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Plasma Transferred ARC (PTA) Hardfacing of Recycled Hardmetal Reinforced Nickel-matrix Surface Composites

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The aim of this work was to apply coarse recycled hardmetal particles in combination with Ni-based matrix to produce wear resistant metal matrix composite (MMC) thick coatings using plasma transferred arc hardfacing (PTA) technology. Assignment of hardmetal waste as initial material can significantly decrease the production costs and improve the mechanical properties of coatings and, consequently, increase their wear resistance. The microstructure of MMC fabricated from a recycled powder was examined by optical and SEM/EDS microscopes, whereas quantitative analyses were performed by image analysis method. Micro-mechanical properties, including hardness and elastic modulus of features, were measured by nanoindentation. Furthermore, behaviour of materials subjected to abrasive and impact conditions was studied. Results show the recycled powder provides hardfacings of high quality which can be successfully used in the fabrication of wear resistant MMC coatings by PTA-technology.
Keywords: tribology, hardfacing, recycling carbide, PTA, MMC, wear behaviour, chemical treatment.

1. INTRODUCTION

Tungsten carbide hardmetals are one of the most known and successful powder metallurgical products mainly used for manufacturing of machinery tools, which operate in environments where severe wear conditions prevail. Due to superior properties of tungsten carbide as hardphases in combination with different alloys of Fe, Co or Ni basis, it provides high wear resistance materials used in cutting, mining, drilling tools and other industrial equipment [1 – 3]. However, the high marked requirements lead to permanently increasing price and wastage of cemented tungsten carbide. Therefore research and development on alternative solutions such as reuse or recycling of the hardmetal scrap containing tungsten carbide became significantly important in recent years.

Recycling technology of hardmetal scrap with worn cermets requires applications of different processes for breakup, disjunction and purification of tungsten carbide particles. One of effectively applied mechanical methods for recycling of worn cermets and hardmetal scrap is disintegrator milling [4 – 7], which provides particle powders of uniform size and shape. Also, this method offers some more advantages in preservation the chemical composition and mechanically activation of materials. Received hardmetal powders by application of disintegrator milling process are successfully used in the fabrication of thin protective coatings by HVOF thermal spray technology [8 – 11]. The studies have shown importance of narrow granulometry and spherical shape of particles on wear resistance of coating. Particle size and shape depend on the duration of milling. An increase in time results in larger sized particle shape approaching spherical with a smooth surface [4]. However increased amount of cycles leads to extensive wear of a grinding media and increased content of contaminations (Fe, Fe-based particles) in powder that significantly influence quality and properties of recycled hardmetal powder. Therefore to decrease content of impurities by processing of coarse, angular (up to 0.4 mm) particles plasma transferred arc (PTA) technology was suggested in present work.

The PTA-process is an efficient technology commonly used for the fabrication of wear resistant metal matrix composites (MMCs) [12 – 14]. PTA as an unique heat source for surface modification exhibits an enormous potential because of its low cost, easy operation and no need in a special surface treatment. Single or multilayer depositions provide strong metallurgical bonding between the deposit and the base metal, as well as porosity-free coating and relatively low dilution with substrate. In the PTA process, the heat of the plasma (arc of ionised gas) is used to melt the surface of the substrate and the welding powder, where the molten weld pool is protected from the atmosphere by the shielding gas. The variations in processing parameters such as preheat temperature, arc current and welding rate affect the welding performance (e. g. deposition rate) and the MMC's quality in terms of cermets homogeneity and hardness. PTA hardfacing is a promising approach for fabricating metallurgically bonded thick coatings of low alloyed steels using recycled cermets powders.

