Arch. Metall. Mater. **67** (2022), 2, 541-545

DOI: https://doi.org/10.24425/amm.2022.137788

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CONSOLIDATION AND CHARACTERISATION OF HARD METAL POWDERS MILLED UNDER DICHLOROMETHANE

This work presents the development of a safer processing route for hard metals. Traditional processing of fine particles under organic solvents presents significant explosion risks. The milling under dichloromethane (DCM) reduces the risks associated with fire hazards. After milling and drying, the samples have been sintered in an industrial sintering furnace under a vacuum at 1380°C. The materials' characterisation has been done by X-ray diffraction, scanning electron microscopy, particle size analysis, optical microscopy, and by magnetic measurements. The present work results reveal the powders' appropriate properties after milling and drying and the desired biphasic (Co-WC) phases obtained after sintering, thus proving the feasibility of such a route, therefore the diminishing of specific fire hazards.

Keywords: hard metal; sintering; milling; particle; dichloromethane

1. Introduction

Hard metals represent one of the most successful products of powder metallurgy (PM) [1-3]. This class of materials is comprised of a hard phase, typically WC particles, and a tough metallic binder which usually is Cobalt, mainly due to its good wettability [4]. As their name suggests, this class of materials combine the tungsten carbide's high hardness and the metallic binder's toughness. These materials' properties can be tailored by modifying the cobalt amount or the carbide particle size based on their applications [1,5]. The carbide particle size varies from nanometric domain up to 10 µm, while the Co content is of practical interest in the 3-30 wt.% range [1,6]. Desired composition, size and homogeneous distributions of the powder is achieved via PM routes [3]. One of the essential processing steps of such materials is milling the powders under an organic solvent to prevent excessive heating or oxidation [7]. Such a process's main drawback is represented by the associated fire hazards of fine particles and flammable organic solvent traditionally employed (isohexane, alcohols, acetone). Most of the hard metals research is focused on developing novel carbide grades with increased hardness and toughness or by developing alternative routes [8-10]. Nowadays, researchers have focused their attention on developing safer and eco-friendly processes to overcome traditional milling media shortcomings. However, by using this approach, there are significant downsides, such as the formation of hard agglomerates and powder oxidation [4,11,13]. Andersson and Bergström's work highlights WC and Co's dissolution in water [11], while reference indicates a method of dispersing WC-Co powders in aqueous media by using polyethyleneimine PEI [13]. Our previous works have focused on preventing agglomeration by tailoring the zeta potential and using corrosion inhibitor to prevent powder oxidation [4].

This paper describes our proposed milling process's results, which aims to overcome such shortcomings by milling under a non-flammable milling media such as dichloromethane (DCM) compared to a traditional milling route. The main advantage of this milling medium over the classical ones is that it is not flammable. The employment of such a solvent should reduce fire hazards considerably. Dichloromethane is considered a borderline non-polar solvent, mainly because its molecule is symmetrical [14]. The use of non-polar solvent ought to reduce the agglomeration tendency due to different sedimentation kinetics [12]. The purpose of the present work is to use develop an alternative route of processing hard metals with reduced fire risks, without affecting the final product properties.

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2. Materials and methods

The milling experiments have been done using one of the most common cemented carbides: WC and Co powders with respect to the 90:10 weight ratio. Once the starting mixtures were dosed, the powders have been blended in a turbula type apparatus for 30 min. The homogeneous mixture is referred to as the starting sample (SS). Two different batches have been prepared by attrition milling starting from the SS to highlight our approach's benefits. For the first batch, isohexane milling has been employed to have a benchmark sample processed in the traditional method. For the second batch, the milling media was changed to the non-flammable dichloromethane (DCM) using the same milling parameters: milling duration of 2 h in a Netzsch PE5 attritor. The attritor milling speed was 350 rpm, and WC-Co milling balls have been used to reduce powder contamination. The solvent removal has been performed by rotary vacuum evaporation in a Büchi Rotavapor 100 using the following parameters, 40 mbar, 60°C and 60 rpm. The determination of the phases existing in the samples after milling has been performed by X-ray diffraction (XRD) using an Inel Equinox 3000. The particle size analysis was done using an Anton Paar PSA 1090 particle size analyser and using a Sigma Gemini Zeiss SEM (Scanning electron microscope). The residual moisture of the milled powders was determined using a Mettler Toledo HC103 scale. The measurement was performed at 200°C for 5 minutes using samples of 3 g for each measurement. The samples have been sintered in an industrial furnace at eutectic temperature (1380°C) in a vacuum. After sintering, assessing the phases present in materials has been done by measuring the saturation magnetisation and compacts' coercivity. The accuracy of such a method in evaluating whether the material is in the desired biphasic region is 0.01%.

