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Powder metallurgy: Sustainable process for the manufacture of cemented carbides in Colombia

Pulvimetalurgia: Proceso sostenible para la fabricación de carburos cementados en Colombia

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Abstract

This paper presents the opportunity to promote the Colombian industry towards the development of new high performance materials manufactured by powder metallurgy (PM) as an alternative to the conventional manufacturing processes, generating new needs for the national industry. The objective of this work describe the manufacturing processes of composite materials, type CERMET, formed by a CERAMIC phase, which is tungsten carbide (WC), and a METAL phase which is cobalt (Co). Additionally, analyze at microstructural level the manufactured materials using vacuum sintering process. The designed alloy was a mixture of 88 % WC and 12 % Co according to ISO K40 standard. The process involved the control of precursor materials, found in powder form, followed by mixing and milling steps, and finally compaction and sintering. The microstructures and chemical compositions obtained by scanning electron microscopy (SEM-EDS) were studied in order to evaluate the mechanical behavior of the CerMet; for that, microhardness tests were performed reaching values of 1289HV0.5, which are related with the low porosity levels such as A02, B00, C00, and average grain size of 1.14 µm. These results indicate that is possible to manufacture wear resistance high performance materials in the country. It highlights the relevance of enhancing the synergy between government entities such as SENA-*Colciencias -Universidad Nacional* to create applied research in the country.

Keywords: Powder metallurgy; tungsten carbide; metallic powders; compaction; CERMET; sintering.

Introduction

Innovation in the industrial sector is key to generating employment and competitiveness of companies; this is why collaboration between researchers, universities, and companies is crucial to generate new sources of knowledge and business opportunities. Hence, the importance of the national industry of adopting innovation based on the challenges it faces in an open and competitive market. In this sense, Colombia in the last decades has taken the position of a net consumer country, where the import of raw material and finished products of high performance has been increased generating deindustrialization at local and national levels. Given this panorama, it is essential that in the country the study of poorly implemented manufacturing technologies be gives solutions to these needs, one of these alternatives is the implementation of powder metallurgy (PM). This manufacturing process consists of the production of pieces by means of powder compaction (pressing) and its subsequent thermal treatment (sintering) at temperatures below the melting point of the material. The manufacture of PM components begins with the mixing of metallic powders, ceramics or mixtures of these with the lubricant and the additives. This mixture is compacted inside a mold with the desired shape by applying pressure, which in the case of sintered steels ranges between 400 and 700 MPa (Randall, 1989). After compaction, the powder takes on the properties of a solid and said state of the process is usually referred to as "green". Subsequently, in the sintering under controlled atmosphere, either in vacuum or with the use of gases (Ar, H2, N2, among others) the metallurgical union between the particles takes place. After sintering, some parts are used directly in the condition of sintering while others are subjected to secondary operations of finishing (machining, calibration, oil impregnation, coatings, among others) or heat treatments (nitriding, quenching, among others).

The components manufactured by (PM) have certain advantages compared to conventional processes since relatively short processing times are required, energy consumption is 40 % less than conventional processes; likewise it is known that 85% of the raw material (powders) of the PM come from recycled material (Metal Powder Industries Federation, 2017) and in addition materials with excellent mechanical, tribological and corrosion properties are obtained; nevertheless it is a technology that requires an initial investment and an important maintenance and that is only economically viable when the production of pieces is high. On the other hand, because the starting material in this manufacturing process is in the form of a powder, the bulk density is much lower than the density of the solid, with which the weight of the finished products is reduced. By means of powder metallurgy, it is possible to obtain materials with very high densities, close to 98 %, with a fine, homogeneous microstructure and uniform distribution in carbides and inclusions. These characteristics are difficult to achieve by conventional methods such as casting where the segregation, produced during the solidification process, is not easy to control and it is feasible to obtain thick and non-homogeneous microstructures accompanied by low cross-sectional properties due to the formation of heterogeneous grains, as well as deficiencies in the control of its size (Hoeganaes, 2002).

The PM is an interesting option in applications that demand alloys of difficult processing by conventional methods, special materials with demanding mechanical and thermal properties added to an excellent behavior against wear and corrosion as it is the case of the tool steels (M2, M3 , among others.) and hard metals (Hillskog, 2003).