The main purpose of this work was to apply recycled cermets (cutting tools) in combination with metal matrix by PTA routine to produce novel advanced MMCs. It should be noted that this is a novel experimental process with no similar precedent found in literature. The principal scheme of the procedure applied in this work is shown in Fig. 1, where tungsten carbide based hardmetal scrap was used as an initial material. WC-Co hardmetals were milled

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with the help of disintegrator technology to produce a powder and chemically treated to clean the surface of the received grains. Then blends were mixed with Ni-based matrix and overlaid on steel substrate, producing wear resistant thick coating.

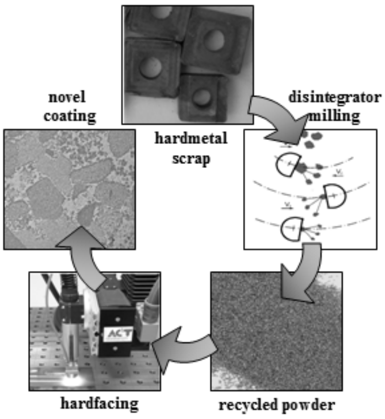

Fig. 1. Schematic view of the work procedure

2. EXPERIMENTAL DETAILS

Powder preparation and characterisation. Recycled WC-Co hardmetal powders were produced from hardmetal scrap by disintegrator milling as described in [5]. Purification of powders was performed by chemical treatment in concentrated sulphuric acid and successive cleaning with water and isopropyl alcohol. These processing steps were done to clean the particle surface after milling and to improve the weld ability and mechanical properties of material.

Table 1. Characteristics of initial powders

Type of powder	Particle size [μm]	Composition [wt %]
WC-Co	150 – 410	9 – 13 Co; 6 – 10 Fe; 2 – 4 Cr; rest WC*
Matrix**	32 – 125	0.2 C; 4 Cr; 1 B; 2.5 Si; 2 Fe; 1 Al; rest Ni
Reference***	45 – 90	4 C; rest WC/W_2C

* Various due to wear of grinding media and Co binder content.
** Castolin 16221 PTA powder.
*** Sulzer WOKA 50005.

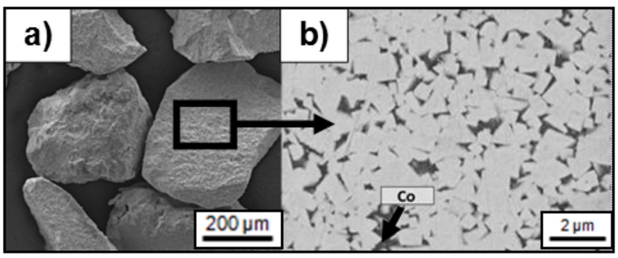

Fig. 2. SEM micrographs of recycled hardmetal particles: a – SE image of WC-Co particles; b – BSE image of grinded and polished grain surface

Castolin Ni-based 16221 powder was selected as a matrix material in the PTA processing of the recycled WC-Co hardmetal powders. The choice of this matrix can be explained by sufficient knowledge about powder properties combined with experience by PTA cladding of this powder with tungsten carbide. Chemical composition and grain size of recycled powder, matrix and reference powder are presented in Table 1. It should be noticed, that coarse carbide grains are agglomerates of fine (3 μm – 5 μm) tungsten carbide particles bonded together by Co-binder. Characterisation of microstructure of powders was performed by optical microscopy (OM) after etching as well as scanning electron microscopy (SEM/EDS). Typical microstructure of recycled WC-Co particles is shown in Fig. 2.

Hardfacing. PTA hardfacing was performed using a EuTronic® Gap 3001 DC apparatus (Fig. 3*).* Welding parameters such as welding current, oscillation and welding speed, substrate, powder feed rate, nozzle distance to workpiece, process gas flow rates are optimised related to the welding behaviour concerning to practical welding procedures. Welding procedure was carried out in a single layer welding without preheating or heat control of the substrate for reduced dilution. The mean welding parameters used in the present study are given in Table 2. The provided PTA-welded specimens were prepared by water jet cutting for further characterisations. This method of metallographic sample preparation avoids overheating of the probes that may induce changes in the properties of substrate and hardfacing [15].

