for Materials Research, Tallinn University of Technology, Ehitajate 5, 19086 Tallinn, Estonia*
[3] *Tampere University of Technology, Department of Materials Science, FI-33101 Tampere, Finland*

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Thermal spray and WC-Co based coatings are widely used in areas subjected to abrasive wear. Commercial cermet thermal spray powders for HVOF are relatively expensive. Therefore applying these powders in cost-sensitive areas like mining and agriculture are hindered. Nowadays, the use of cheap iron based self-fluxing alloy powders for thermal spray is limited. The aim of this research was to study properties of composite powders based on self-fluxing alloys and recycled cermets and to examine the properties of thermally sprayed (HVOF) coatings from composite powders based on iron self-fluxing alloy and recycled cermet powders (Cr_3C_2-Ni and WC-Co). To estimate the properties of recycled cermet powders, the sieving analysis, laser granulometry and morphology were conducted. For deposition of coatings High Velocity Oxy-Fuel spray was used. The structure and composition of powders and coatings were estimated by SEM and XRD methods. Abrasive wear performance of coatings was determined and compared with wear resistance of coatings from commercial powders. The wear resistance of thermal sprayed coatings from self-fluxing alloy and recycled cermet powders at abrasion is comparable with wear resistance of coatings from commercial expensive spray powders and may be an alternative in tribological applications in cost-sensitive areas.
Keywords: hardmetals, recycling, HVOF, composite coatings, wear resistance.

INTRODUCTION

Thermally sprayed coatings are widely used in areas where high wear and corrosion resistance are required [1]. Hence, thermally sprayed coatings are not the cheapest solution due to relatively expensive equipment and running costs, especially powders [2, 3]. Rapidly increasing raw material prices won't be giving any benefit as well [4]. Therefore, use of HVOF technology is limited due to economical reasons. From that point of view recycling materials for thermal spray powders, especially carbides, could give reasonable results [5, 6].

However, pure carbide based coatings, due to brittleness, do not perform well in impact loading conditions [7]. Therefore, there is a need for a tough matrix material with relatively high hardness and low cost. Only iron based alloys meet all these requirements [8]. Up to date, iron based self-fluxing alloys are relatively less studied than nickel based self-fluxing alloys, but are cheaper and harder.

The aim of this study was (a) to investigate the properties of iron based self-fluxing alloys reinforced with hardmetal/cermet particles in different wear conditions (abrasion and solid particle erosion wear), (b) to investigate the structure and hardness of sprayed coatings.

*Corresponding author. Tel.: +372-620-3470; fax.: +372-620-3196.
E-mail address: *heikki.sarjas@ttu.ee* (H. Sarjas)

EXPERIMENTAL DETAILS

As a substrate material carbon steel C45 with dimensions 100 mm × 25 mm × 5 mm was used. The chemical composition and hardness are shown in Table 1.

Table 1. Chemical composition and hardness of steel C45

Grade of steel	Composition, wt %	Hardness HV1	
		as normalised	as hardened
C45	0.45 C; 0.60 Mn; 0.30 Si	200 – 235	300 – 310

Chemical composition of used powders, both self-fluxing alloys and recycled hardmetal are shown in Table 2. From that powders four different powder compositions were mixed containing 60 vol% self-fluxing alloys as metallic matrix and 40 vol% hardmetal/cermet particles as reinforcement produced by mechanical milling. WC-Co recycled hardmetal powder produced by mechanical milling, causes high iron content in the powder due to the intensive wear of the grinding media as can be seen from Table 2 [9, 10].

Fig. 1 illustrates the particle shape and size distribution of typical mechanically milled hardmetal. The powder particles of chromium carbide cermet were primarily equiaxed in form. The shape of WC-Co was more angular.

Table 2. Chemical composition and particle size of the used self-fluxing alloy and hardmetal/cermet powders

Type of powder	Composition, wt %						Particle size, µm
	Cr	Si	B	C	Ni	Fe	
NiCrSiB*	7.5	3.5	1.6	0.25	bal	2.5	–53 +15
FeCrSiB*	13.7	2.7	3.4	2.1	6	bal	–45 +10
Cr_3C_2-Ni**	78 Cr3C2; 2.5 W				14	3.1	–50 +20
WC-Co**	75.6 WC; 11.5 Co					12.9	–50 +20

* Produced by Höganäs.
** Experimental TUT.

