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The properties of laser-clad coatings made of NiCrBSi alloy and recycled tungsten carbides

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Abstract. Tungsten carbide hard metals are one of the most known and successful powder metallurgical products used in environments where severe wear conditions prevail. Since tungsten belongs to the list of critical raw materials for the European Union (EU), its recycling is highly desirable. In this paper, recycled tungsten carbide powders fabricated by the zinc-reclaim process where mixed with NiCrBSi matrix and deposited with one-step laser cladding using a coaxial powder feeding on mild steel substrates. Prepared clads were tested in low-stress rubber wheel abrasion tests and compared with clads produced from commercial macrocrystalline (WC) and cast and crushed eutectoid WC/W_2C reinforced clads. The results showed that recycled WC induced porosity in clads when produced with 'production' laser cladding parameters due to small carbide size resulting in poor wear performance. When laser-clad with lower heat input and productivity, pore-free clads with excellent wear performance were obtained.

1. Introduction

Tungsten carbide reinforced hard-facings produced by laser cladding, plasma-transferred arc (PTA), and metal inert/active gas (MIG/MAG) welding are widely used in such applications as mining & mineral processing, oil & gas drilling, agriculture, and steelworks [1-3]. Tungsten belongs, however, to the EU's list of critical raw materials, which makes its recycling from hard-metal scrap highly desirable [4]. The use of recycled tungsten carbides in hard-facing was already studied in Refs. [5-7]. Zikin et al. [6] and Kulu et al. [7] fabricated, for instance, Ni- and Fe-based clads reinforced with 40 vol.% of coarse (150-400 µm) recycled WC particles by PTA welding. In abrasion and impact-abrasion tests, the clad fabricated from the commercial WC/W_2C showed, however, better wear resistance than the clad made of recycled WC.

Methods to produce recycled tungsten carbide particles can be divided into mechanical and chemical methods. Mechanical methods include disintegrator milling, where hard-metal scrap such as used cutting tools are crushed [7]. Benefits of disintegrator milling include the possibility to fabricate coarse WC particles, which suit for overlay welding and hard-facing processes [7]. Such a coarse single WC particle consists of several smaller WC particles (3-5 µm), which are bound together by cobalt binder. Large or coarse WC particles tend to survive in a melt pool without dissolution and melting better than finer carbides leading to an ideal metal matrix composite, which consists of a ductile matrix reinforced with hard particulates. Long milling times lead, however, to increased content of contaminations from the grinding media (Fe) and atmosphere (oxidation), which necessitates chemical cleaning treatments afterwards [6].

In the zinc-reclaim process, hard metal scrap is exposed to molten zinc at 900-1050°C in Ar/N_2 atmosphere [8]. Zinc forms with cobalt a compound that expands and breaks the hard metal. After the zinc is removed, the result is an easily crushed porous hard metal that can be crushed and sieved to WC-Co powder.

Common for all these recycled tungsten carbides is that they are tungsten mono-carbides (WC) and angular in shape. Tungsten mono-carbide is somewhat softer than the eutectoid WC/W_2C, which is more frequently used in hard-facing. Tungsten mono-carbide is, however, thermally more stable than eutectoid WC/W_2C, which tends to dissolve and melt in the melt pool and embrittle the matrix via the precipitation of secondary carbides.

The objective of this paper is to evaluate the suitability of recycled WC produced by the zinc-reclaim process in laser cladding and compare its wear properties to commercial macrocrystalline WC and eutectoid WC/W_2C in a low-stress three-body abrasion wear test.

2. Materials and methods

The powder used for laser cladding was NiCrBSi mixed with recycled WC, commercial macrocrystalline WC, and cast and crushed eutectoid WC/W_2C. Mechanical mixtures of powders were prepared by weighing the desired amount of powders (40/60 wt.%) and mixing them in a plastic bottle, which was placed in the mechanical mixer for 24 h. Chemical compositions, microhardness of carbides, and granulometry of powders are given in Table 1. Microhardness values were measured from the polished cross-sections of carbides mould in epoxy resin. Eutectoid WC/W_2C was clearly the hardest carbide. The morphologies of powders are illustrated in Figure 1. Tungsten carbide powders were angular in shape with nearly the same size distributions. It should be, however, noted that recycled powder also included particles where small WC particles were bound with cobalt. The substrates employed for the cladding were mild steel plates with a thickness of 20 mm, a width of 60 mm, and a length of 200 mm. Prior to cladding, they were grit-blasted with alumina to a roughness of R_a 4.4 µm.