Table 2. Summary of PTA welding parameters

Parameters	Values
Welding current	90/(100) A
Welding speed	0.9 mm/s
Oscillation speed	19.5 mm/s
Oscillation width	20 mm
Substrate material	mild steel (1.0037)
Substrate thickness	10 mm
Plasma gas	1.8 l/min
Carrier gas	carbide: 0.8 l/min; matrix 1.2 l/min
Shielding gas	15 l/min
Powders feed rate	35 g/min

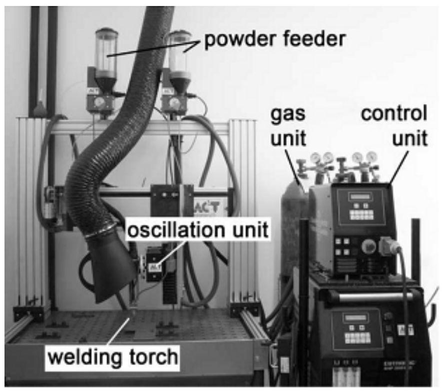

Fig. 3. PTA welding plant at AC²T (European Centre of Tribology)

Materials characterisation and wear examination. Test samples were cut, grinded and finished by 1 μm polish. Hardness measurements were carried out with standard Vickers hardness technique HV10. To determine hardness of each phase in the microstructure, e. g.

hardphases and metallic matrix, micro-hardness HV0.1 tests were applied. Four determinations of the micro- and macro-hardness were repeated for each considered sample for statistic calculation. Characterisation of microstructure was performed by OM after etching with Murakami's reagent as well as by SEM/EDS. The Leica QWin image analysis software (Leica microsysteme GmbH, Austria) was adapted and used to measure carbides/matrix content and grain size of carbides in MMCs. Mechanical properties where determined using nanoindentations. The preparation of samples for nanoindentation was done using standard methods without etching. The nanoindentation measurements of carbides and matrix were performed using a Hysitron TriboIndenter® apparatus (Hysitron inc., USA) equipped with Berkovich indenter operating in line-scan mode. For indentation an applied normal load of 5 mN was used.

In order to simulate field conditions in lab-scale as realistic as possible, wear tests were performed with the ASTM standard G65 method for 3-body-abrasion and the Cycling Impact Abrasion Test (CIAT) for combined impact-abrasion behaviour developed at the Austrian Centre of Competence for Tribology (AC²T) and described elsewhere [16 – 18].

3. RESULTS AND DISCUSSION

Pretreatment of powders. Certain percent of impurities, oxides and wasted adherences on the surface of the recycled tungsten carbide were indicated by EDS (Fig. 4, a). These impurities can influence weldability of the powders and influence the quality of the provided hardfacing, especially aggravate the coating porosity and decrease mechanical properties.

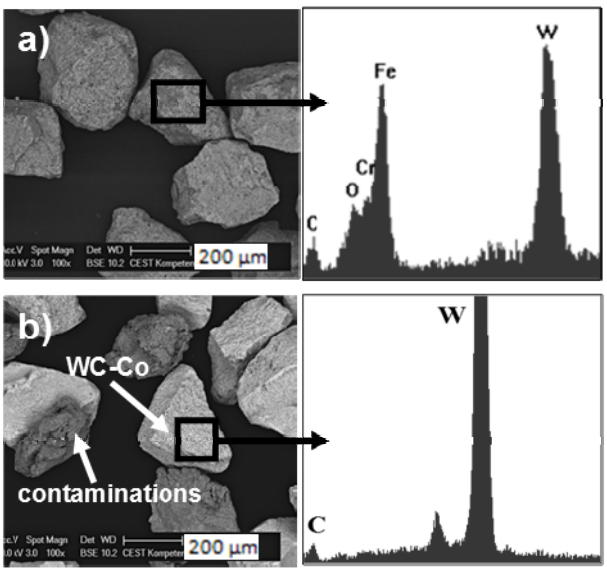

Fig. 4. Effect of cleaning process on surface composition of recycled WC-Co powder: a – SEM image and EDS analysis without chemical treatments of powder; b – SEM image and EDS analysis with chemical treatments of powders

