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INFLUENCE OF DISSOLVED OXYGEN CONTENT ON THE PROPERTIES OF AQUEOUS MILLED WC-Co POWDERS

The research aims to develop a novel and safer milling route to produce Hard Metals. Considering the risks associated with milling fine particles under organic solvents, especially the increased fire and explosion risks, we propose milling under aqueous milling media to diminish the risks associated with fire hazards, while maintaining the oxidation level at a minimum. The samples were sintered in an industrial sintering oven under vacuum at 1380°C subsequent to milling and drying. The characterisation of the materials has been done by X-ray diffraction, scanning electron microscopy, particle size analysis, optical microscopy, and a magnetometer. The obtained results indicate that appropriate properties of the powders after milling and drying as well as the desired biphasic (Co-WC) phases were obtained after sintering, thus proving the feasibility of such a route and diminishing specific fire hazards.

Keywords: Cemented carbides; hard metal; milling; drying; sintering; agglomerate

1. Introduction

Since the discovery of cemented carbides, their industrial application has grown and diversified, especially in many areas of the industry, from rock drilling, steel machining and even to medical applications [1]. The WC-Co composite is nowadays one of the most used materials for tool manufacturing. This composite is made up typically of two main phases, one hard phase (carbide) and one ductile phase (metallic binder), which usually is one of these transition metals: Ni, Fe, Co [1-3]. The most used binder for such materials is Co because of the excellent wetting of the WC particles by liquid phase sintering and because of the good mechanical properties, such as ductility, which, combined with the hardness of WC particles, provides this composite an impressive wear resistance [4]. Usually, the content of the binder phase varies from 3% up to 30% of total weight, based on the type of the application of such materials, while the carbide particle size, the domain ranging from nanometric up to 20 microns is of industrial interest. Based on this combination, the desired mechanical properties can be achieved. In order to limit the excessive grain growth that occurs upon liquid phase sintering, there are several other carbides added as dopants with the sole purpose of grain growth inhibition [5,6]. Further improvement of the mechanical properties of such WC-Co tools can be made by applying a coating by CVD (chemical vapour deposition) or PVD (physical vapour deposition) such as TiN, diamond coating or multilayer coating like (Ti, Al)N or Zr(C, N) [[1]].

Industrially, the production of WC-Co powders is commonly done in large attrition mills. The main advantage of such mills is that the powder is added along with a liquid medium, which forms a slurry, thus inhibiting the direct contact between air and powder. The primary purpose of milling for such materials is to ensure a good homogeneity within the powder and, in some cases, to tailor the desired particle size [7-9]. One of the milling medium‘s functions is to protect the powder from oxidation and local overheating. Industrially, for these reasons, organic compounds such as isohexane, ethanol, acetone are used [10-13] however, by employing such media, besides the desired advantages, a homogeneously distributed powder without any agglomerates, there are certain downsides, which are becoming more and more important nowadays, such as the negative impact on the environment and the CO_2 free production targets.

The classical, industrially employed organic milling media leads to unagglomerated powder with a minimum degree of oxidation, ensuring appropriate properties of the sintered compact [14]. The greener way, milling in water, could result in hard agglomerates and cobalt oxidation. Andersson et al. have clarified that the pH modifications during the WC and Co dissolution in water modify their behaviour, while Chivot’s brings a further understanding of how Co interacts with water [15-18]. According

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to Laarz et al. [19] adding polyethyleneimine to the milling media will provide a good dispersion of powder in the media, which is the key to eliminating the formation of agglomerates. One of our previous studies proved that the milling time in an aqueous medium influences the properties of the sintered products [20], but also, as expected, by increasing the milling duration, smaller particle size can be obtained, and the powder tends to form flake like agglomerates [8]. In another study, an aqueous milling media with the adjusted pH was used as a milling medium, and a hard agglomerates free powder was obtained [21].

One of the challenges the hard metal industry faces is milling under aqueous media without forming any hard agglomerates [22]. The main objective of this work is to determine how the oxygen content of the used milling media influences the powder and, subsequently, the sintered product's properties. Implementing an aqueous way of milling these hard metal powders is in the industry's interest, reducing costs, fire risk, and human health risk factors. The main challenge is obtaining hard agglomerates and oxides free powder. We analysed the powder during the drying period, sintered the probes and characterised the obtained samples. Previous published research on this topic report the oxidation of samples after aqueous milling, as well as some traces of the used corrosion inhibitor. One of the leading causes of oxidation is the dissolved oxygen in water, which interacts with the new surfaces of the powder generated during milling. The novelty of our proposed route is the reduction of the oxidation risks by tailoring the oxide content of the milling media.