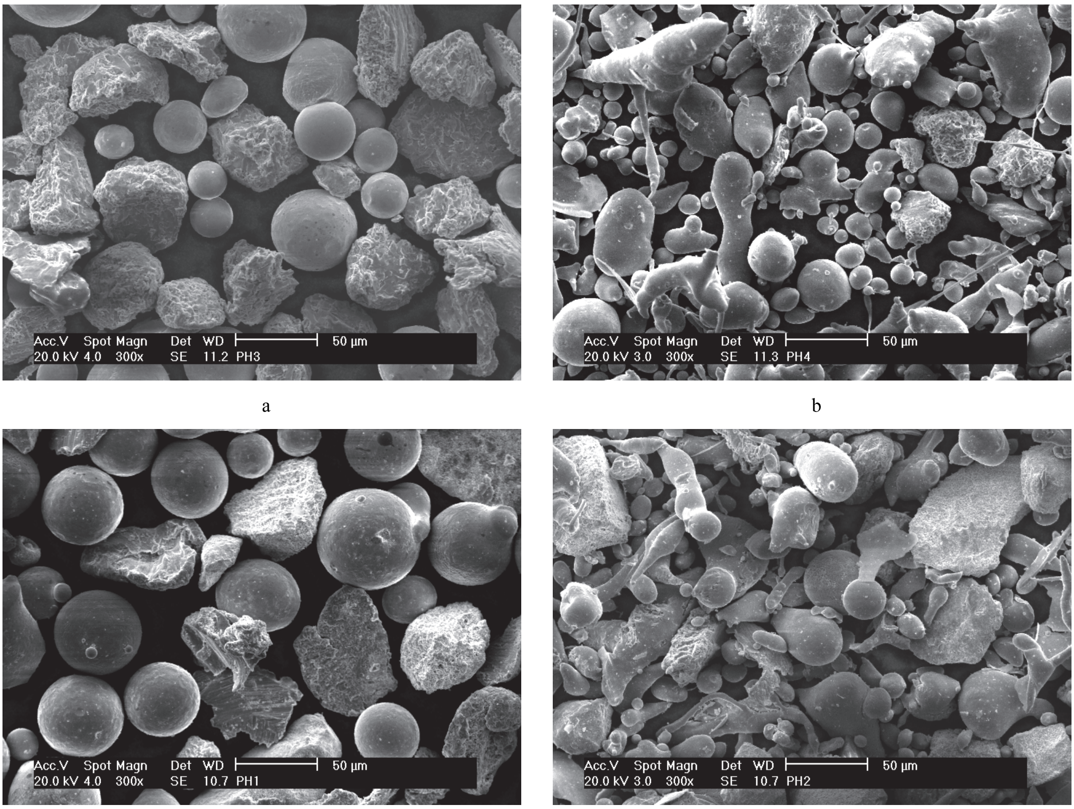

Fig. 1. Micrographs of composite spray powders: a – (Cr_3C_2-Ni)+FeCrSiB; b – (Cr_3C_2-Ni)+NiCrSiB, c – (WC-Co)+FeCrSiB, d – (WC-Co)+NiCrSiB

For deposition of coatings High Velocity OxyFuel (HVOF) spray system Diamond Jet Hybrid 2700 (propane hybrid gun from Sulzer Metco) was used. Parameters of HVOF spray are shown in Table 3.

Polished cross-sections of coatings were observed by light microscope using Omnimet image analysis system and SEM Zeiss EVO MA-15. X-ray analysis (EDS) was performed on Oxford Instruments INCA- Energy system for estimation of the changes in composition of metal matrix.

Surface hardness measurements were performed with universal hardnessmeter Zwick 2.5/TS at load 10 N (1 kgf). Load was selected to obtain the size of indents comparable with sizes of hard phase in the compostie.

For measuring microhardness in cross-section Micromet 2001 was used. The applied load was 2.45 N (300 gf).

Sprayed coatings were tested at two different wear conditions including abrasion (abrasive rubber-wheel wear) and abrasive-erosive wear (AEW).

Table 3. Parameters of HVOF spraying process

Parameter	Value
Propane flow, l/min	68
Oxygen flow, l/min	240
Air flow, l/min	375
Spray distance, mm	250
Surface speed, m/min	120
Distance between passes, mm	6
Powder feed rate, g/min	40
Number of passes	40 30 for (Cr3C2-Ni+FeCrSiB)

Abrasive wear tests were carried out using the block-on-ring rubber wheel (ABRW) scheme (ASTM standard G 65-94) (Fig. 2, a). The diameter of the ring was 228.6 mm, the applied force 130 N, feed rate of abrasives 330 g/min and the speed of rotation 200.8 1/min (linear velocity 2.4 m/s). Testing time was 5 min. The parameters of wear tests are shown in Table 4.

The mass loss of the specimens at ABRW was determined and the wear coefficient calculated as

$$k = \frac{\Delta m}{\rho \cdot F \cdot t \cdot v \cdot r}, \qquad (1)$$

where Δm is the mass loss, kg; ρ is the density, kg/m^3; F is the force, N; t is the time of the experiment, s; v is the rotation speed 1/min; r is the radius of the ring, m.

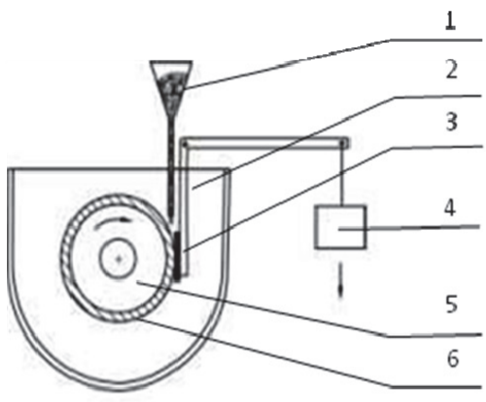

Fig. 2. Principal scheme of block-on-ring wear tester: 1 – abrasive particle vessel; 2 – specimen holder; 3 – specimen; 4 – weights; 5 – steel wheel; 6 – rubber wheel

Abrasive erosive wear (AEW) of coatings was studied by the experimental centrifugal-type wear testers CAK (Fig. 3). The velocity of abrasive particles was 80 m/s, impact angles 30° and 90°. Wear experiments at ABRW and AEW with quartzite sand of fraction 0.1 mm – 0.3 mm were carried out. Hardness of the quartz, measured at the cross-section polishes, was 11.0 HV 0.05 GPa.