Table 1. Chemical compositions in wt.%, microhardness values, and grain sizes of powders. Standard deviations for microhardness values are given in parentheses.

Material	B	C	Si	Cr	Fe	Co	Ni	W	$HV_{0.1}$	Size (µm)
NiCrBSi	1.7	0.25	3.5	7.5	2.5	-	Bal.	-	-	53-125
Recycled WC									1700 (260)	45-100
Macrocrystalline WC		6.1			0.15			Bal.	1628 (249)	45-90
Eutectoid WC/W_2C		3.8-4.1			≤0.3			Bal.	2397 (321)	44-74

Laser cladding was performed using a continuous wave fiber laser (Coherent) with a maximum power of 3 kW. The experimental set-up consisted of a laser-integrated beam delivery system (400 µm fiber, f160 mm collimator unit, f250 mm focus optics), coaxial powder feeding nozzle (Coax 8), rotating disc type of powder feeder (Medicoat), and a Fanuc F-200iB parallel kinematic robot. The optics and powder feeding nozzle were kept static while the base materials were moved by the robot. The laser beam was defocused to a spot size of ~4 mm (Figure 2). The optimized cladding parameters to produce fusion-bonded metal matrix composites with low dilution are summarized in Table 2. Shielding and carrier gases used in the experiments were argon with flow rates of 12 and 6 l/min, respectively. The recycled powder had to be clad with lower specific energy due to porosity issues. After the cladding had been completed, plates were water-cut to the wear specimens (50 x 20 mm^2) and coating surfaces machined to a condition where no as-clad surface remained.

The microstructure of the specimens was studied by means of an optical microscope (OM) and a scanning electron microscope (SEM). Energy-dispersive X-ray spectroscopy (EDS) was employed to

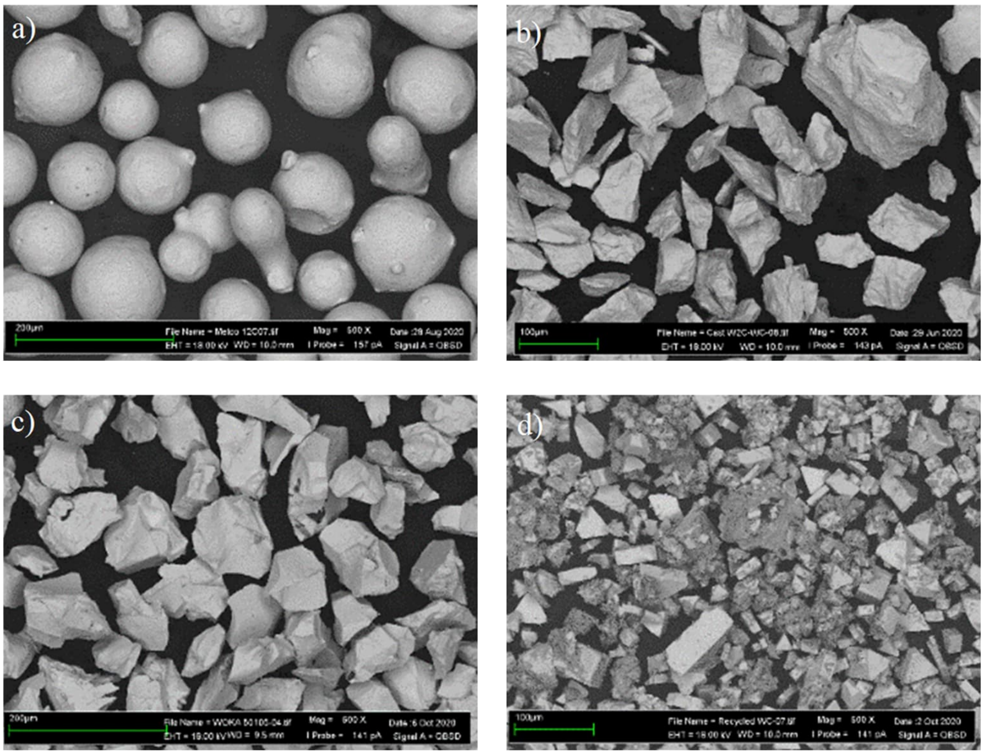

Figure 1. SEM micrographs of powders: a) gas atomized NiCrBSi, b) cast and crushed WC/W_2C, c) macrocrystalline WC, and d) recycled WC.