2. Materials and methods

WC and Co powders were used as base materials for producing WC-Co bulk material. A Netzsch PE5 attrition mill was used for the material milling, which has the shaft and the balls made up of cemented carbide to reduce the chance of contamination. Two hours of milling were employed under aqueous milling media by using distilled water with reduced oxygen content. A certain amount of corrosion inhibitor (2%) was used to inhibit the oxidation further. The corrosion inhibitor we used is triethanolamine, which adjusts and buffers pH, acting as an anti-corossion agent and adjusting the pH of the milling media. The milling was performed for four h at a constant speed of 350 rpm with a filling factor of 100%. The reduction of the oxygen content was made by sparging with CO_2. It is essential to mention that sparging with CO_2 reduced the pH of the water. According to Henry's law, the dissolved gas is proportional to the pressure of the gas above the solution, so during milling above the suspension, a slight CO_2 overpressure was maintained. It is essential to mention that no additional grain growth inhibitor was used for all milling experiments.

After the milling, both powders were dried for 48h in a Büchi rotary vacuum dryer under 40 mbar pressure, and the bath temperature was set to 40°C. The resulting powders' characterisation was performed using a Keyence microscope, SEM Gemini Zeiss equipped with an EDAX spectroscopy sensor to assess the elemental mapping in the powder. Although the milling was performed in an aqueous medium and subsequently dried, there is a certain amount of residual humidity in the powder, which was quantified using a Mettler Toledo HC103 thermobalance. Using a KOERZIMAT 1.097 magnetometer, the sintered samples' saturation magnetisation and coercive field have been assessed. These two magnetic properties give indices regarding the microstructure of the samples. The saturation magnetisation indicates the amount of ferromagnetic cobalt (unreacted with the WC), whereas the coercivity indicates the finesse of the structure. Larger saturation magnetisation values indicate the presence of carbon, while lower values indicate the presence of eta phases, a combination (Co, W)C. The optical micrographs were obtained on polished surfaces using Murakami etching.

3. Results and discussion

In this case, we investigated the effect of reducing the oxygen content on the properties of the powder when milling under an aqueous medium (water + corrosion inhibitor). Using the corrosion inhibitor has two main purposes: to protect the powder of oxidation; and to prevent the powder from forming hard agglomeration at the drying stage. One of the leading causes of oxidation is the dissolved oxygen in water, which interacts with the new surfaces of the powder generated during milling.

Fig. 1 presents the two investigated methods, one by decreasing the pressure to remove dissolved oxygen and the other by sparging water with CO_2. As shown in Fig. 1, after the sparging with CO_2 the reduced amount of low oxygen maintains in time as opposed to when decreasing the pressure, where the dissolved oxygen returns to the initial value.

Since the dissolved oxygen content is not maintained at low values by decreasing the external pressure, the CO_2 sparging route was preferred for further processing. Moreover, a pH decrease is noticed upon sparging, as highlighted by the pH evolution highlighted in Fig. 2.

During this process, the following reactions are possible, and the carbonic acid is formed when water reacts with CO_2 [23]:

$$CO_2(g) \leftrightarrow CO_2(l) \tag{1}$$

$$CO_2(l) + H_2O(l) \leftrightarrow H_2CO_3(l) \tag{2}$$

$$H_2CO_3(l) \leftrightarrow HCO_3^-(l) + H^+(l) \tag{3}$$

$$HCO_3^-(l) \leftrightarrow CO_3^{2-}(l) + H^+(l) \tag{4}$$

In the first case, an inhibitor-free distilled water sparged with CO_2 was used. By analysing the powder by SEM, one can see that the more oversized agglomerates are made up of much smaller ones and that there are larger single particles, as highlighted in Fig. 3. By performing the chemical mapping of the elements, the local distributions of elements revealed that these large, big particles are cobalt particles, as highlighted in Fig. 3. Such behaviour is expected, especially since cobalt is a more ductile material than WC, and for such materials, the fragmen-