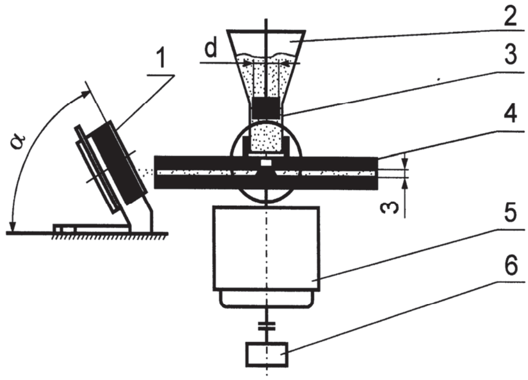

Fig. 3. Principal scheme of block-on-ring wear tester: 1 – specimen; 2 – abrasive particles vessel; 3 – shield; 4 – rotor; 5 – drive motor; 6 – rotation frequency gauge

At AEW the mass loss of the specimens was determined and the volumetric wear rate I_v was calculated, dividing mass loss by abrasive mass per specimen and material density (Eq. (2)).

$$I_v = \frac{\Delta m}{\rho \cdot q}, \qquad (2)$$

where Δm is the mass loss in mg; q is the quantity of abrasive per specimen in kg; ρ is the sample density, mg/mm^3.

The relative volumetric wear resistance ε_v was determined on steel C45 by the following equation:

$$\varepsilon_v = I_v / I_v^{C45}, \qquad (3)$$

where I_v is the volumetric wear rate of tested coating; I_v^{C45} is the same of reference steel C45.

Table 4. Abrasive wear testing parameters

Type of wear	Velocity, m/s	Abrasive and particles size, mm	Amount of abrasive, kg
Abrasion block-on-ring wear (ABRW)	2.4	Quartz sand 0.1 – 0.3	1.5
Erosion wear (AEW)	80	Quartz sand 0.1 – 0.3	3

RESULTS AND DISCUSSION

Thickness of the coatings determined by SEM cross-section images and presented in Fig. 4 was from 300 µm up to 400 µm. Porosity was between 1 % – 3 %. Coating adhesion with steel substrate was good. Only some small pores and SiO_2 particles were found in the border between steel and coating. As a result of high velocity of deposition the hard phase particles (WC-Co and Cr_3C_2-Ni) were destroyed, elongated in a direction of substrate surface and fractured partially (first of all more brittle particles of Cr_3C_2-Ni). According to EDS analysis (Fig. 4, windows and Table 5) the obtained coatings consist mainly of the initial phases – WC-Co, Cr_3C_2-Ni, FeCrSiB and NiCrSiB respectively. Additionally, some Fe areas were found primarily in coatings consisting of WC-Co formed in hardmetal powder production process.

The hardness measurements of surface hardness as well as microhardness of the coating showed that Fe-based self-fluxing alloy matrix proved to be slightly harder than ones of Ni-based self-fluxing alloys as expected. The relationship of harder matrix–higher abrasive wear resistance was proved (Table 7). Hardness of reinforcement particles was from 7.6 – 9.2 and 8.5 – 12.6 for Cr_3C_2-Ni and WC-Co respectively. Impact of harder reinforcement materials on ABRW wear was moderate (Table 7).

Table 5. Detected phases in coatings (Fig. 4)

Composition of spray powders	Phases by EDS analysis			
	1	2	3	4
Cr_3C_2-Ni+FeCrSiB	Cr_3C_2	Ni	FeCrSiB	–
Cr_3C_2-Ni+ NiCrSiB	Cr_3C_2	Ni-Cr	NiCrSiB	Fe
WC-Co+FeCrSiB	WC	Co	FeCrSiB	Fe
WC-Co+NiCrSiB	WC	Co	NiCrSiB	Fe