Cemented carbides or hard metals are one of the most successful composite materials that have been designed, which have outstanding chemical and thermal characteristics; as well as properties of exceptional hardness, resistance to abrasion and erosion (Katiyar, Singh, Singh & Kumar, 2016). This combination of properties is due to the fact that these composite materials are formed by refractory and brittle transition metals such as WC, TiC, TaC, Cr3C2 or Mo2C which are combined with a metal phase (matrix) composed mainly of Co, Ni, Fe (Upadhyaya, Sarathy & Wagner, 2001; Chan & Chan, 2014). These materials are also known as CERMET (Ceramic-Metallic) due to the presence of a ceramic phase, which for this work will be the WC dispersed in a metallic matrix of cobalt. The fundamental role of the ceramic phase is to provide the material with mechanical strength and hardness; while the metallic phase protects the ceramic phase, achieving a considerable increase in ductility, toughness and reducing the possibility of fragile fracture of the composite material (Vinicius *et al*, 2011). This type of material has been preferred for many years for demanding applications such as cutting tools, processes in mining sectors (oil & gas), among others (Katiyar, Singh, Singh & Kumar, 2016; Gant, Gee, Gohil & Jones , 2013).

From the PM, it is possible to manufacture a generation of new sustainable materials as a result of improvements and innovations in all stages of the manufacturing process. Consequently, this process is recognized as a green technology whose sustainability is based on the efficiency of raw materials, energy consumption and environmental impact.

In terms of raw materials, powders, efforts have focused on recycling and reusing them, it is estimated that 85% of powders used in PM come from recycled material (Metal Powder Industries Federation, 2016).

In this context, there is a potential market niche in terms of obtaining powders from hydrometallurgical processes (Shibata, Murayama & Masakazu, 2014) as well as the reuse of the minerals that are produced in the country. In this regard, the support of institutions such as the National University of Colombia and training and research centers such as SENA towards industry is necessary to generate an academic-scientific and industrial synergy. It is important to note that the reduction in energy consumption for components obtained by PM can reach 44% compared to components manufactured by casting or machining (Metal Powder Industries Federation, 2016). This decrease is associated with the net-shape nature of the PM that minimizes the use of post-processing. Finally, the environmental impact is a consequence of the two aspects mentioned above, since both the recycling of raw materials and the reduction of energy consumption result in a highly efficient process.

This paper presents the complete route of manufacturing a conventional hard metal from the compositional design of the alloy to the thermal treatment of sintering. The results of the microstructure of the materials manufactured are analyzed through the use of characterization techniques such as Optical Microscopy (OM), scanning electron microscopy and analysis by energy-dispersive X-ray spectroscopy (SEM-EDS) and microhardness tests. These results show that it is possible to manufacture hard metal or other powder-metallurgical materials at the laboratory and industrial level with qualities equal to and even superior to those used in the country and that are currently imported from Europe, the United States or China (Villar, 2009).

Methodology

Description of the manufacturing process

Figure 1 shows the critical route that has been carried out to obtain cemented carbides manufactured in the *consortium Universidad Nacional - SENA*.

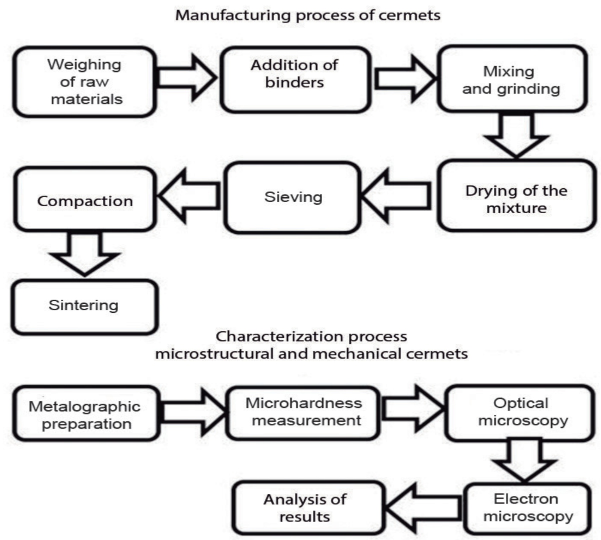

Figure 1. Flow diagram for the manufacture and characterization of CERMETS

Preparation of the mixture

For the mixture, named CERMET 1, WC and cobalt powders were used, in Figure 2 the particle size distribution of the powders used for the manufacture of the alloy is shown. The chemical composition carried out is shown in Table 1 and corresponds to an ISO type K40 alloy (ISO 513, 2004).

