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Effect of Fe impurities and pure Cr additions on microstructure of nanostructured WC-10Co alloy sintered by HIP

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ABSTRACT

The present work evaluates the effect of both, Fe impurities and Cr addition, in nanostructured WC-10Co cemented carbides, which are sintered by hot isostatic pressing. Fe impurities and Cr addition in nanostructured WC-10Co alloy generate a series of microstructural and structural changes in the morphology, present phases, crystallite size and density, which in turn influences the microhardness of the samples. Such changes are mainly related to the nature of binder, generation of a bimodal grain size distribution and an abnormal grain growth of the WC phase and the formation of the η phase.

1. Introduction

Nanostructured WC-Co cemented carbides can be effectively used in all areas where conventional carbides are present. However, recently, a particular interest in the synthesis of nanostructured WC-Co cemented carbides has emerged for the manufacture of cutting tools. In these applications, nanostructured systems are preferred because the useful life of the tooling could be increased by a reduction in the grain size of the WC phase which induces positive improvements in their mechanical properties [1,2]. A typical microstructure of cemented carbides consists of a hard WC phase embedded within a soft and tough Co binder phase [2–4]. There are many works in which the cemented carbides with different ratios WC:Co are studied, many of them with microstructures in the order of microns [2,5]. Nowadays more than 90% of all WC-hard metals utilize Co as the preferred binder metal with contents between 3 and 30 wt % [2] and as cutting tool materials, cemented carbides with 3–12 wt % Co are commonly used [6,7]. The mechanical properties of WC-Co cemented carbides are directly related to their chemical composition and microstructure, for this reason, and depending on each application, their properties can be adapted upon the Co content, size, and quality of the starting powder, sintering techniques, and the use of additives as grain growth inhibitor [2]. Therefore, the uses of nanostructured systems open new possibilities in terms of increasing the working life of cutting tools.

Conventionally, WC–Co cemented carbides are fabricated by mixing, compaction and sintering of powder precursors. The liquid-phase sintering process is carried out above the eutectic temperature of WC–Co (1280–1310 °C). For cemented carbides, the grain growth is favored by their high interfacial free energy. Therefore, the addition of grain growth inhibitors such as VC, Nb_3C_2, and Cr_3C_2 is necessary to control this growth during sintering process either by

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modifying the WC-Co interface or by providing diffusion resistance [8]. The pure Cr has not been used as an inhibitor of grain growth due to the assumption that Cr when interacting with WC will reduce the W and give rise to the formation of the η-phase (Co_3W_3C -M_6C type). However, the influence of Cr element in cement carbides recently has been studied by different researchers, showing the positive effects on such carbides. They reported that as the Cr in cemented carbides is mainly located in the Co binder [9,10]; as well as a decrement in WC grain size as the Cr content is increased [11], the segregation of Cr and Co at both WC/Co and WC/WC boundaries may be closely related to the retardation of growth and changes morphological of WC grain [9,12]. Also it has been reported the formation of M_7C_3 [11,13], which contributes to a fine dispersion of η-phase [11], in addition to suggest that Cr addition would delay Co spreading and enhance differential shrinkage in WC–Co alloys [14].

On the other hand, it is known that during the synthesis of nanostructured WC-Co cemented carbides through high-energy milling, some contamination due to the milling media and container wear is generated. Although many researchers use balls and containers made of WC for minimize such contamination, others still using a variety hard steels due to their low cost. Regarding this issue, few researchers have paid attention to the possible Fe contamination. Some of them concluded that the level of Fe contamination increases if the powder is milled for longer times than required. For example, 20 at.% Fe has been found in a WC mixture milled for 310 h and 33 at.% Fe in pure W milled for 50 h in a SPEX mill [15]; as well as increases in contamination by Fe with milling time of almost 3 wt% after 300 min milling [16]. A large number of scientific articles related to milling of WC alloys have been published, where the use of steel as milling media and in container is reported, however, strangely none of them reported contamination effect or Fe impurities, much less have been evaluated; some of them are indicated in references [17–22]. At a given level of cobalt, the hardness is improved by decreasing the grain size of the WC. Therefore, in the present study a composition of 10% by weight of Co is used in order to evaluate only the Fe impurities generated when reducing the grain size through milling process and by grain growth inhibitor addition (pure Cr). Thus, a study on the effect of Fe impurities and pure Cr as a grain growth inhibitor in WC–Co cemented carbides processed by mechanical alloying and Hot Isostatic Pressing (HIP) is fully justified as the primary objective of this work.