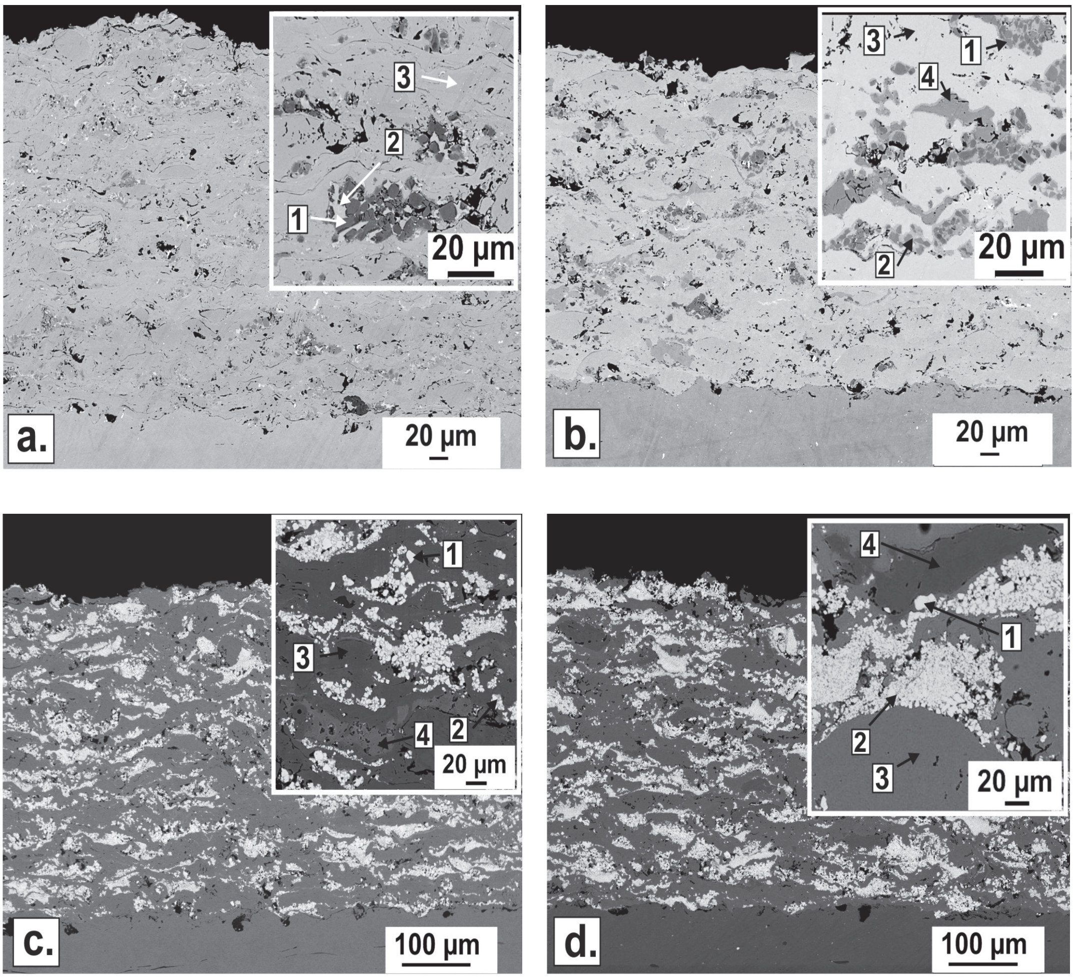

Fig. 4. Coatings cross-sections and EDS phasemaps (window areas): a – (Cr_3C_2-Ni)+FeCrSiB; b – (Cr_3C_2-Ni)+ NiCrSiB; c – (WC-Co)+FeCrSiB; d)– (WC-Co)+NiCrSiB

The predominant wear mechanism at abrasion is the loss of the softer matrix phase and often leads to the loss of hard phase (Fig. 5). Results of abrasion of coatings tested at ABRW showed 1.5 – 2.7 times better wear resistance than reference material steel C45 (Table 7). The relative wear resistance of Fe self-fluxing alloy based and hardmetal/cermet consisting hardphase coatings compared with Ni-based reference coating proved to have slightly higher wear resistance.

Erosion resistance of coatings proved to be quite poor at 30° angle and extremely low at 90° angle (Table 8). It can be explained with fracture of hard phase, first of all Cr_3C_2 particles at high energy spray process as it follows from the structure studies (see Fig. 4). Wear at high and low velocity and at high impact angles from carbide based particles fracture or removal at sprayed matrix metal microparticles due to low-cycle fatique process (see Fig. 5) [11].

Table 6. Hardness of sprayed coatings

Composition of coatings	Thickness, µm	Hardness HV, GPa	
		Surface	Matrix / reinforcement
		HU	HV1
Cr3C2-Ni+ FeCrSiB	300	3.5 – 4.3	4.9 – 5.9/7.6 – 8.3
Cr3C2-Ni+NiCrSiB	400	3.2 – 3.8	4.4 – 5.1/8.0 – 9.2
WC-Co+FeCrSiB	400	4.3 – 5.0	4.7 – 5.6/8.5 – 12.6
WC-Co+NiCrSiB	400	2.9 – 3.5	4.8 – 5.2/8.8 – 12.6