3. Results and discussions

In Figure 1 are given the X-ray diffractions recorded on the starting sample as on the samples milled under DCM and isohexane. As shown in the figure, there are four phases identifiable in the material before and after milling.

Besides the majority stoichiometric WC (6.12 wt.%), there is a residual amount of W_2C detected in the material and the two allotropic forms of Co, hexagonal close-packed (HCP) and face centred cubic (FCC). The occurrence of residual W2C is indicated by the presence of its three most intense diffraction peaks, and a small amount is expected considering it is an intermediary product of the synthesis of WC from tungsten trioxide (WO_3) by carburisation [5,15]. It is worth mentioning that FCC cobalt and α-W_2C phase are not thermodynamically stable at RT under normal conditions; their presence has been previously reported [4,5,16]. The milled samples' XRD patterns reveal decreased HCP Co peaks, even for such short processing times. This behaviour has been assigned to the mechanically induced allotropic transformation of Co, highlighted in previous studies [17,18].

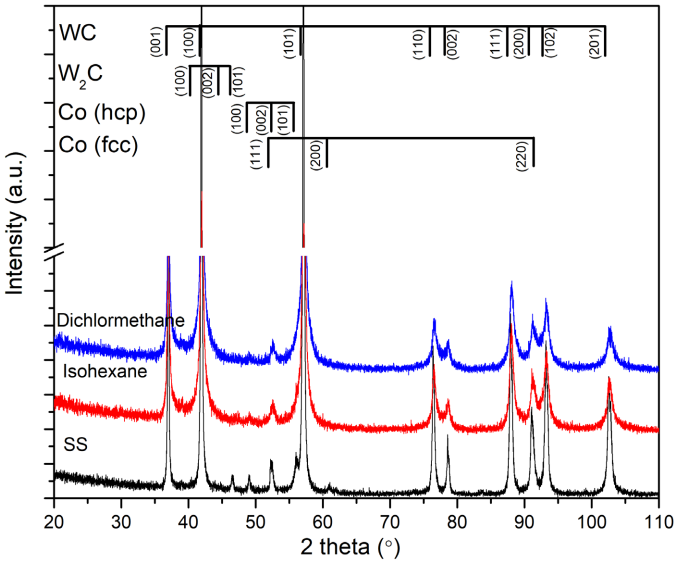

Fig. 1. XRD patterns recorded on the WC-Co samples milled under isohexane and dichloromethane. For comparison, the XRD pattern of the starting sample is also given

On the other hand, one can also notice a slight peak broadening, which results from a slight decrease in the mean crystallite size and the accumulation of internal stresses during milling [7].

No significant difference between the XRD patterns is observed by comparing the milled samples' diffractions in the two different milling media. Considering this, we concluded that the milling medium's substitution does not play a vital role in the material's structural evolution upon sintering. However, from a morphological point of view, specific differences were observed, as shown in the optical microscopy images given in Figure 2.

As shown in figure 2, the particles are agglomerated into larger rounder aggregates, which is expected considering the drying method. It is worth mentioning that for isohexane (non-polar), the agglomerates were smaller and more friable than DCM (borderline non-polar). It is well known that the milling media's polarity influences the hardness of the agglomerates obtained after drying and their friability [12,19-21]. The obtained results are following this expected behaviour. On the other hand, the materials' SEM investigation reveals similar morphology and size for both employed solvents, as shown in figure 3.

The SEM investigation reveals that the used solvent influences the powder agglomeration behaviour only at the microscopic scale and that in the nanometric domain, thus the particles morphology is not influenced by the substitution of the processing media. Moreover, the powders' macroscopic analysis has revealed a pronounced agglomeration tendency intro larger aggregates ranging up to millimetric domain in some cases. It is worth mentioning that the agglomerates can be disintegrated easily and do not require any other additional mechanical treatment. In both cases, friable agglomerates were obtained, an essential aspect of the powders' further processability. The determined residual moisture was 0.86% for isohexane, while for DCM was 0.94%. These results could also be explained by

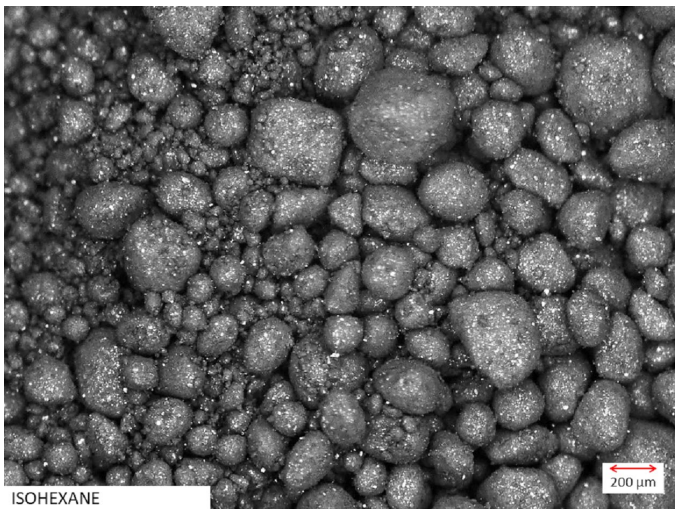

Fig. 2a. Optical microscopy images recorded on the samples milled under isohexane