a)

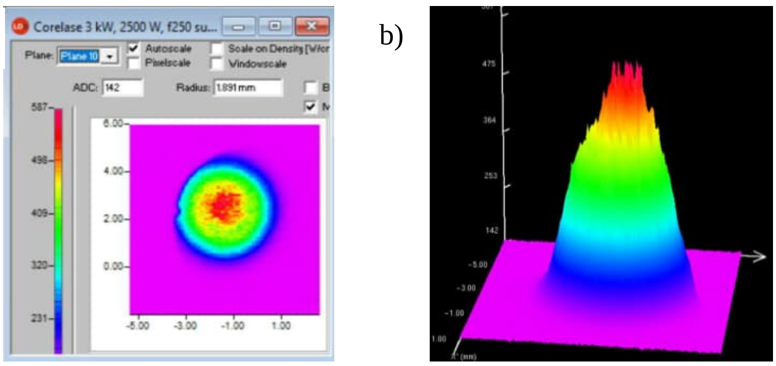

Figure 2. Intensity distribution of defocused fiber laser beam measured at working distance: a) plane and b) spatial distribution.

analyse local chemical compositions. To reveal crystal structures and phases present in studied materials, an X-ray diffractometer (Panalytic Empyrean Multipurpose Diffractometer) was used using the monochromatic Cu Kα radiation at the voltage of 45 kV and the current of 40 mA. The scanning angle 2θ covered a range of 20-80°. The Vickers microhardness measurements from the coating cross-sections were taken with a Matsuzawa MMT-X7 hardness tester using indentation loads of 1, 3, and 10 N applied for 10 s.

Three-body abrasion wear tests at room temperature were conducted with a rubber-wheel abrasion test device, a modified version of ASTM G65, where crushed dry quartz (SiO_2) sand abrasives (0.1-0.6 mm) flow between the surfaces of the rotating rubber wheel (Durometer A84-88) and the test specimen. The test device and parameters are described in more detail in Ref. [9]. The worn specimen surfaces were examined by SEM. The volume losses were calculated based on the mass loss and the theoretical density of the materials. Reference material in abrasion tests was quenched & tempered steel with a hardness of 450 HV.

Table 2. Laser cladding process parameters.

Material	Power (kW)	Traverse speed (mm/s)	Powder feed rate (g/min)	Specific energy (J/mm^2)	Inter-track advance (mm)
NiCrBSi + Recycled WC (40/60 wt.%)	0.6	10	12	20	1.25
NiCrBSi + Macrocrystalline WC (40/60 wt.%)	1.8	18.3	39	33	1.50
NiCrBSi + Eutectoid WC/W_2C (40/60 wt.%)	1.8	18.3	38	33	1.50

3. Results and discussion

3.1. Microstructure

The representative low-magnification cross-sectional OM images of coatings manufactured with process parameters given in Table 2 are illustrated in Figures 3a-c. Coatings are generally characterized by low dilution, a thickness of ~1.1 – 1.3 mm, homogeneous distribution of primary carbides, slight porosity, and varying amounts of vertical cracks, which stop at the fusion line and do not propagate to the base material. Some essential coating characteristics are shown in Table 3. It can be, for instance, seen that the primary carbide content is the highest and size the smallest in recycled WC coating.