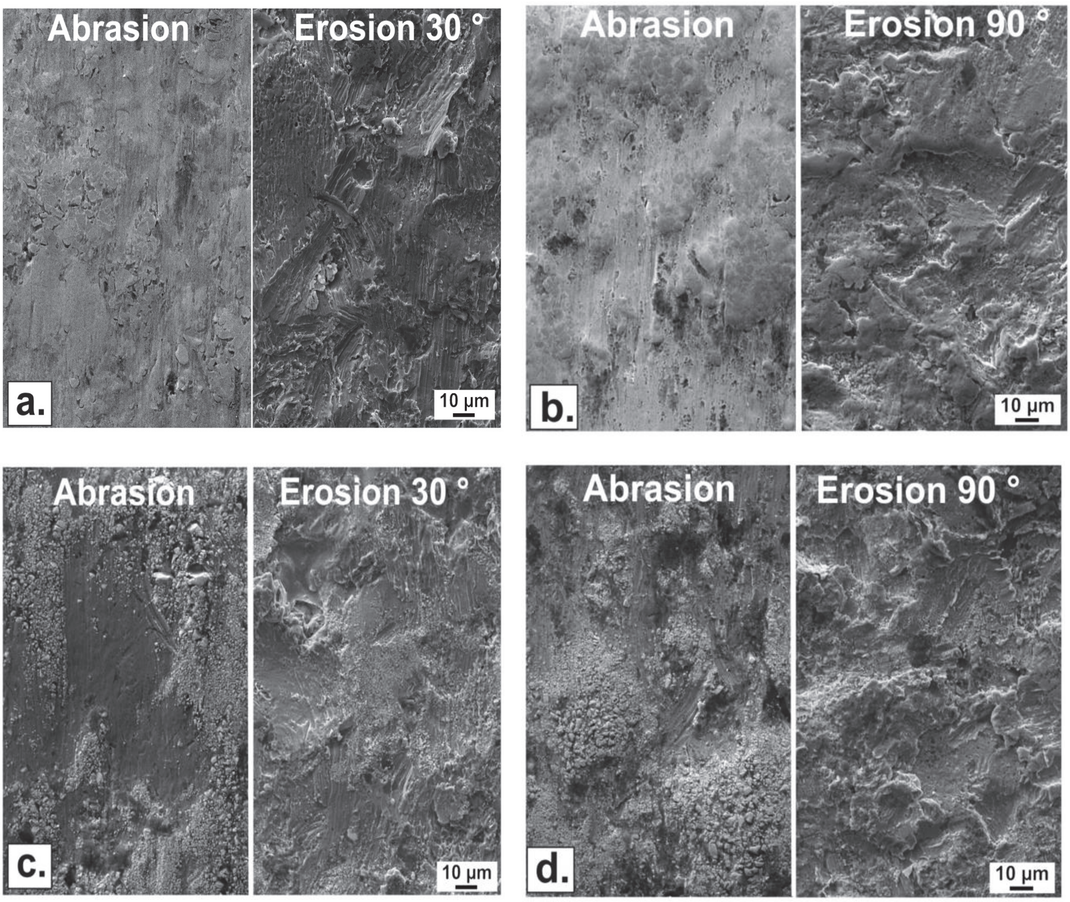

Fig. 5. Worn surfaces of the coatings after abrasive wear: a – (Cr_3C_2-Ni)+ FeCrSiB; b – (Cr_3C_2-Ni)+ NiCrSiB; c – (WC-Co)+ FeCrSiB; d – (WC-Co)+ NiCrSiB

Table 7. Abrasion resistance of tested coatings

Material	Wear coefficient K, $mm^3/Nm\ 10^{-5}$	Relative wear resistance to ε_v
Cr3C2-Ni+FeCrSiB	10.0	2.2
Cr3C2-Ni+NiCrSiB	14.0	1.6
WC-Co+FeCrSiB	8.3	2.7
WC-Co+NiCrSiB	11.1	2.0

Table 8. Erosion wear resistance of coatings

Material	Volumetric wear rate I_v , mm^3/kg	Relative wear ε_v resistance
	30°/90°	30°/90°
Cr3C2-Ni+ FeCrSiB	47 / 125	0.8 / 0.2
Cr3C2-Ni+ NiCrSiB	46 / 100	0.8/ 0.2
WC-Co+ FeCrSiB	31 / 78	1.2 / 0.3
WC-Co+ NiCrSiB	34 / 79	1.1 / 0.3

CONCLUSIONS

1. High Velocity deposition of Fe and Ni matrix based hardmetal/cermet hardphase consisting coatings leads to formation of high defective lamellar structure.
2. Wear resistance at abrasion of Fe-based matrix coating with WC-Co reinforcement is three times higher and depends primarily on the microhardness of surface, caused by hardphase content in coating (needs further study).
3. Abrasive impact wear resistance at erosion of studied composite coatings is low due to high defective of the hardphase in coatings and high energy of impact (at velocity of 80 m/s.

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PAPER IV

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Novel WC-Co Spray Powders and HVOF Sprayed Coatings on their Bases

H. Sarjas*, P. Kulu, K. Juhani,
Department of Materials Engineering,
Tallinn University of Technology,
Ehitajate tee 5, 19086 Tallinn, Estonia.

P. Vuoristo
Department of Materials Science,
Tampere University of Technology,
Fi-33101 Tampere, Finland.
*Email: heikki.sarjas@yahoo.co.uk

Abstract

Coatings produced by HVOF spray have become more popular over last decades and are used in industrial areas where high wear resistance is needed. However, relatively high cost of feedstock materials is hindering the use of HVOF sprayed coatings more widely than of today.

The aim of the current study is to produce spray powders and wear resistant spayed coatings from them, whose properties are comparable to coatings produced from industrially manufactured powders. As feedstock materials for WC-Co hardmetal powders produced by mechanically activated synthesis (MAS) W, Co and C were used. The following aspects were studied: (a) production and characterization of spray powders, (b) spraying of coatings by HVOF and (c) characterization of coatings as structure as well as wear resistance.

For the deposition of the coatings, the HVOF spray system Diamond Jet Hybrid 2700 (propane-hybrid gun from SulzerMetco) was used. Thickness of coatings was approximately 250–300 μm.

The structure and composition of the coatings was determined by SEM and XRD methods, surface hardness and constituents of coatings were measured. Abrasive rubber-wheel wear according to standard ASTM standard G65 and abrasive erosive wear tests were performed. Wear resistance of coatings produced form experimental powders was compared to similar industrial ones.

1.0. Introduction

Thermal spray technology popularity and annual turnover has increased rapidly over long period and they are expected to do so in future as well[1,2]. Different thermal spray processes offer high throughput, are simple to operate and versatile, which gives clear advantages over competing technologies[3]. One of main areas of application for HVOF sprayed coatings are wear and corrosion protection (or wear + corrosion) for very different industries like aviation, metal processing, petrochemical and pulp/paper industry etc.[4]. Though HVOF spray equipment and accessories are relatively expensive to purchase, running costs, high turnover, greater performance, relatively no waste and longer wear lifetime gives clear economic benefit compared to for example hard chrome plating[5]. However, the fact that around 75% of running costs are coming from feedstock material[6] limits the use HVOF spray.

Reactive sintering (also named Mechanically Activated Synthesis − MAS or Integrated Mechanical and Thermal Activation – IMTA) is the process, which has been developed and used successfully for producing bulk materials from WC-Co with promising results[7]. Feedstock material is produced by activating initial materials at first mechanically and then thermally by sintering. During thermal activation carbides are formed. Mechanical activation enables to use lower sintering temperatures than those of conventional methods[8].

The aim of the study is to produce spray powders for wear resistant applications via IMTA and compare the properties of experimental coatings with similar commercial ones. As a reference, industrially widely used powder for high wear resistance applications, Amperit 558 from HC Stark was selected and coating properties were compared.

2.0. Experimental

2.1. Powder production

As initial materials for producing experimental powders 99.5% pure tungsten carbide (Sylvania Tungsten) with grain size 1−3 μm, carbon black KS6 and cobalt with particle size under 10 μm were used. Chemical composition of feedstock materials are given in Table 1. In the current study two different types of powders consisting 6.2% and 6.7% of carbon were prepared. Carbon content and sintering temperature were selected to avoid free carbon in structure[9]. Powders used for spraying were manufactured according to procedure shown on Fig.1.