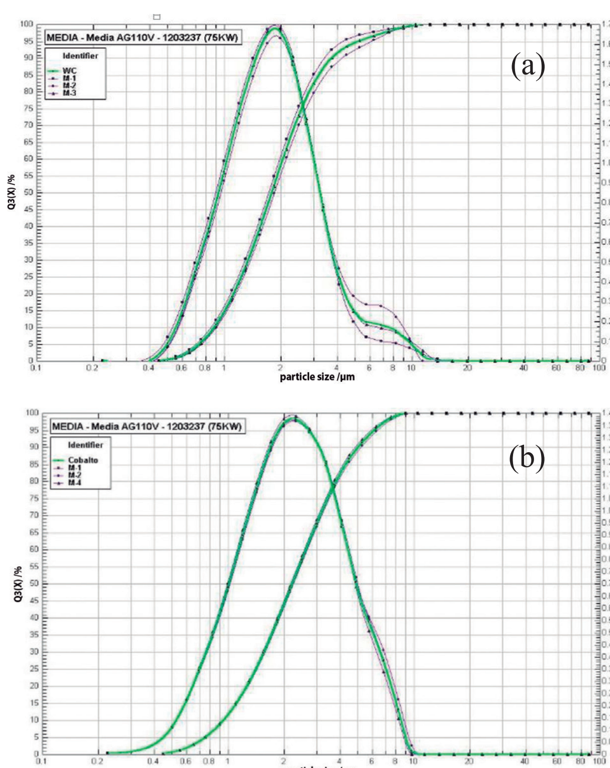

Figure 2. (a) Particle size distribution of WC powder **(b)** and cobalt

According to laser diffraction analysis, carried out with an SYMPATEC HELOS device (H0852) & RODOS, the particle distribution for WC (Figure 2a) is 1.6 µm; while for cobalt it is around 1.4 µm as seen in Figure 2b.

Table 1. Chemical composition of the study material

Designation	WC	Co
CERMET 1(ISO K40)	88%	12%

For the preparation of the mixture, we first weighed the powders, tungsten carbide and its cobalt binder, which were added in a tungsten carbide (WC) container together with spheres of the same material, as shown in Figure 3a. This process is carried out in a wet way with hexane in order to facilitate the homogenization of the materials and also to facilitate the elimination of heat during the process.

Mixing and grinding

Figure 3b shows the mixing process that was carried out in a planetary mill, where the objective is to homogenize and mix the powders that make up this alloy, the process is favored by the impact of the tungsten carbide spheres as well as the rotary movement of the container. To ensure that the material manufactured meets the desired requirements (microstructure and mechanical properties) it is essential to control parameters of this process such as the ratio of spheres-material, speed of rotation and grinding time.