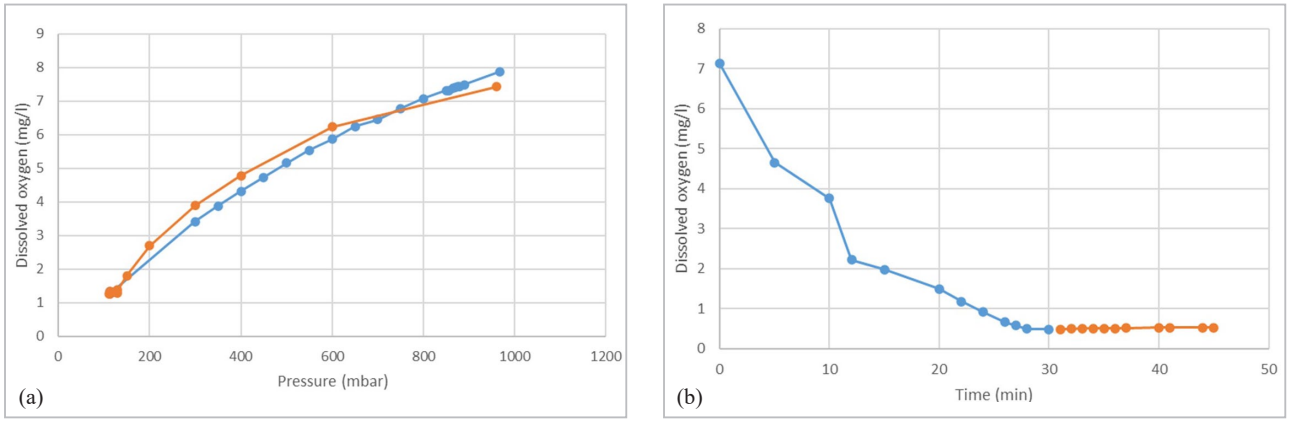

Fig. 1. Evolution of dissolved oxygen content as a function of external pressure (a) and (b) CO_2 sparging duration

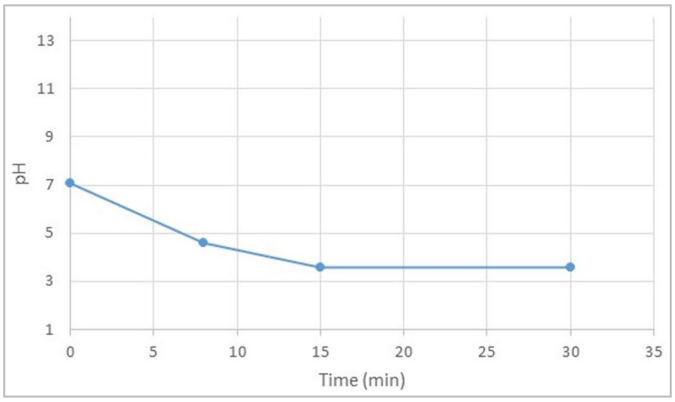

Fig. 2. Evolution of the suspension pH as a function of CO_2 sparging duration

tation occurs only after longer milling durations. In the early stages of milling, ductile materials will suffer plastic deformation induced by milling bodies, which in the later stages of milling, work-hardening will lead to fragmentation.

In the case of milling such materials, especially under an aqueous medium, the residual humidity represents an essential factor. In this case, the measured residual humidity of the milled and dried powder is 0,79 wt.%. An appropriate humidity can ensure the proper flow of the particles, which represents an important technological parameter for further implementing such materials. Besides this, another major technological characteristic that the residual humidity can affect is the shelf life of such a powder, considering that the residual humidity could continuously oxidize the powder upon storing. Powder oxidation can lead to undesired eta phases after sintering such materials.

Milling the WC-Co powder in an aqueous medium with the addition of the corrosion inhibitor and subsequent drying resulted in a powder consisting of one with soft and low size agglomerates. It is worth mentioning that during the milling process, the slurry started to foam, which suggests that an antifoaming agent could also be added during milling. The foam formation was assigned to the corrosion inhibitor, which reduces the superficial tension of the water, thus forming more easily foam. The residual humidity of the resulted powder is higher (1,2 wt%) than the powder milled without corrosion inhibitor. This has been assigned to the nature of the corrosion inhibitor, which influences the remanent humidity of the powder. Given that the measurement records the mass loss upon increasing temperature, another reason for the larger measured value is

