



Short communication

Microstructure and mechanical properties of cemented carbides recycled by a novel recovery process

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ABSTRACT

Hardmetal (HM) sector faces growing supply risks due to the criticality of tungsten (W) and cobalt (Co), the main components of WC-Co cemented carbides. To reduce dependence on raw material suppliers, recycling HM waste is becoming increasingly important, and sustainable recovery processes are being developed to meet both environmental regulations and industrial demands. The properties of HMs are strongly influenced by microstructural features such as WC grain size, binder content, and possible residual phases, which are not always easy to control in new recycling systems. In this study, WC-Co samples were produced entirely from recycled scraps through an oxidation–reduction–carburization treatment combined with eco-friendly leaching based on organic acids. Microstructural analysis and mechanical tests showed that the recycling process does not significantly affect the main microstructural parameters or the mechanical performance, apart from minor differences in WC grain morphology. These results demonstrate that fully recycled WC-Co HMs can achieve quality standards comparable to conventional materials.

1. Introduction

The recovery of secondary raw materials (SRM) reduces the exploitation of resources, which are increasingly scarce on Earth. Regarding WC-Co cemented carbides – also known as hardmetals (HMs) – their main components, tungsten (W) and cobalt (Co), are listed among Critical and Strategic Raw Materials by the European Union and their recovery is becoming increasingly important [1]. Regulations on waste and pollution prevention also push companies towards the design of more sustainable recovery processes. Besides the most versatile HM recovery process, the Chemical Recycling, which involves numerous energy- and chemicals-demanding stages and produces virgin-like materials, the most established direct recycling exploits the Zn-process. Zn-process typically produces four or five different powder grades, including three Co-based grades with different WC grain sizes (submicron/fine, medium, and coarse), one Ni-based grade, and one γ -phase-containing grade. These powders exhibit a quality suitable for a wide range of applications; however, their incorporation is typically limited to a maximum content of 50 wt% [2,3].

Within the above framework, a novel recycling process which consists of a series of pyrometallurgical treatments – oxidation, reduction and carburization (ORC) – applied to hard WC-Co scraps, combined with a green hydrometallurgical leaching based on the use of bio-derived organic acids, was designed. This process demonstrated its potential in tuning the W/Co ratio in the treated material, providing a desired final composition of the recovered WC-Co powders [4,5].

This work is an immediate follow-up of the studies referred to above, and the main goal is to assess the microstructural and mechanical integrity of 100% recycled HMs. In doing so, HM samples were produced by sintering powders obtained from the described novel method. After leaching, the treated powders underwent reduction, carburization, and then sintering, to give a first evaluation on the quality of recycled material pointing out possible leaching stage effects occurrence. Thus, recycled HMs were characterized both in terms of microstructure and mechanical properties. The results obtained were compared with those measured for HMs with a similar composition (Co content and WC grain size) produced from virgin raw materials. The results show good quality recycled HM with comparable mechanical properties.

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Table 1

Microstructural parameters of recycled HMs and their counterpart reference samples.

Sample name	Co (wt%)	d_{WC} (μm)	V_{Co}	C_{WC}	λ_{Co} (μm)
Reference	18.9 ± 0.8	0.6 ± 0.3	0.28	0.36	0.3
1 N	16.1 ± 0.3	0.7 ± 0.3	0.26	0.32	0.4
1H	16.1 ± 0.3	0.7 ± 0.4	0.26	0.32	0.4
2 N	16.2 ± 0.2	0.7 ± 0.4	0.26	0.32	0.4
2H	16.4 ± 0.1	0.7 ± 0.4	0.26	0.32	0.4
3 N	16.3 ± 0.2	0.7 ± 0.3	0.27	0.31	0.4
3H	16.3 ± 0.2	0.7 ± 0.4	0.26	0.32	0.4

2. Experimental procedures

2.1. Materials

Recycled and reference HMs were produced at OMCD TEK HUB (Anzola d'Ossola, Italy). The reference grade was selected as a candidate to be produced with the largest amount possible of the recovered powder. Powders for reference samples were provided by H.C. Stark (Goslar, Germany) and Umicore/Eurotungstene (Grenoble, France) for $0.8 \mu m$ WC and $1.2 \mu m$ Co powders, respectively. Recycled powders were obtained through HM scrap thermal oxidation followed by a metal leaching step on oxidized powders at $100^\circ C$ with a 4 M aqueous lactic acid solution at $pH = 4$ (NaOH addition for adjusting the acid pH), as