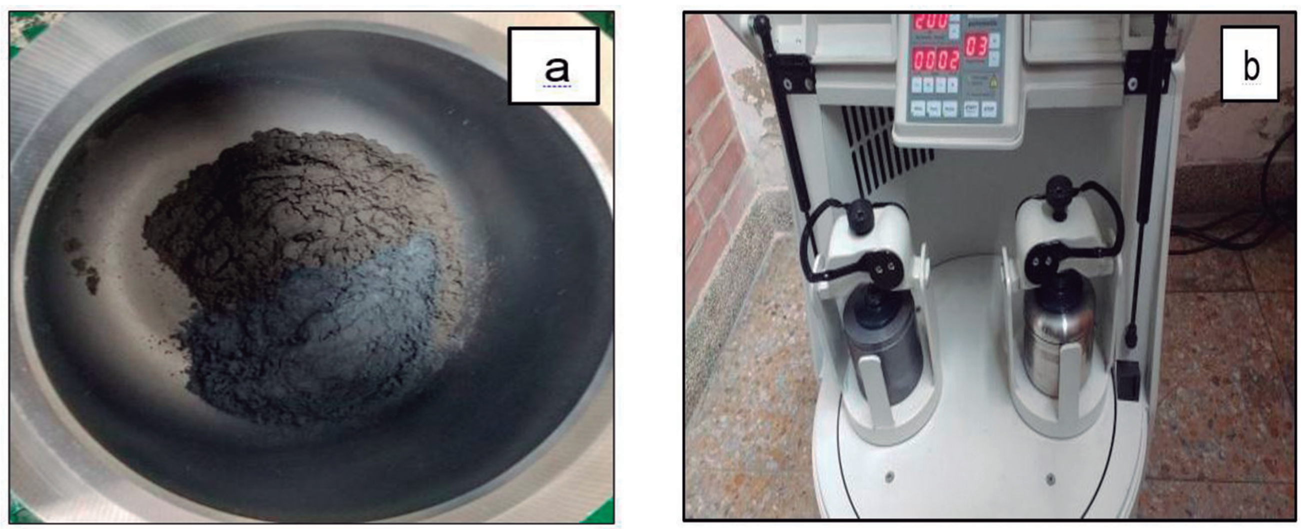

Figure 3. (a) Ceramic and metallic powder inside the container
(b) The planetary mill where the mixing and grinding of the powder is carried out

Once the mixing and grinding process are completed, the powder is dried with the help of a thermostatic bath at a temperature of 90 °C, in Figure 4a the appearance of the mixture is observed once the hexane has evaporated. After this the mixture is extracted and sifted to eliminate the agglomeration of the powder and homogenize it as shown in Figure 4b to then continue with the compaction stage.4b

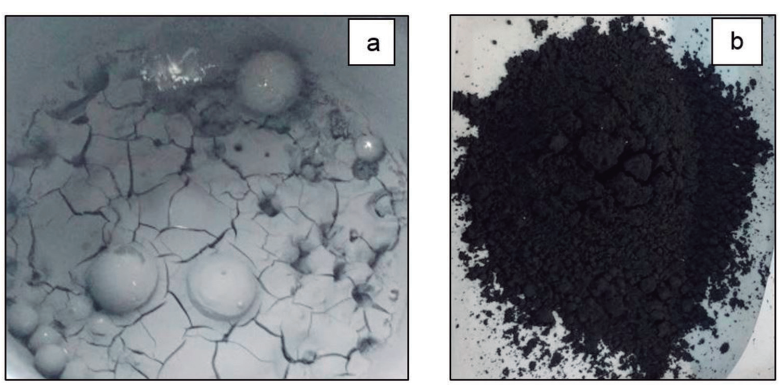

Figure 4. (a) Final state of the mixture after drying
(b) Sample of powder ready for compaction

Stage of powder compaction

For this stage, quantities of approximately 10 grams were weighed for compaction, in order to obtain cylindrical specimens with a diameter of 16 mm and 4 mm in thickness. The compaction of the powder consists of applying loads in two opposite directions towards the center of the mold by means of two punches in a matrix that contains the determined form; first the positioning of the lower punch inside the mold, followed by this the powder is added to the mold and finally the upper punch is placed. Using a universal testing machine (Shimadzu UH-50A) compaction pressures between 140 MPa and 230 MPa are applied, as shown in Figure 5 (a and b). This compaction process is called a floating matrix.

When the powder is compacted, the extraction of the cylindrical specimens is carried out, which are in the green state (see Figure 5c), which is why they are very fragile materials with very low mechanical resistance.

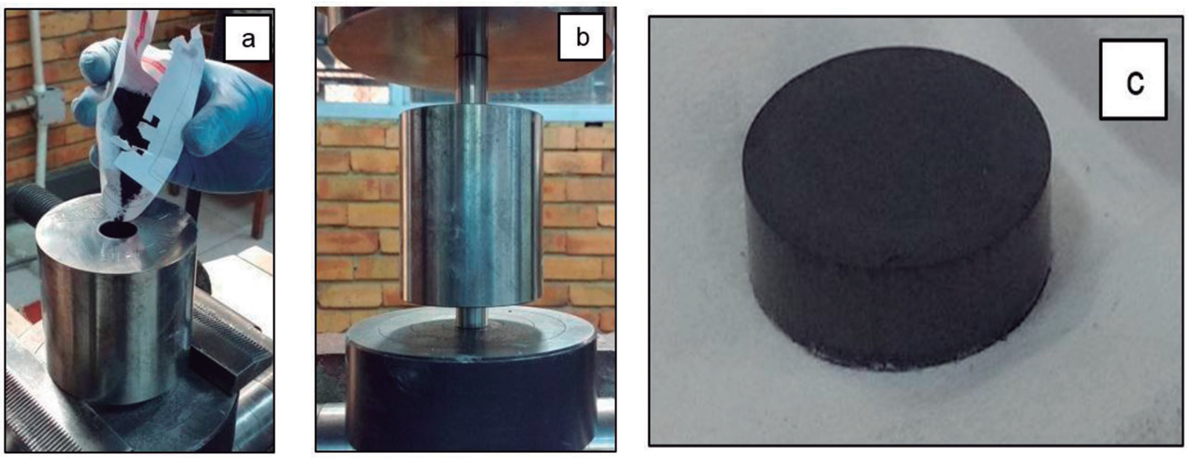

Figure 5. (a,b) Addition and compaction of the powder respectively and **(c)** Cylindrical test piece in the green state