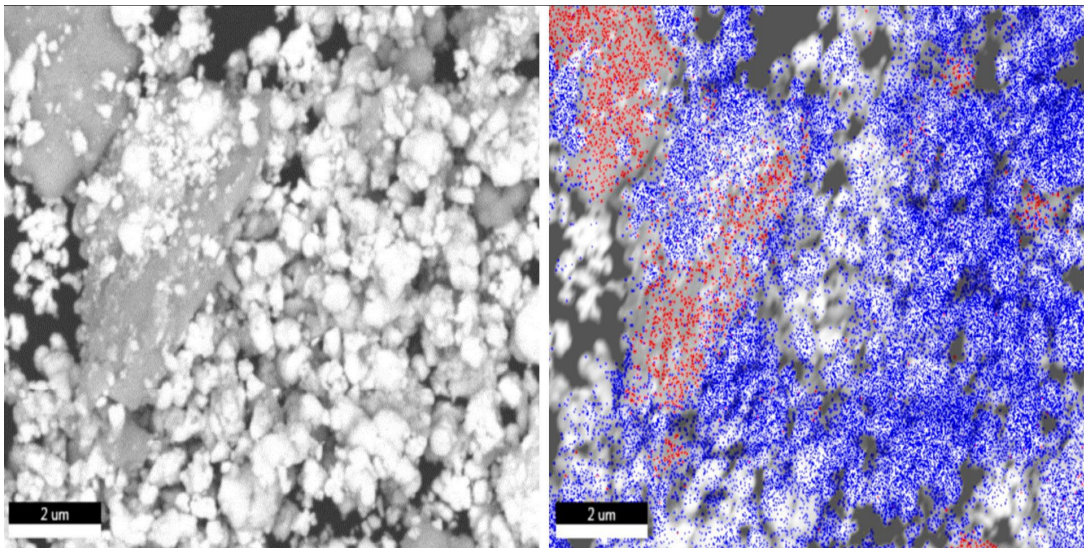

Fig. 3. Elemental distribution of the W and Co in the milled and dried WC-Co powder

the incipient decomposition of a part of the corrosion inhibitor under the temperature condition (200°C).

In Fig. 4 is presented the morphology of the powder, which, in this case, reveals a well-distributed particle size arrangement and morphology. One can notice that particles range from the submicronic domain to particles with a few microns diameter. Such a distribution helps press the powder in form because it enables a denser green shape.

For the other batch of samples, we used sparged water with the addition of a corrosion inhibitor. In this case, no foam was formed. This behaviour has been assigned to the reduced pH level of the water. The resulted powder forms hard and middle-sized agglomerates. In our previous studies, we proved the correlation between the pH of the water and the presence of hard agglomerates [21]. Besides the pH of the milling suspension, the Zeta potential influences the sedimentation of the powder. The powder was milled using sparged water with the addition of corrosion inhibitor as milling media presents a high humidity level, 1,53 wt%. Analysing the powder by SEM, one can see that the powder is well dispersed and has a suitable particle size distribution, as highlighted in Fig. 5.

The SEM images show that the morphology and particle size distribution are very close to the powder milled using corrosion inhibitor without sparging. The particles were subsequently pressed and sintered into cylindrical shapes and then analysed, primarily to determine the metallic binder's chemical nature through non-destructive analysis methods. The sintering was done under industrial SinterHIP ovens under the same parameters employed in production for traditionally processed materials. Although there was no plasticiser added to the powder, two different sintered cycles were employed to determine whether the more reductive (H_2 cycle) or the less reductive (Ar partial pressure) is more suitable for such materials. The magnetic saturation (given by the percentage of magnetic phase), the coercivity, and hardness were measured for the resulting probes. The results are presented in TABLE 1.

The coercive force indicates how many magnetic domains are in the material; thus, more magnetic domains mean more