Mechanical activation was carried out in ball mill, where milling time was 72 h and ball-to-material (BM) ratio was 7:1. Mill and balls were made of WC-Co hardmetal. Thermal synthesis was done at temperature of 1310°C followed by mechanical milling to achieve feedstock powder with particle size 20−53 μm for spraying via High Velocity Oxy-Fuel (HVOF).

2.2. Spraying of coatings

As a substrate material for spraying carbon steel C45 with dimensions 100x25x5 mm were used. For deposition of coatings HVOF spray system Diamond Jet Hybrid 2700 (propane hybrid gun from SulzerMetco) of Tampere University of Technology was used. Parameters of HVOF spray are shown in Table 2. Prior to spraying the steel substrates were grit blasted by using mesh 36alumina for improved coating adhesion.

Polished cross-sections of coatings were observed by light microscope using Omnimet image analysis system and SEM Zeiss EVO MA-15. X-ray analysis (EDS) was performed on Oxford Instruments INCA-Energy system for estimation of the changes in composition of metal matrix.

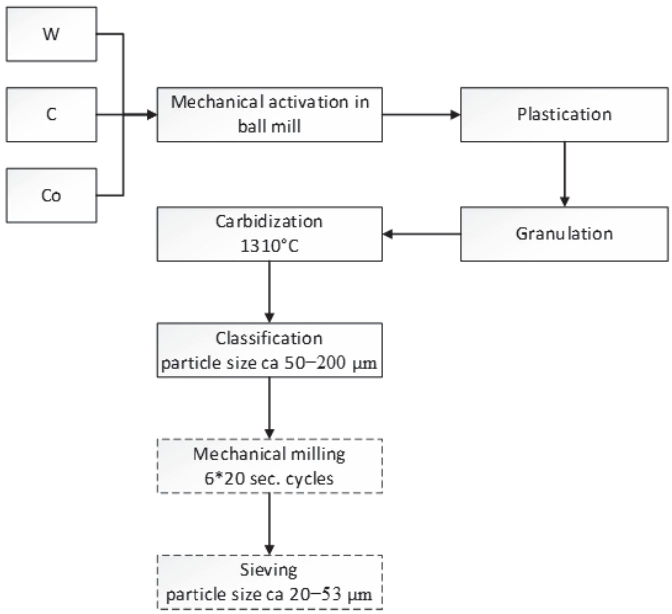

Fig.1: Powder production process via mechanically activated synthesis

Table 1: Chemical composition of studied powders

Type of Powder	Chemical composition, wt%			
	W	C	Co	Cr
Z5	76.8	6.2	17	–
Z6	76.3	6.7	17	–
Amperit 558	bal.	5–6	8.5-11.00	3-5

Table 2: Spraying parameters

Parameter	Value
Propane flow, l/min	68
Oxygen flow, l/min	240
Air flow, l/min	375
Carrier gas l/mim	12.5
Powder feed rate, g/min	60
Spray distance, mm	230

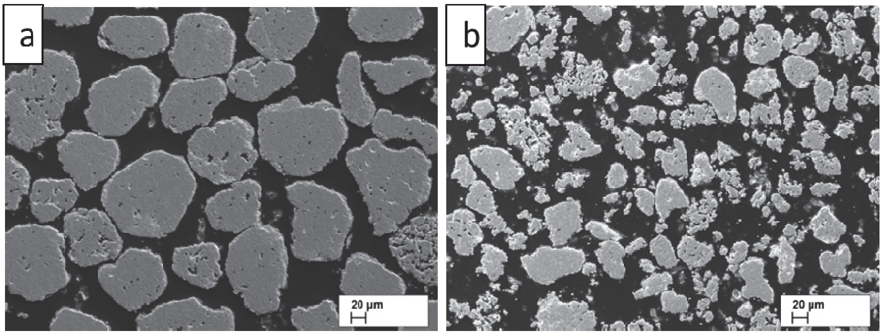

Fig. 2: Particle size and shape **(a)** before and **(b)** after disintegrator milling

2.3. Hardness measurement and wear testing

Surface hardness (HU) measurements were performed with universal hardness meter Zwick 2.5/TS at load 9.8 N (1 kgf). Load was selected to obtain the size of indents comparable with sizes of hard phase in the composite. Microhardness in cross-section was measured using Matsuzawa MMT-X. The applied load was 2.94 N (300gf). On both occasion Vickers indentor was used and standard deviation (STD) of measurements were calculated.

Abrasive wear testing of the coatings was performed using abrasive rubber-wheel wear(ARWW) according to (ASTM standard G 65–94). The diameter of the ring was 228.6 mm, the applied force 130 N, feed rate of abrasives 330 g/min and the speed of rotation 200 1/min (linear velocity 2.4 m/s). Testing time was 5 min.

Abrasive erosive wear (AEW) of the coatings was tested at impact angles 30° and 90° at velocity of abrasive particles speed of 80m/s, feed rate of abrasives 400g/min. Testing time was 5 min.

As abrasive quartz sand with size of 0.1−0.3 mm was used. The relative wear resistance to steel C45 was calculated at ARWW and AEW based on mass loss of specimens before and after wear tests.

3.0. Results and Discussions

3.1. Production of spray powders

Both Z5 and Z6spray powders produced by the IMTA process were spherical in form (Fig. 2(a)). As, the particle size was too coarse (around 50−200 μm), additional size reduction for achieving finer powder was needed. Mechanical size reduction using disintegrator mill was performed[10,11] – particle size of the milled powder was in the range of 20−53 μm. Image analysis with SEM showed that milling had negative effect on powder homogeneity and sphericity, which can be a factor of lower spraying efficiency and therefore coating quality (Fig. 2(b)).