Fig. 2b. Optical microscopy images recorded on the samples milled under DCM

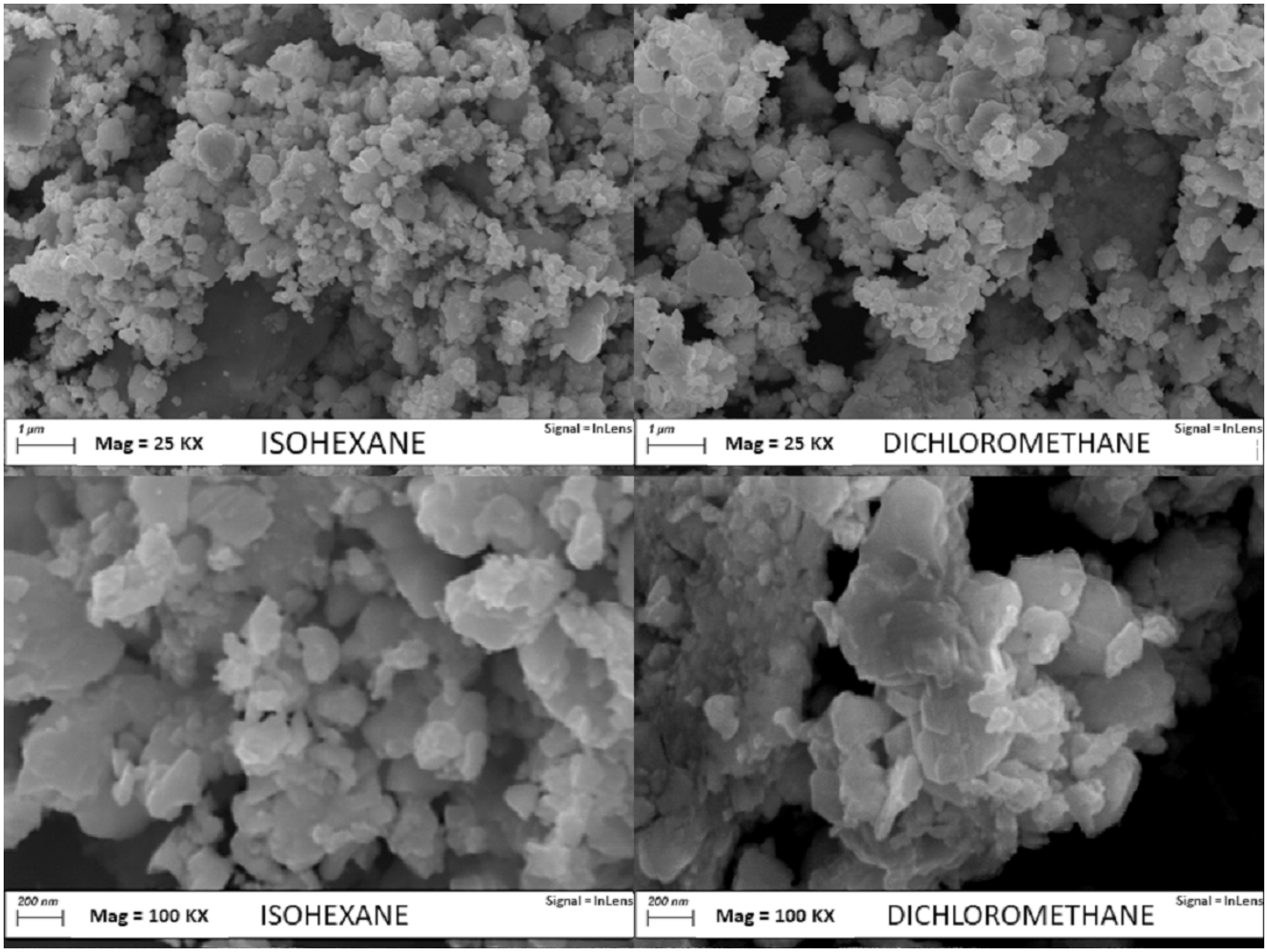

Fig. 3. SEM images of the HM powders milled under isohexane (left) and DCM (right) at different magnification levels

the slightly larger agglomerates obtained for DCM, which could entrap a more considerable amount of water.