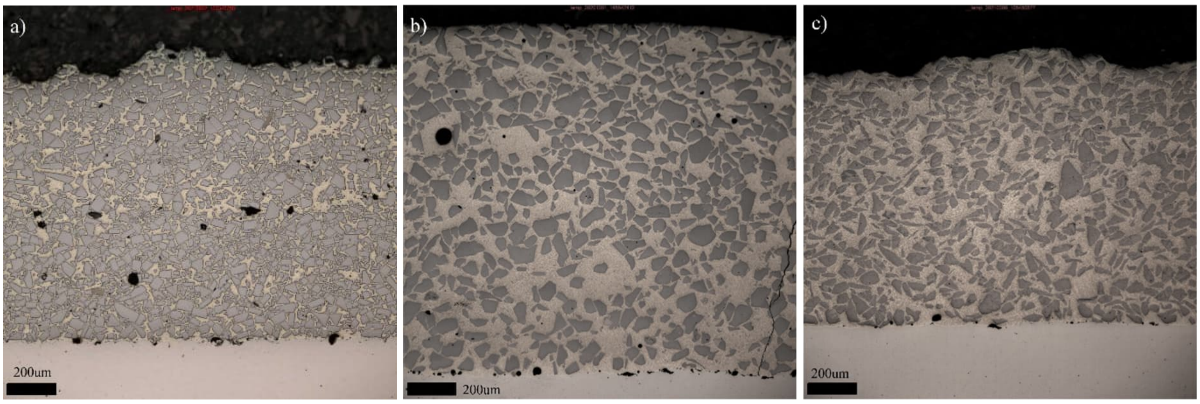

Figure 3. Low magnification OM images of a) Recycled WC, b) Macrocrystalline WC, and c) Eutectoid WC/W_2C coatings.

Table 3. Summary of coating and process characteristics.

Material	Primary carbide content	Average primary carbide size	Secondary carbide content	Thickness	Coverage rate
Recycled WC	56 vol.%	24 µm	5 vol.%	1.1 mm	0.02 m^2/h
Macrocrystalline WC	48 vol.%	57 µm	7 vol.%	1.3 mm	0.1 m^2/h
Eutectoid WC/W_2C	42 vol.%	48 µm	11 vol.%	1.1 mm	0.1 m^2/h

Low and high magnification SEM images and image analysis revealed that the amount of secondary carbides in the matrix due to the dissolution of primary carbides is the highest in the coating made of eutectoid WC/W_2C as displayed in Figures 4a-f, 5, and Table 3. This is attributed to the lower chemical stability of W_2C than WC [10]. According to Ref. [11] eutectic WC/W_2C decomposes into W and WC below 1250°C. Whereas monocrystalline WC is thermally stable up to 2757-2777°C. Dissolution in

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recycled WC is less than in monocrystalline WC due to lower specific energy in the cladding process despite finer WC granulometry. Secondary carbides are mainly tungsten-based mixed carbides in Macrocrystalline WC and eutectoid WC/W_2C. Whereas the matrix of recycled WC coating includes also small black dots which are probably chromium carbides, borides, and/or silicides. Common for all the secondary carbides is that they locate in the interdendritic region of the Ni-based matrix. Light regions in the matrix are richer in chromium, iron, and tungsten compared to dark regions.