2. Experimental procedure

2.1. Powder processing

The starting materials consisted of commercial WC (99.95% pure), and elemental powders of Co and Cr (99.5% pure). The nominal compositions of the studied systems were WC-10Co and WC-10Co-1Cr with conditions of mixed and milled. The reference sample was not milled; it was only mixed. Nanostructured powders for the milled condition were synthesized through the milling process. The millings were performed in a high energy ball mill Spex 8000 M, the used milling media and container were made from hardened steel. Milling conditions were set to 5 h of milling time, powder mass 8.5 g with a ball-to-powder ratio of 5:1. All milling runs were performed with N-heptane as process control agent and argon as an inert atmosphere (to avoid oxidation). The ceramic powders are more difficult to compact compared to metals, and therefore, very high pressures need to be are applied. To obtain WC-10Co compacts free of any additives, ultra-high pressure in piston/cylinder die at ~1.6 GPa for 5 min has been used for both conditions, mixed and milled. A drawback when substantial pressures are applied is increasing of residual stresses in ceramic powders that may result in fracture upon subsequent handling; however, this issue is not addressed in the present study.

On the other hand, abnormal grain growth often takes place during liquid phase sintering of ceramics with faceted or even partially faceted grains. Based on the above, Yang et al. [23] attempted to reduce the time of liquid phase sintering through solid state densification by pre-sintering the compacts below the liquid formation temperature with acceptable results. Thus, in the present study, the process mentioned above will be followed using pre-sintering the samples at 1200 °C for 2 h. Finally, the sintering process was carried out by HIP, using ~186 MPa of pressure under two temperatures: 1300 and 1400 °C for 1 h.

2.2. Structural and microstructural characterization and microhardness

The structural characterization of the mixed and milled powders and sintered samples was performed by X-ray diffraction (XRD) analysis, in a Panalytical X'pertPRO diffractometer operated at 40 kV and 35 mA. The crystallite size (powder and consolidated samples) were estimated based on XRD peak broadening using the Williamson–Hall method [18].

$$\beta \cos\theta = \frac{\lambda}{D} + 2\sqrt{\varepsilon^2}\sin\theta$$

where θ is the Bragg diffraction angle, D is the average crystallite size, ε is the average internal strain, λ is the wavelength of the radiation used and β is the diffraction peak width at half maximum intensity. To determine crystallite size {0 0 1}, {1 0 0}, {1 0 1} WC peaks were used. Microstructural characterization and phases evolution in both, powders and sintered samples were evaluated through a scanning electron microscope (SEM) Hitachi model SU3500. The samples analyzed by SEM were prepared under conventional metallographic techniques. Density measurements of sintered samples were determined following the Archimedes method. The Vickers hardness test was performed using a LECO LM 300AT equipment, reporting the mean value of at least 10 indentations. Vickers microhardness tests were carried out on a polished surface using 300 g of load and 15 s of dwell time.