A method of fast chemical treatment was developed for cleaning of the milled powder, which significantly improves the properties of recycled WC-Co powders. The impurities in the powder surface were removed by the treatment, whereas no dilution of the main elements (WC with Co binder) was observed. Fig. 3, b, presents EDS analysis of the surface of recycled powder particles after the chemical treatment where no additional elements on the grain surface were indicated. The measured weight lost during the chemical processing of the powders is less than 1.5 %. Cleaning is found to significantly improve the hardfacing weld layer quality by decreasing porosity (Fig. 5).

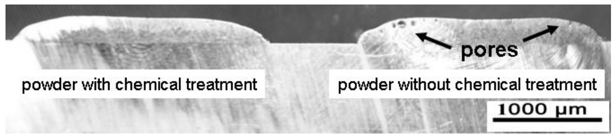

Fig. 5. Cross-section of weld deposit: effects of cleaning process on hardfacing quality

Formation of pores and concaved form of hardfacing during PTA-process can be explained by additional energy required to oxidise the adhered surface contaminations by the reaction with plasma. It should be noticed that chemical treatment of hardmetal powder surface is an experimental process and future investigations with process improvement steps are required.

Microstructure and hardness. For the developing of high quality MMCs certain amount of hard particles homogeneously distributed in the matrix and low dissolution of carbides in the matrix material are required. Preliminary investigations with 25 vol. % – 30 vol. % of hardmetal powder provide no homogenous distribution of carbides in the hardfacings caused by sinking of the heavy carbide particles (Fig. 6, a) leaving a huge area of the deposit without particles. Similar problems were observed by laser cladding of WC in combination with Ni-matrix [19]. In the present study a homogeneous distribution of carbides was performed only by addition of 40 vol. % of hardmetal powder in coating (Fig. 6, b).

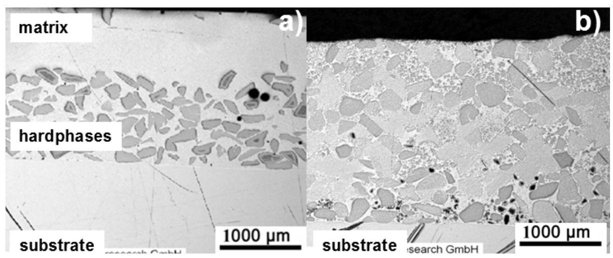

Fig. 6. OM micrographs of coatings: a – 30 vol. % of hardphases unetched; b – 40 vol. % of hardphase etched with Murakami`s reagent

Fig. 7 illustrates a typical cross-sectional SEM micrograph of the received coating with 40 vol. % of hardmetal powder, where formation of three different main phases was observed. Phase A responds to a complex matrix structure with Ni and Fe as the main elements. Chemical composition of the matrix phase A is shown in Table 3 as indicated by the dispersive X-ray analyser (SEM/EDS). The certain content of Fe and Cr in the matrix can be explained by contamination with Fe and FeCr containing wear particles of grinding media in the recycling process. Tungsten carbide and Co inclusions inside the matrix are dissolved and re-precipitated WC-Co grains are formed the double-dispersed structures. Hardness of the matrix is determined to be in the range between 380 HV10 and 550 HV10.