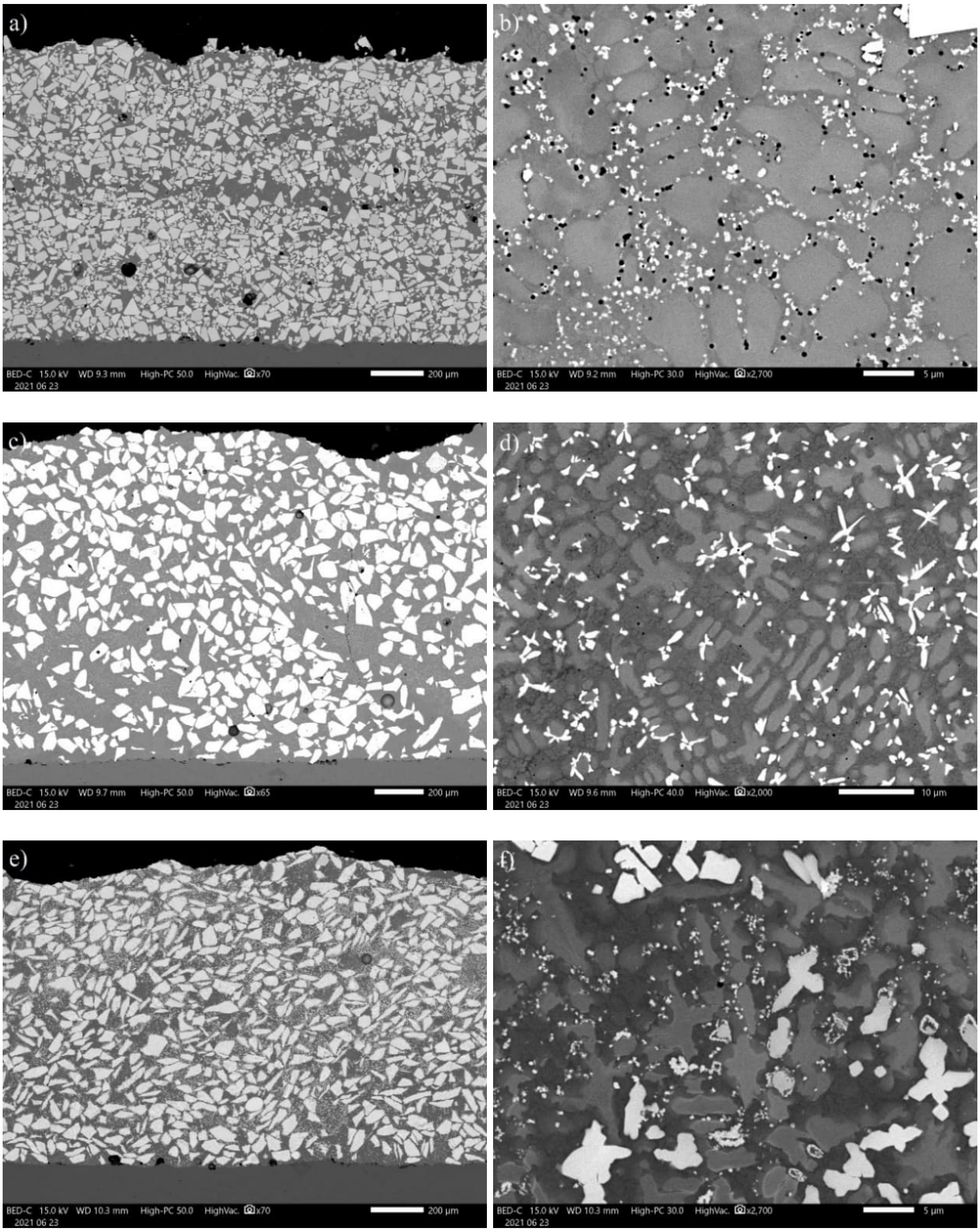

Figure 4. Low and high magnification SEM images of a,b) Recycled WC, c,d) Macrocrystalline WC, and e,f) Eutectoid WC/W_2C coatings.

According to XRD scans shown in Figure 6, the secondary carbides could be Ni_3W_3C, Ni_2W_4C, and $Ni_2W_{11}C_4$. Other phases in the matrix could be Ni_2Si, Cr_5B_3, and Ni_4B_3. As evidenced by the EDS analyses taken from the matrix, all the coatings are chemically only very little diluted (Table 4). Iron contents of the matrix are at the level of 2.0-2.8 wt.%.

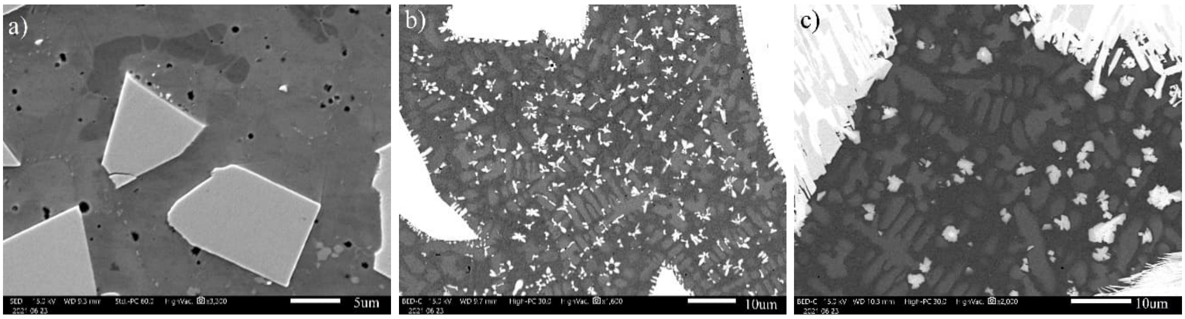

Figure 5. High magnification SEM images of primary carbide and matrix interface a) Recycled WC, b) Macrocrystalline WC, and c) Eutectoid WC/W_2C.