3. Results and discussion

3.1. Morphological evolution of phases during different stages

The WC grain growth during the sintering process is due to their high interfacial energy which is the main driving force for the growth process; thus large grains grow at the expense of smaller grains. Fig. 1 shows micrographs obtained by SEM of WC-10Co and WC-10Co-1Cr systems, in two conditions, mixed and milled. Besides, is presented several images corresponding to three different stages of the process: powders, pre-sintered and sintered by HIP at 1300 and 1400 °C. In the images corresponding to the powders (first row) a different arrangement of particles in the milled powders in comparison to the mixed ones can be observed; the mixed powders show a rounded morphology and small size while the milled powders exhibit different particle sizes and agglomeration. The above could be related principally to Fe impurities and to a possible effect of the mechanisms of the milling process: deformation, welding, and fracture. For the pre-sintering stage (second row), in mixed samples, an incipient diffusion between particles forming a network is observed. In milled samples, the onset of abnormal grain growth as well as the formation of faceted WC grains, and rounded WC grains characteristic of the starting WC–Co powder is detected. For the HIP sintering stage (third row), in the

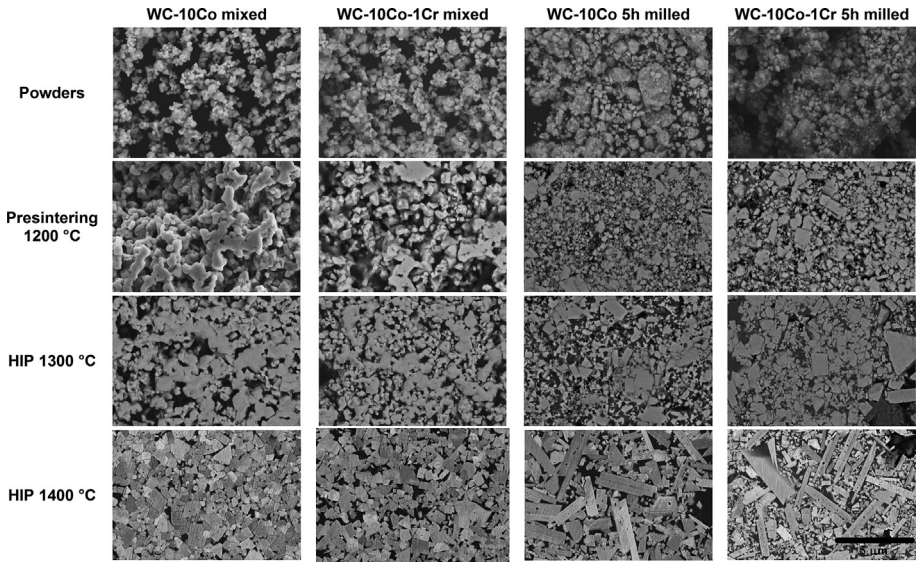

Fig. 1. Micrographs obtained by SEM of WC-10Co and WC-10Co-1Cr systems mixed and milled corresponding to powders, pre-sintered samples at 1200 °C and HIP sintered samples at 1300 and 1400 °C.

case of sintering at 1300 °C, an increase in densification and grain size for all samples are observed. In the mixed samples, larger particles from network previously generated are formed, meanwhile in milled samples, the greater number density of faceted carbides is observed. The last row shows representative micrographs HIP sintering at 1400 °C; these samples showed that most grains have a faceted morphology. Furthermore, two types of grain growth are identified, anisotropic grain growth in the mixed samples and abnormal grain growth in the milled samples. The hexagonal symmetry of WC explains the faceting of the grains. The most common form of WC is the so-called truncated trigonal prism, which is considered the equilibrium form of WC grains. The WC structure contains three types of dense planes formed, the pinacoid {001} and the two prismatic planes {100} and {010}, which determine the morphological characteristics [24]. Abnormal grain growth can be explained in terms of interface mobility, thus rounded grains with isotropic interfacial energy have a disordered interface, while faceted grains with highly anisotropic interfacial energy exhibit an ordered interface. For rounded grains, the energy barrier of the atom near the interface is negligible, and the growth rate is limited by the diffusion of the solute atoms resulting in normal growth [25]. In the case of the growth of faceted grains with atomically flat surfaces, it is generally assumed that further growth is possible only by two-dimensional surface nucleation or a defect-assisted growth process. In faceted grains, there is essentially a critical driving force for substantial growth. If some larger grains have higher driving forces than the critical value, they can grow easier, while the growth of other grains with smaller driving forces than the critical value, it is suppressed, causing abnormal grain growth and leading to a bimodal grain size distribution as shown in Fig. 1 [26,27]. The above explains the cause of the abnormal growth; however, other studies have suggested other causes such as segregation of impurities, matrix viscosity, and mixed liquid presence. Therefore, the abnormal grain growth should be evaluated concerning the effect of CoFe binder (Table 1). The effect of Cr as grain growth inhibitor becomes evident from the presence of a bimodal grain size distribution for the milled sample in the presence of Cr; this distribution allows inferring a decrease in the growth rate in comparison to WC-10Co mixed and milled samples. The dissolution and reprecipitation phenomena of WC has been altered probably because of a lowering of the interfacial free