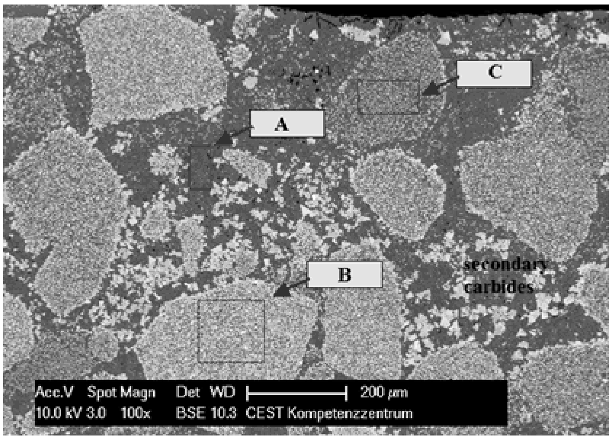

Fig. 7. SEM image of typical microstructure of PTA hardfacing with 40 vol. % of recycled hardmetal powder

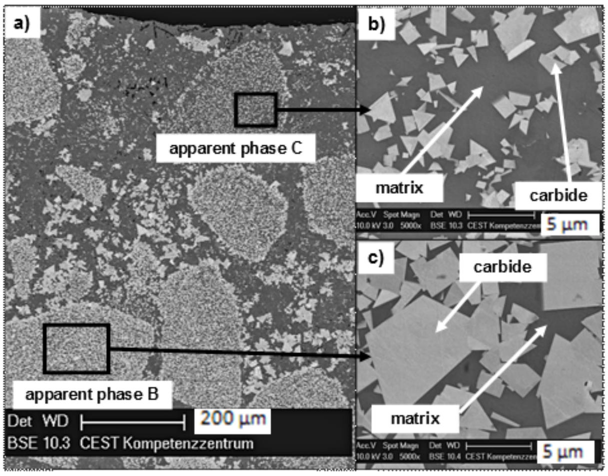

Fig. 8. SEM image of typical cross-section of received coating with detailed phases' analysis: a – overview image of weld deposit; b – BSE image of apparent phase C (more dissolved hardmetal particles); c – BSE image of apparent phase B (less dissolved hardmetal particles)

Two different modifications of carbide grain structures (apparent phases B and C) were received after hardfacing process. Microstructural analysis indicates penetration of the matrix elements (Fe and Ni) into Co binder between hardmetal agglomerates and partial dissolution of carbides. However carbides retain the angular grain shape developing the micro-sized MMC-particles in the coating with a "double-dispersed" MMC-structure (micro carbides with metal matrix). The main difference between phases B and C is matrix composition inside the carbide MMC and average grain size reduction of micro carbides in hardmetal MMC (Fig. 8). It was assumed that various level of hardphases dissolution is due to different binder element content in recycled powder grains. The difference between binder content responds to quality of recycled powder, whereas the Co content is always dependent on cutting tools waste material.

Apparent phase C shows only 30 vol. % of carbide particles with average grain size of 1.3 µm (Fig. 8, b), whereas apparent phase B (Fig. 8, c) indicates mirrored structure of the metal matrix components with 70 vol. % of carbides between matrix and a factor of two coarser average particles size compared to phase C (2.5 µm). The micro hardness of more dissolved matrix was determined to be 750 HV0.1 and hardness value of MMCs in phase C is 1240 HV0.1. This difference in hardness can be explained by influence of matrix content. Table 3 illustrates analysis of chemical composition by EDS of matrix region in both hardmetal MMC phases, which showed differences in elements content (especially Co and W).

Table 3. Chemical composition of matrix in phase A, B and C

Element	Matrix, phase A	Matrix, phase B	Matrix, phase C
	wt %	wt %	wt %
W	9	8	12
Co	10	9	20
NI	50	52	43
Fe	28	28	22
Cr	3	3	3

Nanoindentation. Micro-mechanical properties of the phases (hardness and reduced Young's modulus) were determined by nanoindentation measurements and statistically analysed using Box and Wishker plots (Fig. 9). The results for the received coating showed mean nanoindentation hardness of 4.7 GPa in the matrix phase, whereas no significant difference were found for the hardness of micro carbides in apparent phases B and C (27.2 GPa). This hardness level was in close approximation to hardness of tungsten carbide (whole WC/W_2C particles) measured as reference.