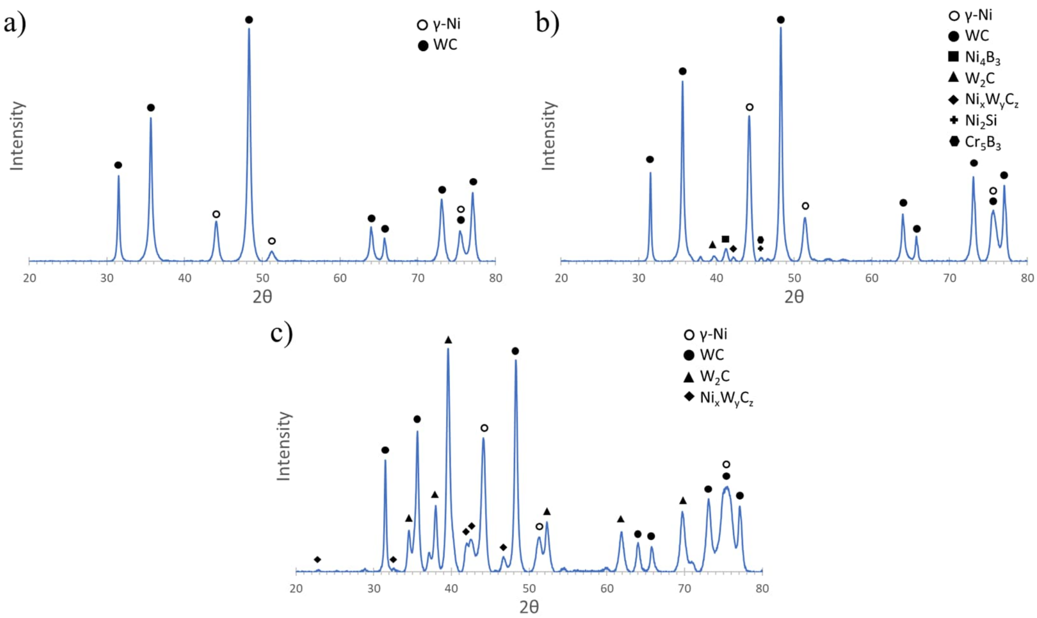

Figure 6. XRD patterns of a) Recycled WC, b) Macrocrystalline WC, and c) Eutectoid WC/W_2C.

Table 4. Average chemical composition of matrix without carbon and boron in wt.%.

Material	Ni	Co	W	Cr	Si	Fe
Recycled WC	61.8 ± 0.1	17.6 ± 0.9	11.2 ± 0.7	5.5 ± 0.1	2.0 ± 0.1	2.0 ± 0.1
Macrocrystalline WC	75.1 ± 0.7	-	12.9 ± 0.6	6.8 ± 0.0	2.4 ± 0.1	2.8 ± 0.1
Eutectoid WC/W_2C	73.1 ± 2.4	-	16.7 ± 2.8	5.5 ± 0.2	2.3 ± 0.1	2.4 ± 0.0

3.2. Microhardness

Hardness profiles measured from the coating cross-sections are illustrated in Figure 7. Average coating hardness values vary from ~730 to 950 HV_1 eutectoid WC/W_2C coating being the hardest and the macrocrystalline WC the softest. Hardness values were also measured from the primary carbides and Ni-based matrices (Table 5). Eutectoid WC/W_2C was the hardest and recycled WC was the softest primary carbide. The Ni-based matrix was the hardest in eutectoid WC/W_2C coating and softest in the recycled WC coating.

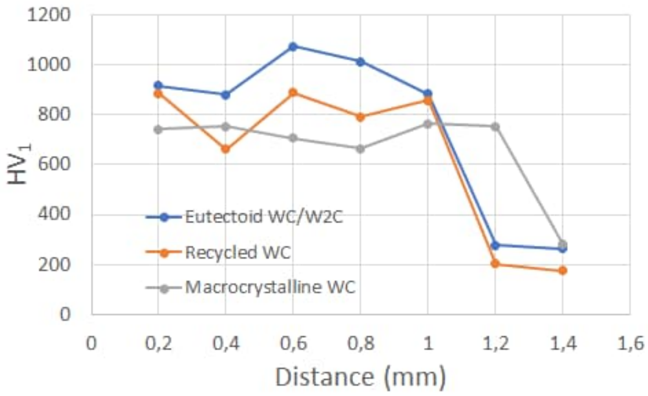

Figure 7. Microhardness values of coatings measured from cross-sections.