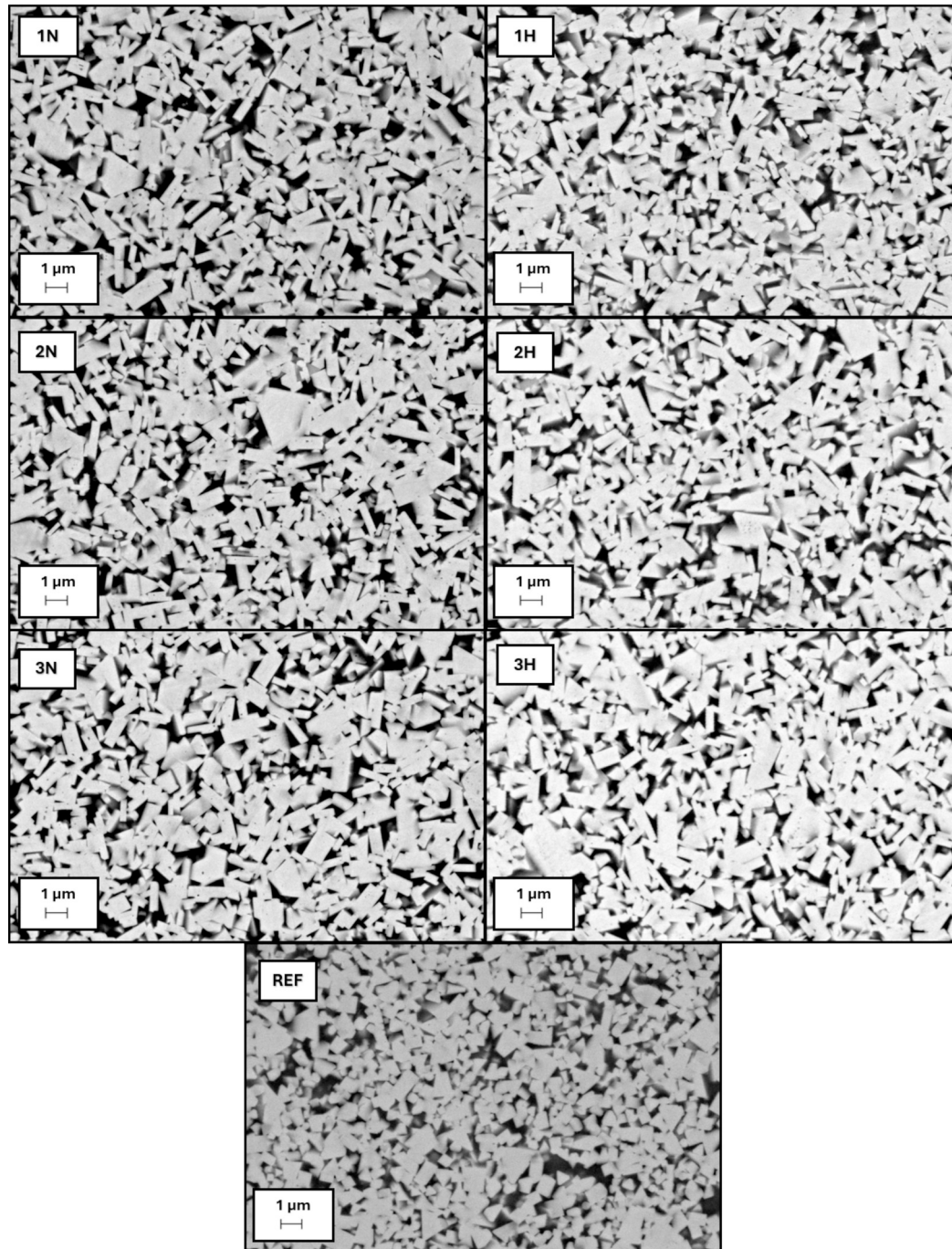


Fig. 1. FESEM images of test specimens obtained from recycled powders (1 N, 1H, 2 N, 2H, 3 N and 3H) and from raw materials (REF).