Sintering

The sintering process is a thermal treatment consisting mainly of generating densification of the material that is conventionally produced in the liquid phase, the WC-Co system forms a eutectic liquid between 1320 °C and 1370 °C, so the sintering temperatures used in the hard metal industry range between 1350 ° C and 1650 ° C, which are chosen depending on the chemical composition. The sintering cycle was carried out in an electric oven marked Protech PT-V1700 34L as shown in Figure 6. The process was developed at 1450 °C under vacuum (0.045 mbar) with the heating of 5 °C / min with the aim of ensuring adequate reduction of oxides; as well as avoiding temperature gradients in the compact; after reaching this temperature, an argon overpressure of 100 mbar was introduced for 60 min (maintenance stage) in order to minimize the evaporation of the metal phase.

Figure 6. Electric sintering furnace PT-V1700 34L

Results and Discussion

Density measurement

The density, as well as the of the material, are properties that are used as quality control of the material. In the case of density, this indicates in general if the manufacturing process has been satisfactory according to the chemical composition of the sample. For CERMET 1, geometrical measurements of the test pieces were made before and after the sintering, in order to obtain the densities of the specimens in each of these stages, as shown in Table 2.

Table 2. Densities in green and sintered of the test pieces and their shrinkage

Green density	7.90 g/cm^3	Shrinkage after the sintering process
Sintered density	14.34 g/cm^3	16.70%

These results show the effect of the densification of these materials after the sintering process, the contraction for the K40 was 16.70 % and is within the expected ranges for this type of materials.

Microstructural analysis by optical and electronic microscopy

To be able to carry out observations at the level of optical and electronic microscopy of the sintered sample, it is necessary to prepare the sample by metallographic routes. The metallographic preparation was carried out under the ASTM B 665 standard, this preparation differs from the ferrous and non-ferrous alloys in the roughing phase where the use of diamond discs is necessary because the cemented carbides have high hardness; Subsequently, the polishing of the sample was carried out with diamond suspensions of 6 µm and 1 µm, obtaining a mirror-like finish for subsequent characterization.

For metallographic observation, a metallographic microscope (ZEISS Axio Observer.Z1m) was used, to verify the quality of the material manufactured as a function of porosity. Since porosity is one of the most important factors in the manufacture of cemented carbides, quantification was performed under the ASTM B 276 standard, which consists of observing magnifications of 100X and 200X and comparing it against visual patterns. During the analysis, it was observed that all the pores analyzed had a size below 10 µm, and their quantification gave a value of 0.07% of the total area analyzed. The porosity for this type of material is classified as A, B, and C. The porosity type A for the manufactured material presented values of A02 and A04, predominating the porosity A02; because the pore sizes did not exceed 10 µm, the porosity type B is B00. Finally, the presence of free carbon is classified as type C and since the cermet does not present this type of porosity, its value is reported as C00. In summary, the porosity presented for the alloy is of type A02, B00, C00 and for this reason meets the minimum requirements for this type of material. Figure 7a shows an optical microscope image of the material and in Figure 7b the reference against which it was compared.