3.2. Sprayed coatings

The thickness of the HVOF-sprayed coatings determined by SEM analyses of cross-section of investigated images was in range of 250−300μm. In general, the coatings were homogeneous, consisting of WC-Co (Fig. 3), only some pores in cross section and small particles of Al_2O3 (used for substrate activation before spraying) was found between substrate and coating.

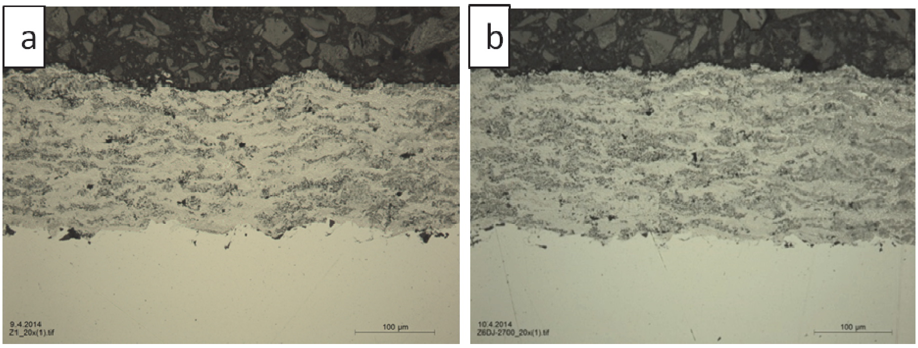

Fig. 3: Coating's structure **(a)** Experimental powder Z5 **(b)** Experimental powder Z6

Table 3: Hardness of sprayed coatings

Composition of coatings	Thickness, µm	Hardess HV, GPa	
		Surface	Cross-section
		HU (STD)	HV0.3(STD)
Z5	250	6.9 (0,66)	9.91 (1,14)
Z6	250	6.2 (0,59)	10.52 (0,58)
Amperit 558	300	7.5 (0,60)	10.64 (1,75)

Table 4: Wear resistance of tested coatings on different conditions

Material	AEW		ARWW	
	Volumetric wear rate I_v mm3/kg	Relative wear ε_v resistance	Wear coefficient K, $mm^3/Nm\ 10^{-5}$	Relative wear resistance to ε_v
	30°/90°	30°/90°		
Z5	14 / 20	2.1 / 1.3	0.42	5.0
Z6	15 / 26	1.9/ 0.7	0.43	5.0
Amperit 558	7 / 8	4.6/ 3.3	0.18	11.7

3.3. Characterization of coatings

Microhardness in cross-section and surface hardness was roughly the same for all sprayed coatings, reference material Amperit 558 showed only slightly higher results (Table 3).

Results of abrasive wear tests are given in Table 4. At ARWW experimental coatings Z5 and Z6 both showed 5 times better wear resistance than reference material steel C45. Compared to coating produced from commercial powder (Amperit 558), the wear resistance was about 2 times lower.

At AEW relative wear resistance of experimental coatings compared to steel C45 was approximately 2 times higher at 30° and basically same at 90°. To compare with reference material Amperit 558 coating, the relative wear resistance of experimental coatings was 2–2.5 times lower. As particle size of experimental spray powders is smaller, more homogenuous and spherical, the wear rate is higher as well.

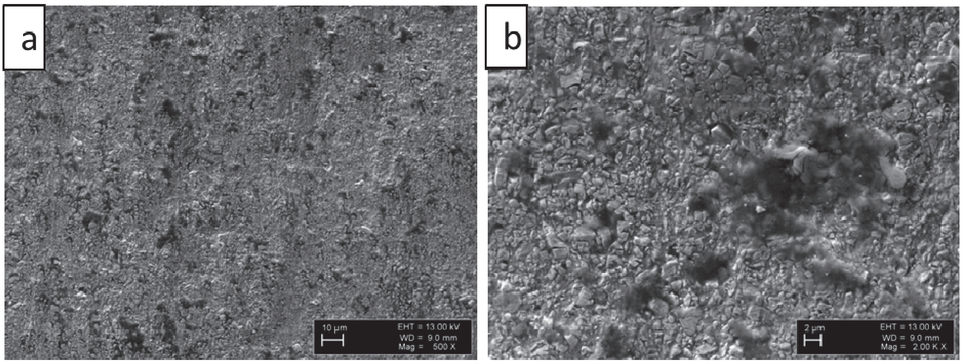

Fig. 4: Abrasive rubber-wheel wearof Z5 at magnification **(a)** 500X **(b)** 2000X

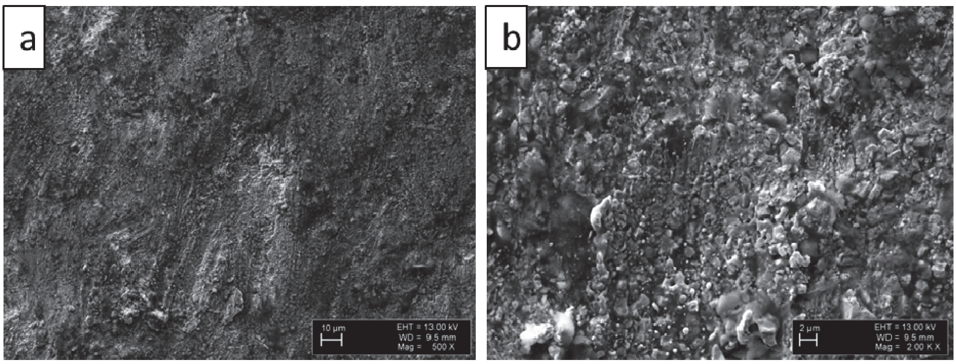

Fig. 5: Abrasive erosive wear of Z5 at 30° at magnification **(a)** 500X **(b)** 2000X

The Dominating wear mechanism at ARWW was removing of hardmetal particles from coating leaving pores on surface (Fig. 4.).