Table 2

Vickers hardness with loads of 10 and 30 kgf, fracture toughness, Weibull modulus (m) and characteristic strength (σ_0) values for reference and recycled test specimens.

Sample name	HV10 (GPa)	HV30 (GPa)	K_{Ic} (MPa $\cdot$ m $^{1/2}$)	m	σ_0 (MPa)
Reference	12.2 $\pm$ 0.1	12.8 $\pm$ 0.1	13.8 $\pm$ 0.3	28	3760
1 N	13.5 $\pm$ 0.3	13.2 $\pm$ 0.2	14.1 $\pm$ 1.2	18	3703
1H	13.4 $\pm$ 0.2	13.2 $\pm$ 0.3	14.0 $\pm$ 0.5	29	3768
2 N	13.4 $\pm$ 0.1	13.3 $\pm$ 0.1	14.6 $\pm$ 0.7	19	3614
2H	13.3 $\pm$ 0.2	13.1 $\pm$ 0.1	13.0 $\pm$ 2.0	17	3781
3 N	13.3 $\pm$ 0.2	13.1 $\pm$ 0.2	13.4 $\pm$ 0.4	9	3455
3H	13.3 $\pm$ 0.2	13.2 $\pm$ 0.1	14.0 $\pm$ 0.2	14	3361

described in a previous study [6]. The obtained material was then reduced and carburized obtaining a WC-Co powder with the desired composition, ready for manufacturing.

Powder mixtures were prepared using standard lab scale Powder Metallurgy methods, involving 48-h ball milling in 1 L volume rotating drums in ethyl alcohol, with a 1:3 powder-to-balls ratio followed by vacuum drying. The powders were pressed at 160 MPa to obtain standard ISO 3327 “B-type” prismatic samples after grinding, with $20 \times 6.5 \times 5.25$ mm 3 size. These samples underwent de-waxing, pre-sintering and sintering in a sinter-HIP furnace at 1400 °C under a 50-bar Ar atmosphere.

Three different carbon contents were considered for powder mixtures to collect information about the carbon window of the recovered powders. Considering the process carbon losses, ± 0.1 m% C was added to the mean standard value for that composition. In the sample ID the increasing carbon content is simply identified from “1” to “3”. In order to further investigate the carbon content consistency of the recovered powders after treatment with a different carburizing activity, two different de-waxing and presintering atmospheres were employed: pure nitrogen and a mixture of nitrogen with 5% hydrogen (“N” and “H” in the sample ID, respectively). The reference samples were pre-sintered just in the 5% hydrogen atmosphere. After sintering, the bar test specimens were polished on the four main faces, according to the ISO 3327 standard.

2.2. Methods for materials characterization

Microstructural parameters – carbide size (d_{WC}), binder content (V_{binder}), contiguity (C) and binder mean free path (λ_{binder}) – were measured from micrographs acquired using a Zeiss Neon40 Field Emission Scanning Electron Microscopy (FESEM). Before image acquisition, all sintered bar samples were grounded and polished until mirror-like surface finish. Measurements were conducted by means of image

analysis, by applying the linear interception method. Semi-quantitative phase measurement was made by using an EDX coupled with the FESEM. To ensure high accuracy, the EDX system was calibrated prior to the measurements using a high-purity Cobalt (Co) reference sample and data was collected from multiple representative areas across each specimen. Contiguity and mean free path were calculated by using the equations proposed by Roebuck and Almond [7] and Lee and Gurland [8], respectively.

Vickers hardness (HV10 and HV30) was determined by performing 5 indentations for each load onto the same face where the microstructural characterization was carried out.

Although fracture toughness is commonly assessed in cemented carbides by means of sharp indentation, it could not be implemented in the studied grades because a well-defined imprint-cracking system was not attained. Indeed, because the relatively tough-like character of the materials under consideration, no cracks emerged from the corners of the HV imprints. In this context, an alternative method was applied by using notched specimens. It involved the use of ultrashort pulsed laser ablation (UPLA) to introduce through-thickness notch/cracks in the HM grades studied, following the successful implementation of this technique for such purpose in different hard and brittle materials, including HMs [9,12,13]. Information on the laser and conditions used to create the micro-notches are described elsewhere [9,13–15]. Then, a three-point bending test was performed on three specimens per group of samples using a universal mechanical testing machine. The value of the stress intensity factor K_{Ic} , was calculated using the following Eq. 1 [14]:

$$K_{Ic} = \sigma Y \sqrt{a} \quad (1)$$

where a is the crack length in μ m, σ the flexural strength in MPa and Y is a dimensionless geometry factor that depends on the configuration of the sample with the notch and the way the load is applied. For the particular testing configuration used, Y is given by Eq. 2 [9]:

$$Y = \frac{1.1215 \cdot \sqrt{\pi}}{\beta^{3/2}} \left[\frac{5}{8} - \frac{5}{12} \alpha + \frac{1}{8} \alpha^2 \beta^6 + \frac{3}{8} \exp\left(-\frac{6.1342 \alpha}{\beta}\right) \right] \quad (2)$$

where $\alpha = a/W$ and $\beta = (1-\alpha)$ [10], with a and W being the crack length and specimen height respectively expressed in μ m. After testing the samples, fracture surfaces of broken samples were assessed by means of FESEM in order to measure the actual notch depth at the failure of origin.

Transversal rupture strength (TRS) was measured under three-point bending test following the ISO 3327-B. Tests were conducted using a universal servo-hydraulic testing machine (Quasar 50 by Galdabini). Flexural strength was calculated as Eq. 3 [11]:

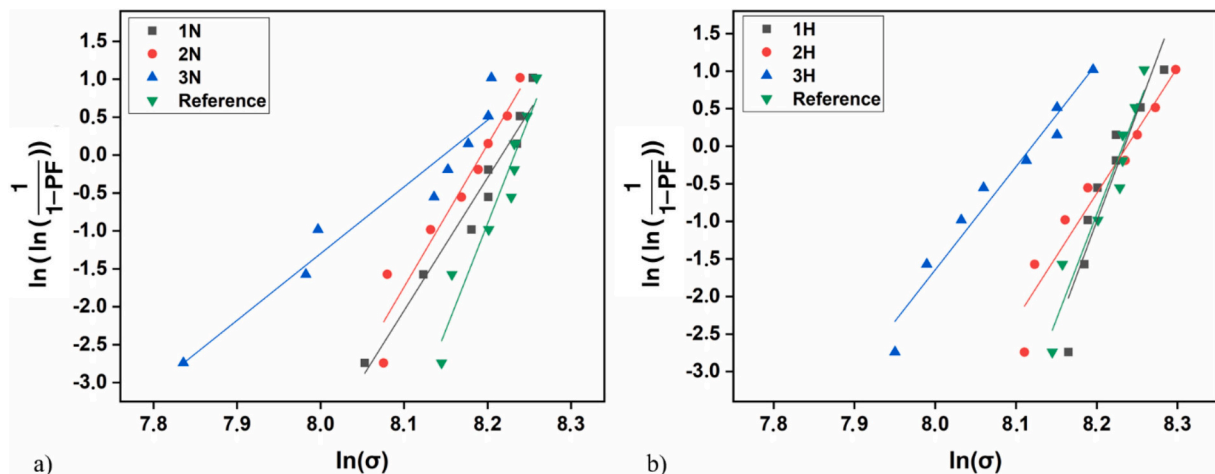


Fig. 2. Linear regression of the natural logarithm of TRS values for reference and: a) N recycled test specimens; b) H recycled test specimens.