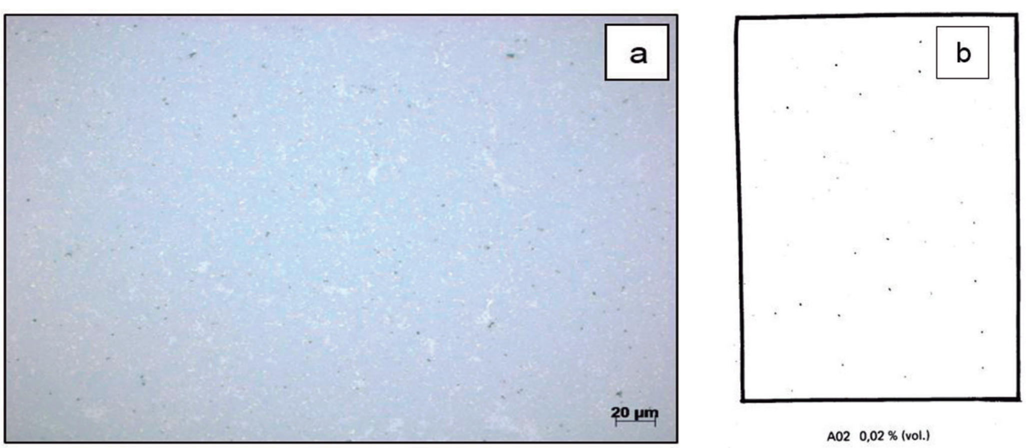

Figure 7. (a) Metallographic image showing the low degree of porosity obtained, **(b)** Comparative image according to norm ASTM B276

For the microstructural characterization of the sintered sample, scanning electron microscopy (SEM) was used. The primary or backscattered electron detectors were used to obtain material contrast, which is related to the chemical composition of this (phases) and the secondary electrons that provide information about the topography of the surface of the material as homogeneity in the microstructure and possible manufacturing defects (cracks, porosities, among others).

Through the manufacturing process already described, cemented carbides have been obtained according to commercial composition type K40 (ISO) where the ceramic phase is dispersed in the metallic phase; as seen in Figure 8.

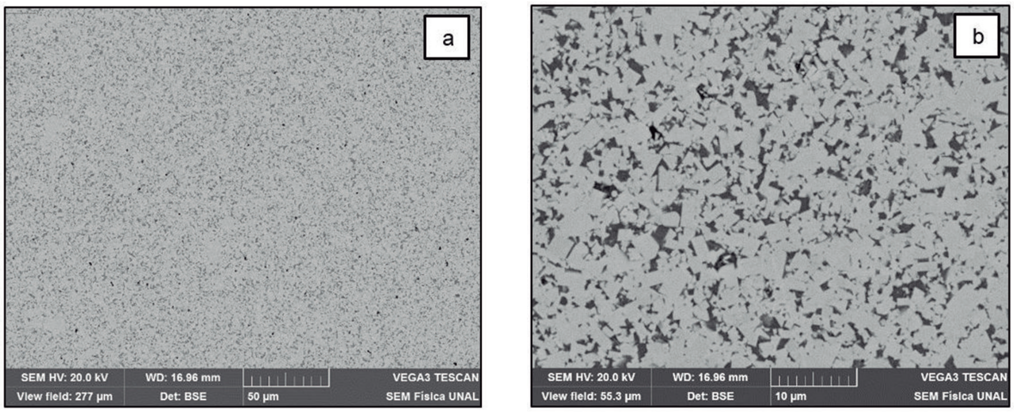

Figure 8. Microstructural distribution of cermets type K40 **(a)** low magnification and **(b)** high magnification

These images show a homogeneous distribution of the material, which is composed of a dark metallic contrast phase, as well as a bright phase of tungsten carbide grains with faceted morphology.

Chemical analyses were carried out by means of specific measurements as shown in Figure 9a where the measurement is made in the area that is delimited by the box, in addition to considering the detection limits of the technique, a semiquantitative analysis is estimated since it is done using the X-ray dispersive energy probe coupled to the SEM where the quantification of light elements is not representative, as shown in the spectrum in Figure 9b. Table 3 summarizes the results of chemical composition obtained by this technique, said values they present small variations in the order of 0.61% for cobalt and for tungsten carbide of 0.64% compared to the values given in Table 1 regarding the average value of each element. Additionally, from the images obtained in SEM, WC grain size was quantified using image analysis software to create segmentation and binarize the image, obtaining shape factors, projected areas and equivalent diameters for statistical study. Figure 10a shows the original photo at 5000X from which the size of WC grain of the cermet is calculated. Figure 10b shows the image after the digitization treatment known as "watershed" to obtain representative data of the measurement of the size of WC three images were analyzed where each image contains around 1200 grains.