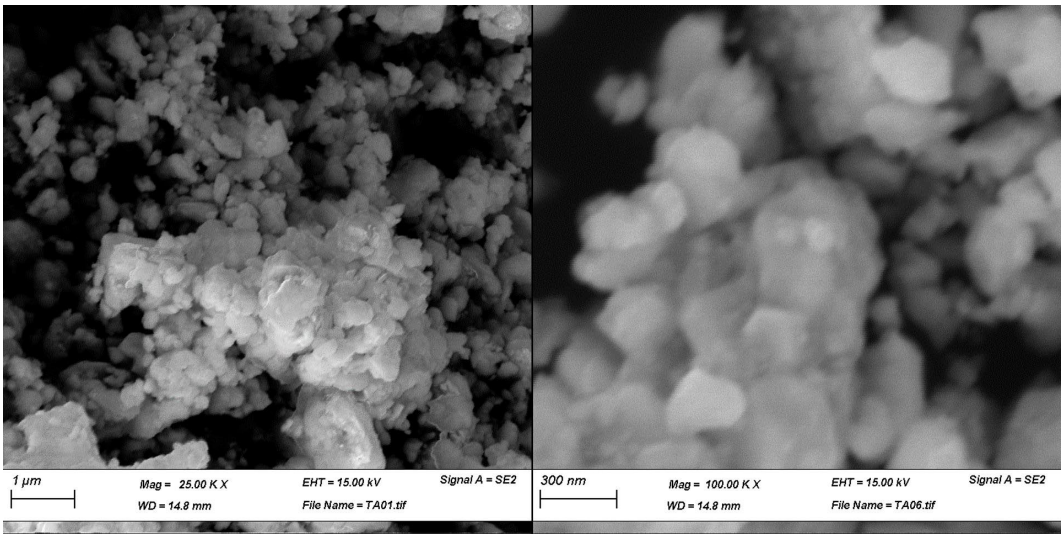

Fig. 4. Morphology of the powder milled in aqueous suspension (water + corrosion inhibitor) at different magnification levels

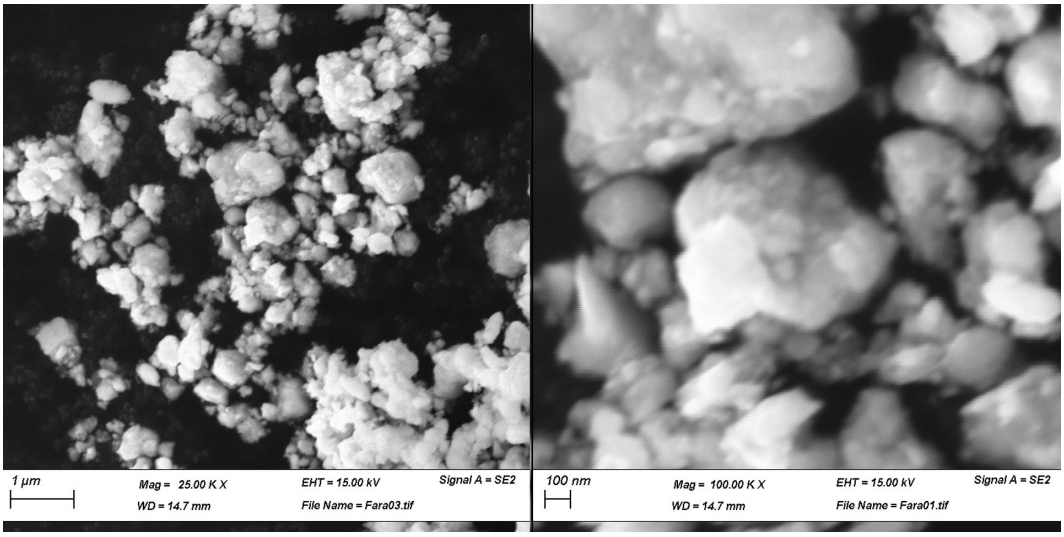

Fig. 5. Morphology of the powder milled in aqueous suspension (water + corrosion inhibitor) sparged with CO_2 at different magnification levels

TABLE 1

Mechanical and magnetic properties of the compacts from powders milled under different milling media

	Hydrogen sintering cycle		Argon sintering cycle	
Probe	**C.I.+CO_2**	**CI.**	**C.I.+CO_2**	**CI.**
HC [Oe]	260	254	258	255
Ms [0,1 × μTm³/kg]	125	123	134	106
feromagnetic phase (wt%)	6,1%	6%	6,6%	5,2%
Hardness HV30	1663	1658	1632	1658

(C.I. = corrosion inhibitor; CO_2 = water sparged with carbon dioxide)

refined WC grains and vice-versa. The coercive force of the probes indicates a fine WC grain size with a neglectable deviation between probes. On the other hand, the magnetic saturation indicates the magnetic phase quantity (unreacted metallic binder). From the obtained results, saturation magnetisation situated in the 12,3-13,4 μTm³/kg, we can conclude that a secondary phase, η-phase, has been formed, which lowers the magnetic saturation value due to its paramagnetic nature. This phase also provides a higher hardness and brittleness, therefore not desired in the samples, except for some special applications, where its occurrence is desired [24]. The magnetic saturation results reveal that changing the dewaxing program can influence the total amount of unreacted Co in the final sample. The recorded micrographs also confirm these aspects after polishing these samples, presented in Fig. 6.