The main wear mechanism at AEW at low impact angle is based on removal of material from surface due to microcutting by abrasive particles and separating carbide particles itself (Fig. 5). At normal impact low-cycle fatigue of material and cracking of hardmetals particles causes the mass loss (Figs. 6(a) and (b)).

4.0. Conclusions

IMTA technology can be used to produce feedstock materials for HVOF spray. However, the limitation of coarse powder should be solved to increase the quality of initial powder for thermal spray.

Surface as well as microhardness of coatings produced by experimental powders is relatively same as similar industrial ones with only slightly lower hardness.

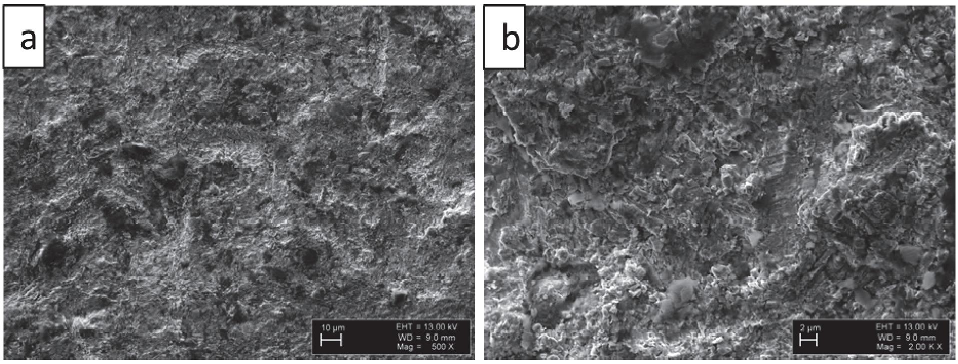

Fig. 6: Abrasive erosive wearof Z5 at 90° at magnification **(a)** 500X **(b)** 2000X

Experimental coatings properties are not influenced by carbon percent in initial powder (expect wear resistance at AEW on 90°).

Lower wear resistance of experimental powders can be explained by lower quality of feedstock material (particle spherity, homogeneity and size), compared to commercial ones.

5.0. Acknowledgements

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CURRICULUM VITAE

1. Personal data

Name	Heikki Sarjas
Date and place of birth	08.07.1984, Rapla, Eesti
Citizenship	Estonian
E-mail	hsarjas@yahoo.co.uk

2. Education

Educational Institute	Graduation year	Education (field of study/degree)
Rapla Ühisgümnaasium	2003	High School
Tallinn University of Technology	2008	Bachelor of Science
Tallinn University of Technology	2010	Master of Science

3. Language competence (basic, average, fluent)

Language	Level
Estonian	Mother Tongue
English	Fluent
Finnish	Basic
Russian	Basic

4. Professional Employment

Period	Organisation	Position
2007	Galvex OÜ	Quality inspector
2008	Tallinn University of Technology	assistant
2010-2013	ABB AS	Quality Assurance Engineer
2013-2014	ABB OY	Quality & Process Development Engineer
2014-2015	ABB AS	Process Engineer
2016-	Ensto Ensek AS	Quality Manager

5. Field of research

Natural Sciences and Engineering. Process Technology and Materials Science (thermal sprayed coatings)

6. Main areas of scientific work

Finished Projects:

ETF7227, Modelling of wear resistance of composite materials and coatings. 2007-2009
SF0140091s08, Hard coatings and surface engineering. 2008-2013.

Publications – 10 (source: www.etis.ee)

ELULOOKIRJELDUS

1. Isikuandmed

Ees- ja perekonna nimi	Heikki Sarjas
Sünniaeg ja -koht	08.07.1984, Rapla, Eesti
Kodakondsus	Eesti
E-posti aadress	hsarjas@yahoo.co.uk

2. Hariduskäik

Õppeasutus	Lõpetamise aeg	Haridus (eriala/kraad)
Rapla Ühisgümnaasium	2003	Keskharidus
Tallinna Tehnikaülikool	2008	Tehnikateaduste bakalaureus
Tallinna Tehnikaülikool	2010	Tehnikateaduste magister

3. Keelteoskus (alg-, kesk- või kõrgtase)

Keel	Tase
Eesti keel	emakeel
Inglise keel	kõrgtase
Soome keel	algtase
Vene keel	algtase

4. Teenistuskäik

Töötamise aeg	Tööandja nimetus	Ametikoht
2007	Galvex OÜ	kvaliteedikontrolör
2008	TallinnaTehnikaülikool	abitööline
2010-2013	ABB AS	kvaliteedi tagamise insener
2013-2014	ABB OY	kvaliteedi ja protsesside arendusinsener
2014-2015	ABB AS	protsessi insener
2016-	Ensto Ensek AS	kvaliteedijuht

5. Teadustegevus

Loodusteadused ja tehnika. Protsessitehnoloogia ja materjaliteadus (termiliselt pihustatud pinded)

6. Uurimisprojektides osalemine

Lõpetatud Projektid:

ETF7227, Komposiitmaterjalide ja -pinnete kulumiskindluse modelleerimine. 2007-2009
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