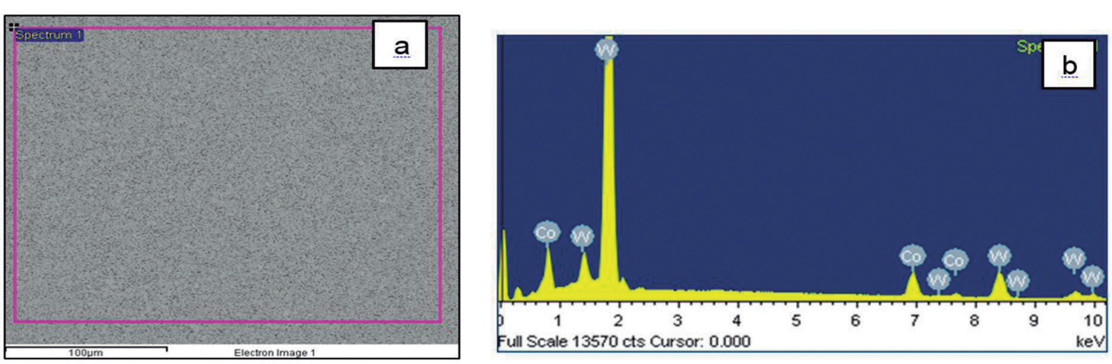

Figure 9. (a) SEM image of the area where the analysis is performed using the EDS probe.
(b) The spectrum of X-ray dispersive energies

Table 3. Chemical composition obtained

Material	Element	Weight percentage (%)				
		Central Zone	Exterior Zone	InterM Zone	Average	Standard deviation
CERMET 1 (ISO K40)	Co K*	11.86	10.27	12.06	11.39	0.98
	W M*	88.14	89.73	88.05	88.64	0.94
	Total	100.00				

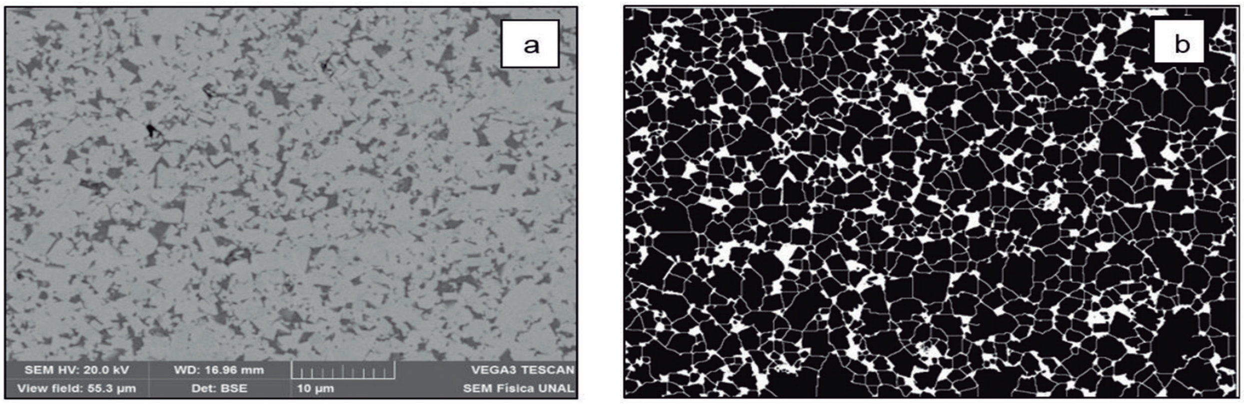

Figure 10. (a) Original image without treatment
(b) Image after the binarization treatment

Mechanical characterization

As is known, the grain size and hardness of material are closely related and the case of cemented carbides is no exception and there is correspondence between grain size, cobalt content, and hardness (Gille, Szesny, Dreyer , & van den Berg., 2002). In this sense, Figure 11 shows the WC grain size distribution obtained by analyzing three electron microscopy images, which corresponds to the measurement of approximately 3600 grains of the ceramic phase (WC).