As shown in Fig. 6, reducing the total amount of dissolved oxygen in the milling media reduces the amount of undesired η-phase is reduced significantly for both employed sintering cycles. The WC particle distribution is similar in all cases; however, Argon partial pressure sintering cycle has led to the best results in this case.

4. Conclusions

Milling hard metals in aqueous media to obtain soft and small agglomerates is possible with the addition of a corrosion inhibitor under the current parameters. By sparging the milling media with CO_2, the amount of dissolved oxygen can be reduced efficiently, while on the other side, decreasing the pressure only leads to a temporary reduction of the dissolved oxygen, which returns to the initial value when returning to normal pressure. The magnetic properties of the sintered powders indicate that η-phase formed (low magnetisation), and on the other hand, the coercive force for all probes is in the correct interval. The optical micrographs recorded on these samples reveal the benefits of reducing the total oxygen content of the milling media. The current study proves the benefits of reducing the dissolved oxygen content of the milling media. However, one of the current shortcomings of the proposed route is the presence of a small amount of η-phases which are undesired. Further investigations are in progress to inhibit the formation of and thus expand the application domain of such materials.

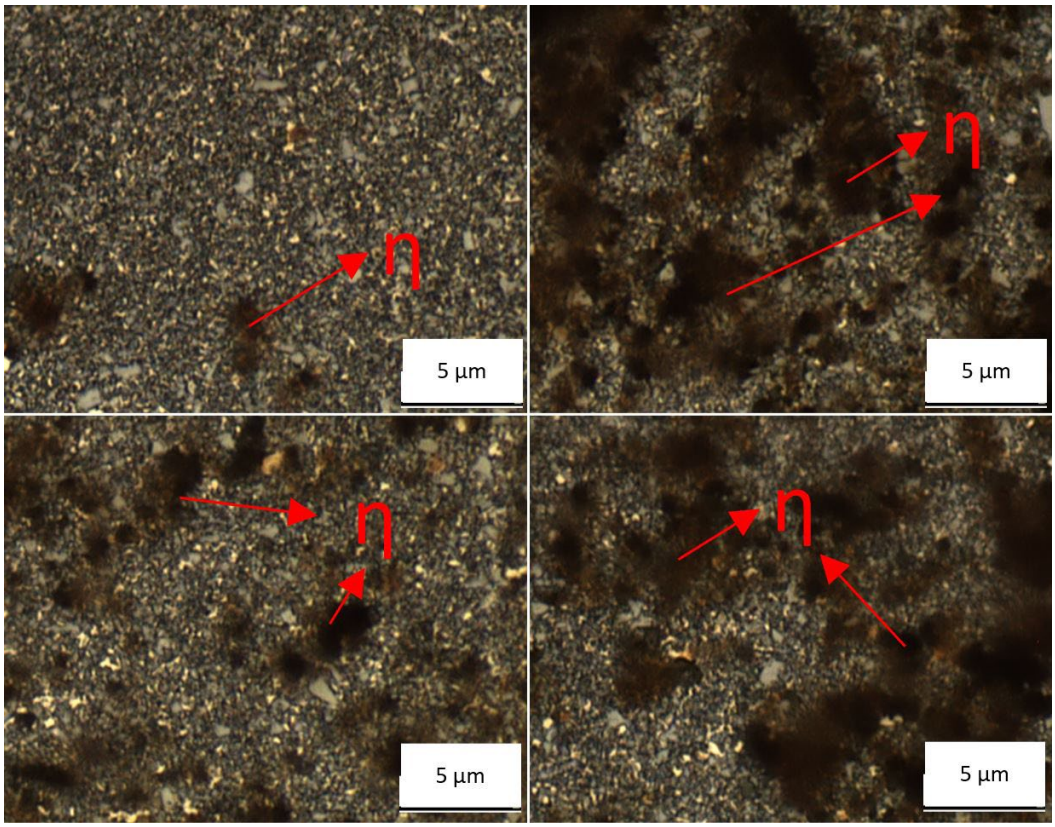

Fig. 6. Optical micrographs of the WC-Co samples milled in aqueous media (water + corrosion inhibitor) with CO_2 sparging (left) and without CO_2 sparging for the two sintering cycles. The Argon cycle is presented in the top two images and the Hydrogen cycle in the bottom two images

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