Table 5. Hardness values measured from the primary carbides and Ni-based matrices together with average mean free path values between primary carbides. Standard deviations are given in parentheses.

Material	Primary carbide ($HV_{0.1}$)	Matrix ($HV_{0.3}$)	Mean free path between primary carbides (µm)
Recycled WC	1478 (274)	562 (20)	~16
Macrocrystalline WC	1687 (206)	584 (15)	~45
Eutectoid WC/W_2C	2372 (164)	703 (96)	~33

3.3. Abrasion wear

The rubber wheel abrasion test (RWAT) results are presented in the form of weight and volume losses as column charts in Figures 8a and b. The results are the average of three test runs per studied material. As indicated by the results, the differences in wear resistance between different coatings are rather obvious, which suggests that the coatings can be ranked in terms of wear performance. Eutectoid WC/W_2C coating, which showed the highest primary carbide and matrix hardness, exhibited the best wear performance. Recycled WC coating was slightly better than macrocrystalline WC coating owing obviously to its higher primary carbide content (56 vs 42 vol.%) and shorter mean free path (16 vs 45 µm) between carbides given in Table 5.

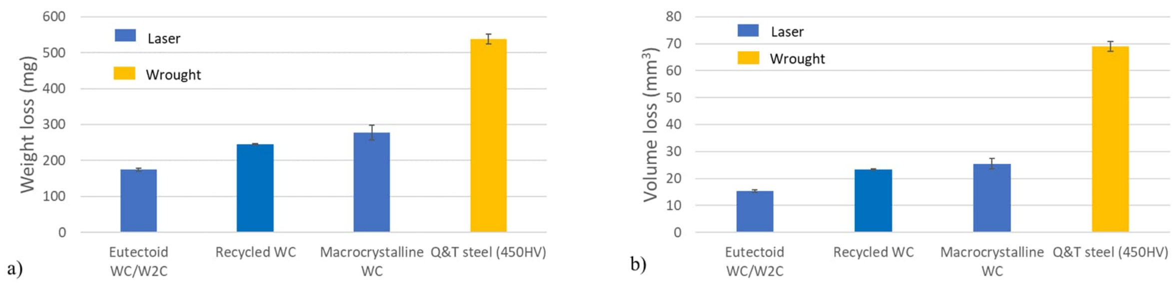

Figure 8. a) Mass and b) volume losses of tungsten carbide reinforced Ni-based coatings and reference material subjected to RWAT.

High-magnification SEM images of wear scars are displayed in Figures 9a-f. Common for all the wear scars is that matrix wore down preferentially leaving primary carbides protruding from the matrix. Obviously, abrasion conditions were hard for the matrices since the average hardness of the abrasive (~750-1200HV) was clearly higher ($H_{abrasive}/H_{material} > 1.2$) than the hardness of the matrices [12]. It was also observed that all the primary carbides remained rather intact under the used abrasion conditions. Not any differences in cracking were detected even if it is known that monocrystalline WC has lower fracture toughness than eutectoid WC/W_2C [11]. Despite only partial dissolution or modest melting of primary carbides, they were well bonded to the matrix, and carbide 'pull-outs' were not observed.