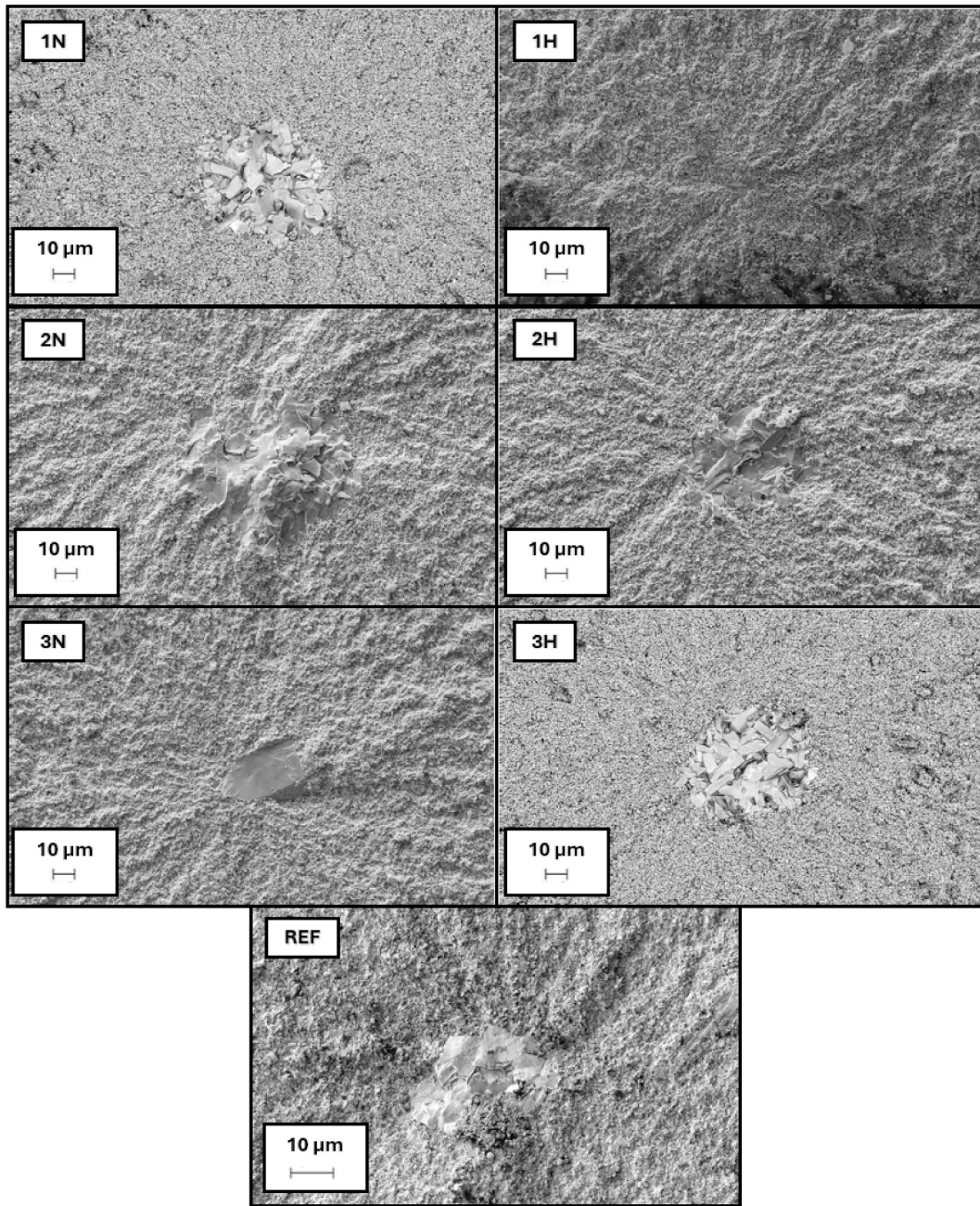


Fig. 3. FESEM images of failure origin in the fracture surface of recycled test specimens (1 N, 1 H, 2 N, 2 H, 3 N and 3 H) and reference test specimen (REF). Only one image per group of samples is reported as a representative.

$$\sigma_f = \frac{3FL}{2bd^2} \quad (3)$$

where F is the maximum load in N , L is the length of the support span (14.5 mm), b is the width of the sample and d is the thickness, both expressed in mm.

It is well-known that fracture behavior of cemented carbides is of stochastic nature due to their brittle nature. Therefore, strength of HMs depends on the size of the major and most critical flaw. It gives a wide scatter due to the variability of size, distribution and nature of the defects. Within this context, a two parameter Weibull distribution is commonly recalled to analyze flexural strength, by Eq. 4:

$$P_f = 1 - \exp \left[- \left(\frac{\sigma_f}{\sigma_0} \right)^m \right] \quad (4)$$

where P_f and σ_f are the experimentally determined failure probability and strength data respectively, while σ_0 and m are material constants which rule the fracture distribution. σ_0 is defined as the characteristic strength and corresponds to the stress at which the failure probability is 63%. Meanwhile m , referred to as the Weibull modulus, describes the scatter of the strength data, and thus, accounts for its variability. Afterwards, fractographic inspection (by optical microscope and FESEM) of all the broken samples was carried out to identify the sites of fracture origin.