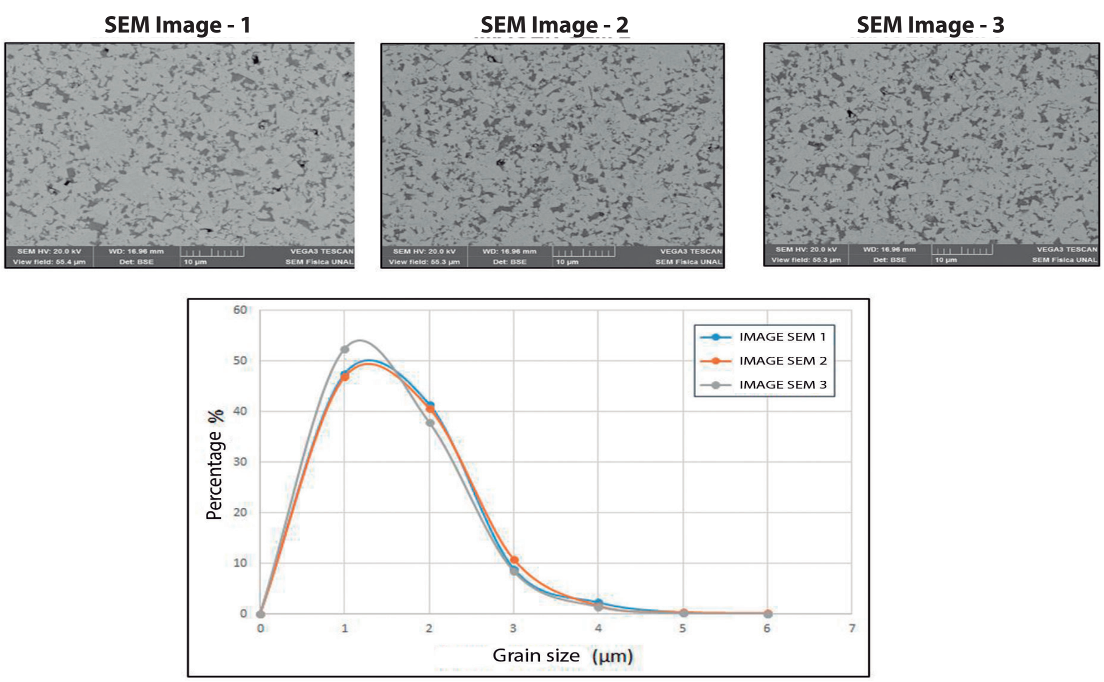

Figure 11. The grain size distribution of CERMETS type K40 alloy

The repeatability of the curves shows that the material has a homogeneous distribution in terms of WC grain size, this indicates that the manufacturing process was controlled since there was no excessive grain growth which is usually associated mainly with the variables of the sintered as the sintering time and temperature.

The was 1.14 µm, with a distribution of 48.89 % between 0 and 1 µm, 39.94 % between 1 and 2 µm, 9, 29 % between 2 and 3 µm and 1.85 µm % between 3 and 4 µm. According to this distribution, the manufactured K40 cermet reveals a medium grade size (Sandvik, 2016).

Table 4 shows the hardness value obtained for the manufactured cermet, this value is adjusted to that reported in the bibliography, as shown in Figure 12.

It is important to note, as already mentioned, that this level of hardness is related to low levels of porosity, grain size, and cobalt content.

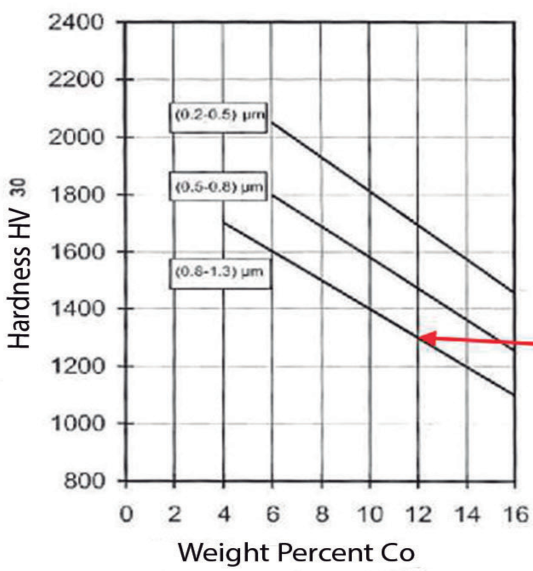

Table 4. Microhardness values

Alloy	Vickers Units
CERMET 1 (ISO K40)	1289*±5

*** Average of five measurements**

Figure 12. Hardness for cermets depending on WC grain size and cobalt content (Gille, Szesny, Dreyer, & van den Berg., 2002)

Conclusions

A methodology has been developed and optimized for the fabrication of hard metals through the powder metallurgical route which can be extrapolated to other types of high performance materials such as tool steels, composite materials, ceramics among others. The manufactured alloy meets quality standards such as porosity, microstructure, and hardness associated with an ISO K40 medium grain hard metal. The results obtained throughout the implementation of this manufacturing technology open many fronts to continue with research, development, and innovation related to PM; this must be linked to the technological transfer of this knowledge to the national industry, with the aim of creating new business opportunities that allow increasing competitiveness, innovating technology and diversifying current manufacturing processes towards more efficient, cleaner and more environmentally friendly technologies.

Acknowledgments

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