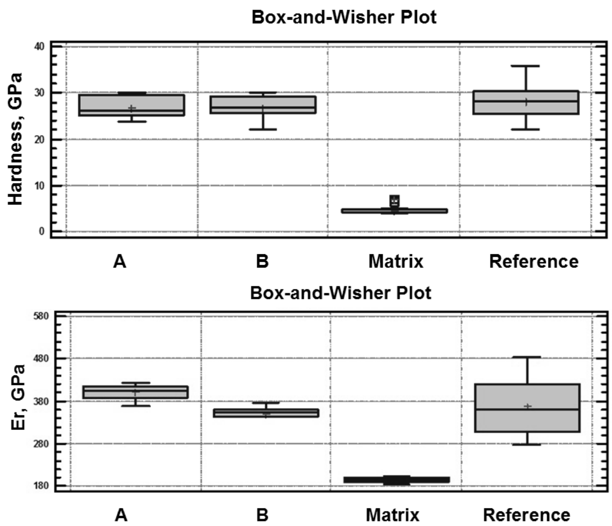

Fig. 9. Box and Whisker plots of the measured hardness and reduced modulus: A – carbides in apparent phase B (less dissolved); B – carbides in apparent phase C (more dissolved); Matrix – apparent phase A; Reference – WC/W_2C

Some differences in values of the reduced elastic modulus were observed between hardmetal with less dissolved micro carbides (A) and hardmetal with more dissolved micro carbides (B). This decrease from 320 GPa to 290 GPa of the elastic parameter can be explained by influence of the increased content of matrix elements (Ni, Co, Fe, etc.) and formation of solid solutions in the more dissolved hardmetal regions. However, the elastic modulus of these both recycled phases was within the measured values of the reference carbide (conventionally used WC/W_2C). These results indicate the micro-mechanical properties of the recycled hardphases were close to the micro- mechanical properties of the tungsten carbides used as the reference. However, the distribution broadness as indicated by standard deviation (Fig. 9) for the measured micro-mechanical properties of the recycled hardphases show close values as the measurements for the reference tungsten carbides. These indicate the high quality of the obtained hardphases in the recycling process of the present study.

Wear testing. It is generally assumed that abrasive wear behaviour of materials influenced by their hardness, microstructural features and wear conditions. Some previous studies [20 – 22] have shown the importance of hardness of both the matrix and the hardphases, whereas type, content, homogeneous distribution and size of the hardphases have a significant influence on wear properties of the material. The microstructure of investigated coating consists of coarse carbide MMCs, homogenously distributed throughout the matrix. The relatively large difference in hardness due to partial dilution of some hardmetal grains leads to a higher wear rate. However, decrease in hardness corresponds to changes in material ductility. In conditions where impact wear is a dominative factor, increased plasticity and high content of fine grained hardphases result in improved wear resistance of a material [18].

Quantitative wear analysis was determined by volume loss and the results are given in Fig. 10, where the summary of wear data obtained in different tests is listened. The relative wear resistance of the coating was compared to Ni-based reference hardfacing consisting 40 vol. % of WC/W_2C grains.

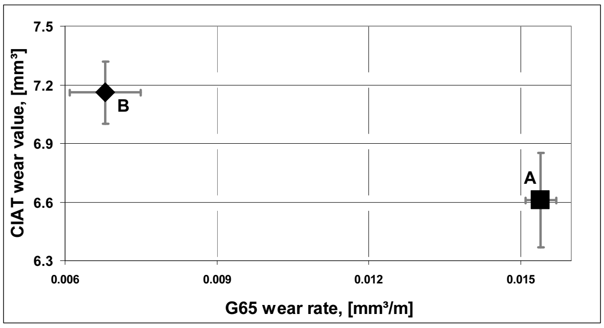

Fig. 10. ASTM G65 and CIAT wear values: A – produced MMC coating; B – reference material with 40 vol. % of WC/W_2C