3. Results and discussion

In Table 1 the microstructural parameters of tested specimens obtained by reference and recycled powders are listed.

As shown in Table 1, different carbon content and pre-sintering gas

do not seem to affect significantly the microstructural parameters, for which very close values were recorded. This is supported by the microstructure images from recycled and reference specimens, Fig. 1. From them, shape differences of the carbide grains were detected. Recycled materials show carbide grains with an elongated and flattened shape, while the typical block shape of WC grains was found for the reference sample.

The assessment of carbon balance in this work relies primarily on systematic microstructural and fractographic examination, in which no evidence of η -phase or free graphite was observed across all samples analysed.

Results of Vickers hardness, fracture toughness, and TRS are reported in Table 2 for both reference and recycled test specimens.

Hardness values for the different recycled samples are very similar among them, following the homogeneity of the microstructure for the different types of specimens. Co content and grain size of recycled samples (about 16 wt% Co and 0.7 μm WC) are not the same as those from the reference sample (about 19 wt% Co and 0.5–0.6 μm WC). Even so, materials with lower Co content and bigger WC particles yield alike hardness values as those determined for materials with higher Co content and smaller WC particles. In this context, HV values measured are similar among them and in agreement with the ones reported in the literature [16]. Fracture toughness values measured were around 14 $\text{MPa}\cdot\text{m}^{1/2}$ for all the samples. This is in complete agreement with the measured hardness values and with the literature values found for cemented carbides with similar microstructural features and/or hardness [17].

Fig. 2 shows the linear regression of the natural logarithm of TRS values per each group of samples. Fig. 3 documents SEM images of representative failure origins for recycled and reference samples.

Weibull modulus (m) and characteristic strength (σ_0) measured exhibit expected values for similar HM grades [17–19]. In all the samples, an agglomerate of carbides was identified as the origin of the fracture, including the reference specimen. Although all sample groups present a similar characteristic strength, some difference in terms of Weibull moduli can be highlighted. The samples sintered under hydrogen atmosphere presents better Weibull moduli than the ones sintered under nitrogen atmosphere for the same carbon content. Besides, samples 3 N and 3 H have values of the Weibull moduli very low compared to the others. These findings should be related to the fact that the defects found during the fractographical inspection present a wide range of sizes and shapes, Fig. 3. Despite this, the origin and type of defect are similar across all grades, with carbide agglomerations or individual carbides tens of micrometres larger than the average carbide size. It would allow to rationalize the relatively lower reliability exhibited by them in comparison of the other ones. It seems that the recycled sample 1 H exhibits a similar strength behavior to the one documented for the reference sample, pointing it out as the best combination, at least within the framework of the gathered data. Nevertheless, more samples shall be tested for each condition to verify this trend.

4. Conclusions

This study presents a first evaluation of the microstructure and mechanical properties of recycled HMs obtained through a new versatile process, demonstrating to have good quality, meeting the market standards for HM tools. Indeed, despite the recycling process affects in some way the WC grain morphology – a phenomenon currently under investigation – it does not appear to have an influence on other microstructural parameters and mechanical properties. In fact, these values are in satisfactory agreement with those measured for a conventional, non-recycled commercial HM grade, that in the future is expected to be produced with the larger fraction possible of recycled powders.

These findings provide a solid basis for the innovation in current recycling techniques, supporting the use of low environmental impact

reagents such as lactic acid, which can itself be produced from agro-industrial waste. Further investigations into recycled materials obtained applying the entire process, including the recovery of W and Co from the leaching solution, are currently in progress.

CRediT authorship contribution statement

M. Cera: Writing – review & editing, Writing – original draft, Methodology, Investigation, Formal analysis, Data curation. **L. Cabezas:** Writing – review & editing, Writing – original draft, Methodology, Investigation, Formal analysis, Data curation. **G.P. De Gaudenzi:** Writing – review & editing, Supervision, Resources, Methodology, Conceptualization. **S. Tedeschi:** Writing – review & editing, Methodology, Investigation, Data curation. **A. Serpe:** Writing – review & editing, Supervision, Project administration, Methodology, Funding acquisition, Conceptualization. **L. Llanes:** Writing – review & editing, Supervision, Resources, Methodology, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

L. L. is serving as Associate Editor for IJRMHM. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Data availability

No data was used for the research described in the article.

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