It is worth mentioning that the particle size analysis presented in figure 4 confirms the observed behaviour and abovementioned interpretations: the particles tend to form larger agglomerates, up to more than 100 microns, which are comprised of smaller submicronic particles as highlighted in the SEM images. The slightly larger value of the D_{50} parameter for

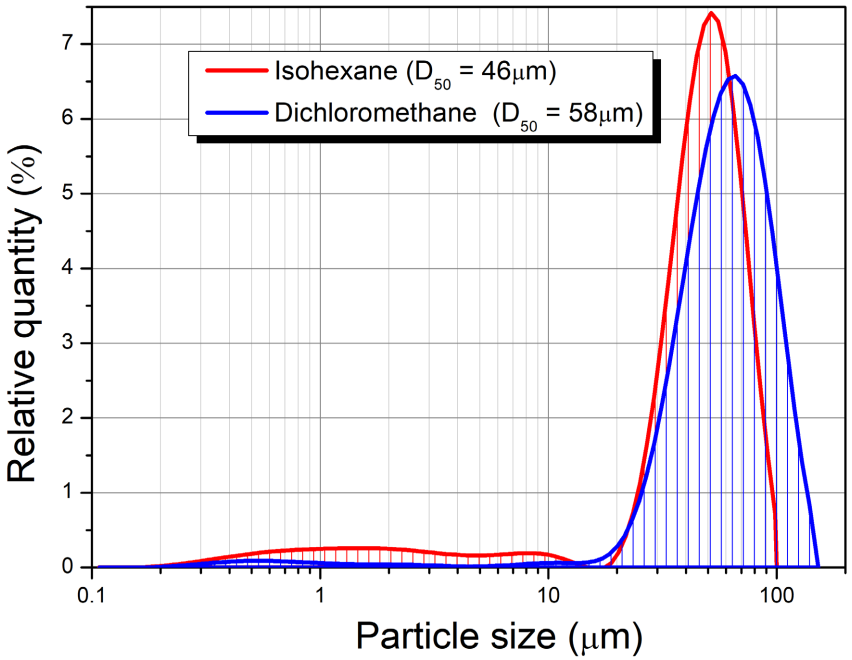

Fig. 4. Particle size distributions recorded on the WC-Co samples milled under isohexane and dichloromethane. For a better understanding, the values of the D_{50} parameter are given

the DCM sample suggests that the agglomerates formed after drying are less friable or that their size is slightly larger. This behaviour is expected since DCM is borderline non-polar while isohexane is non-polar. To assess the agglomerates' friability, the powders have been pressed in cylindrical shapes with the same pressure (430 MPa). For the sample milled under DCM, the obtained green density was 7.38 g/cm^3, representing a 50.8% relative density. For isohexane, where softer agglomerates were encountered, the green density was 7.69 g/cm^3 (53% relative density). The 2% relative density difference did not play a vital role in the sintering behaviour. The obtained magnetic properties suggest that compacts with appropriate microstructure have been obtained after sintering [5]. In table 1 are presented the values of the saturation magnetisation and coercivity for the samples milled under different milling media and sintered.

TABLE 1

Magnetic properties of the sintered WC-Co powders milled under different milling media and dried under a protective atmosphere

Milling Media	Saturation magnetisation [0,1 × μTm³/kg]	Coercive field [Oe]	η phase
Isohexane	139	257	No
Dichloromethane	134	240	No

The sintered compacts' magnetic characterisation revealed that both milling methods obtain appropriate properties. The saturation magnetisation value indicates that the material is situated in the biphasic region of the pseudobinary WC-Co phase diagram [22,23]. The slightly larger coercive field obtained for isohexane suggest a more refined microstructure, which is expected considering the particle size distributions given in figure 4.

4. Conclusions

This research aimed to substitute the traditional milling process to make the manufacturing process safer by reducing any fire hazards associated with traditional organic solvents. Dichloromethane represents a promising candidate considering that it is a non-flammable solvent, which is borderline non-polar. Processing the powders in this media is not adding any other supplementary operations or any significant decrease in the samples' quality. The XRD, SEM and optical microscopy revealed similar behaviour. The particle size distributions revealed a 12 microns increase of the D_{50} parameter for dichloromethane due to the formation of slightly larger agglomerates, which also influence the samples' total residual humidity. The samples' magnetic properties do not reveal any differences, highlighting that the proposed method does not deteriorate the final product properties. Changing the milling media does not influence the structural and morphological characteristics of these samples as revealed by the performed measurements. The imployment of such milling media is possible, however DCM compatible sealings should be foreseen for the equipments.

Acknowledgements

This paper was supported by the project POCU/380/6/13/123927 – ANTREDOC, "Entrepreneurial competencies and excellence research in doctoral and postdoctoral study programs" co-funded from the European Social Fund through the Human Capital Operational Program 2014-2020. Besides this, the infrastructure available from the European Development Fund and the Romanian Government through the Competitiveness Operational Pro-

gramme 2014-2020, project ID P 34 466, MySMIS code 121349, contract no.5/05.06.2018 is highly acknowledged.

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