The volume loss of the produced material under abrasive conditions is increased by a factor of two as compared to the reference coating, which is in a good agreement with [23]. Representative worn surfaces of the produced material are presented in Fig. 11, a. The predominant wear mechanism is dissection of tungsten carbides resulted in matrix material's wear. In the present study it was found that there is no significant wear of secondary MMCs regions with high carbides content (Fig. 11, b). From the other hand the hardmetal regions containing more dissolved hardphases do not give enough protection against wear, resulting in ductile deformation of the matrix showing microcutting scares on the surface and failure of small carbide particles (Fig. 11, c). Therefore the reason for the increased volume loss can be found in the lack of secondary MMCs regions with high carbides content in the surface regions which are exposed directly to abrasive wear attack.

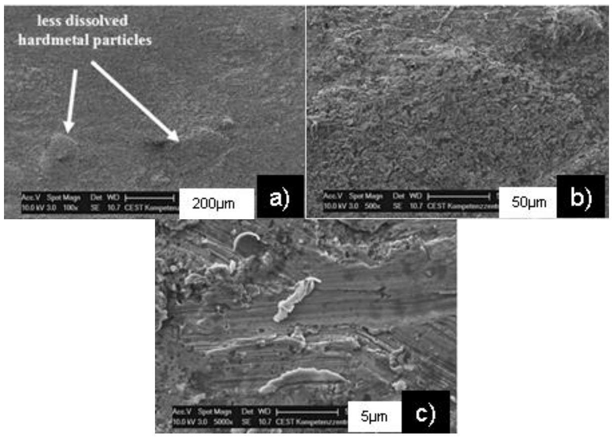

Fig. 11. Typical SEM images of worn of produced MMC coating after abrasion testing

The results observed after cycling impact abrasion test (Fig. 10) show relatively low wear rate of the produced material and higher wear resistance as compared to the reference material. The main mechanisms of material damage are related to plastic deformation of surface through microploughing and microcutting, whereas the brittle fracture of carbides region and breakouts of carbides is negligible as compared to reference material (Fig. 12).

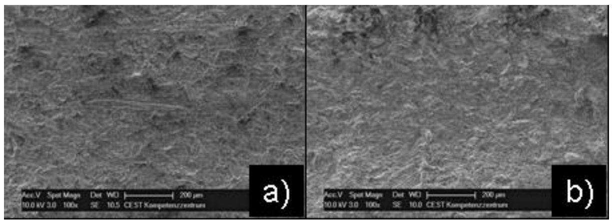

Fig. 12. Typical SEM images of worn surface after impact/abrasion testing: a – produced MMC coating; b – reference material with 40 vol. % of WC/W_2C

4. CONCLUSIONS

Based in the study within this work, the following conclusions can be drawn:

1. Hardmetal scrap was successfully applied by fabrication of wear resistant coatings using PTA hardfacing technology.

2. Chemical treatment of the milled powders has significantly improved quality of the produced hardfacings.

3. A certain amount of WC-Co particles is required (min. 40 vol. %) to achieve homogeneous distribution of carbides in the matrix during PTA processing.

4. Formation of two different secondary MMC apparent phases with different microstructure and mechanical properties in both matrix/carbide areas was observed.

5. Under pure abrasion conditions, reduced wear resistance by a factor of two as compared to conventionally

used WC/W_2C was obtained. This fact can be explained by significant difference in hardness in secondary MMCs (less dissolved hardmetal grains – 1250 HV0.1; more dissolved hardmetal grains – 780 HV0.1) as well as by certain percent of contaminations (up to 10 % of Fe and FeCr particles inside of recycled powder).

6. Under combined impact/abrasion conditions produced coating has shown promising results with high wear resistance.

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