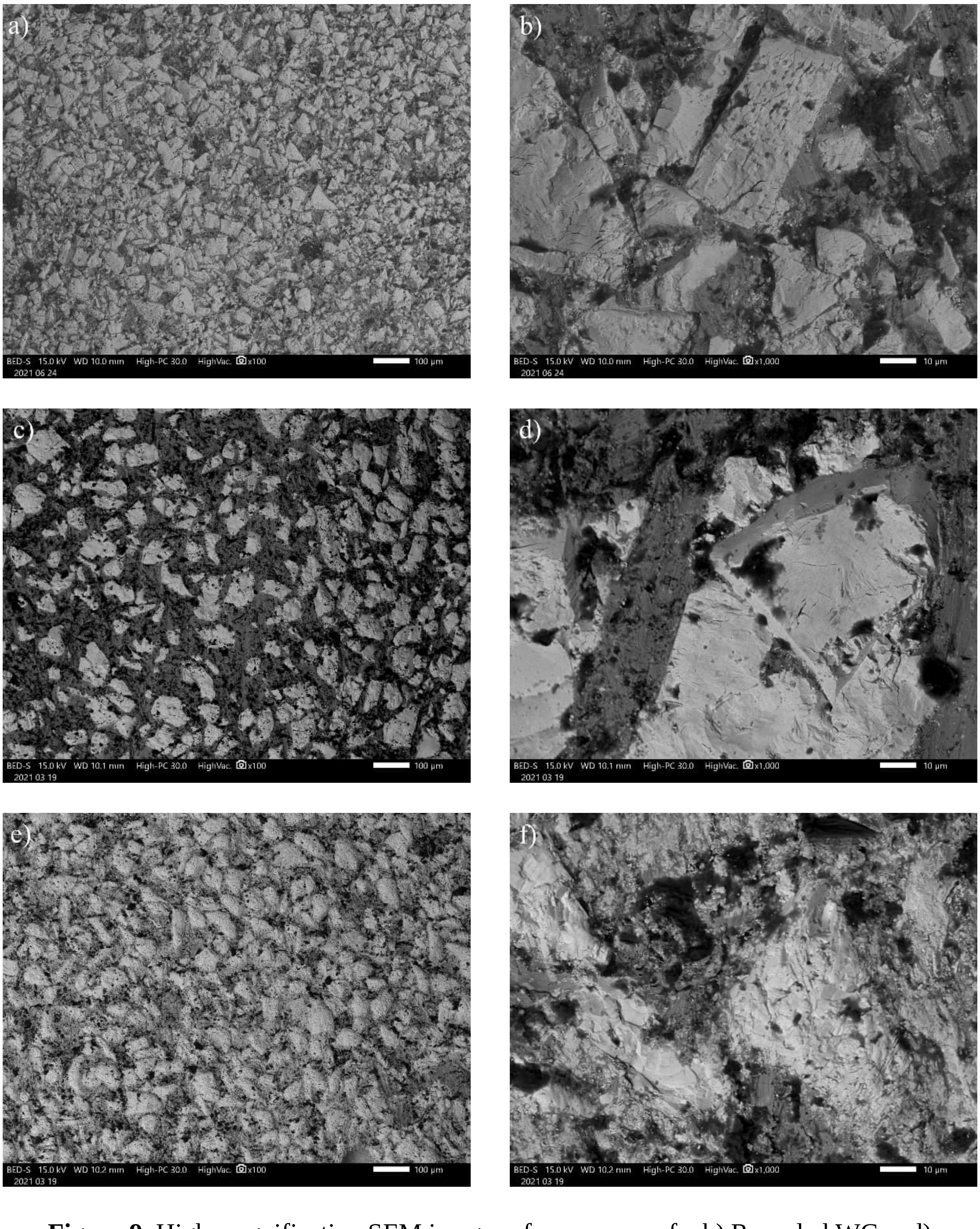

Figure 9. High magnification SEM images of wear scars of a,b) Recycled WC, c,d) Macrocrystalline WC, and e,f) Eutectoid WC/W_2C coatings.

4. Conclusions

The following conclusions can be drawn from the study:

1. Due to the small carbide size of recycled WC, specific energy (J/mm^2) in the laser cladding process needed to be reduced to obtain pore-free clad layers.
2. In a low-stress three-body abrasion recycled WC exhibited wear resistance equivalent to commercial macrocrystalline WC.
3. Eutectoid WC/W_2C showed, however, the best wear performance due to the highest primary carbide and matrix hardness.

The successful introduction of recycled carbide in conventional laser cladding would require a significant increase in carbide size. Potential applications could be machines and components that are subjected to impact and impact-abrasion wear, as tungsten monocarbide is less prone to embrittle the metal matrix due to diminished dissolution in the melt pool. In the future, the use of recycled carbide should be investigated in the novel extreme high-speed laser cladding (EHLA) process, which may allow a smaller carbide size due to the lower specific energy (J/mm^2) of the process.

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