Table 1
Concentration of Co, Cr and Fe elements in studied systems, WC-10Co, and WC-10Co-1Cr with conditions of mixed and milled.

Powder/Element	Co	Cr	Fe
WC-10Co mixed	11.254	–	–
WC-10Co1-Cr mixed	11.121	0.978	–
WC-10Co 5h milled	9.509	–	6.535
WC-10Co-1Cr 5h milled	10.544	1.292	7.161

energies due to Cr segregation to the WC/Co interface boundaries and changes in the array of the binder (Co → CoFe). In this regard, Wittmann et al. [28] reported that the nature of the binder changes the growth behavior by influencing the metal-carbon bonding relationship. Fe has the highest affinity to carbon compared to Co, so it can form metal-carbon bonds (as in the liquid phase), which masks carbon and prevents transport and carbon precipitation by increasing activation energies for the nucleation and grain growth processes. The above seems to be a possible explanation for the low coarsening rate of the WC in the case of the binder with Fe, in comparison with the WC-Co system. Besides, Fe has good wettability and solubility with WC [29] and has a ternary eutectic temperature less than Co [6]. However, other authors reported that exist other different explanations for the abnormal grain growth induced by mechanical milling; this is related with the generation of lattice defects, dislocations (microstrain) and the existence of free carbon inside the sample. Both explanations seem to be independent of each other, but probably can act simultaneously, since both effects support the diffusion of W atoms, which is a prerequisite for grain growth. The higher driving force and flow of material, the greater the probability that the system will approach the state of thermodynamic equilibrium, that is, a coarse grain structure with a small interface area [30]. Since that abnormal growth of the grain is more highlighted in milled samples in comparison to mixed samples, and Cr addition generates free carbon within the sample due to the possible formation of carbides; a deeper study to determine the precise cause of abnormal grain growth is necessary. With regard to the reported by Yang et al. [23], a more homogenous microstructure in the mixed sample was obtained, which reveals that the effect of abnormal grain growth is reduced through a presintering stage. The results also showed twinned WC crystals,

which may have different origins: twins might be originated from the starting WC powder (as growth twins) or might result from powder milling in ball mills (by the introduction of defects) and subsequent recrystallization on heating (recrystallization twins). However, they can also be caused by chemical reactions which take place during sintering and which might result in the formation of growth twins and subsequent plate formation. A strong indication of formation mode is given in the present research, which showed enhanced twinning as a result of powder milling. Also, a fraction of binder might be entrapped within the growing crystals, as shown in Fig. 1. This binder inclusion in twinned WC crystals suggests that the WC crystal is growing through multilayer growth [27,31].

3.2. Phases identification

Fig. 2 shows XRD diffractograms of WC-10Co and WC-10Co-1Cr systems mixed and milled corresponding to the three stages of our process: powders, pre-sintered and HIP sintered at 1300 and 1400 °C. In all diffractograms, the strongest diffraction peaks correspond to the WC phase; this is due to the high proportion of the WC phase (90 wt%) in the sample. For WC peaks the width becomes slightly narrower, and the intensity becomes stronger, indicating that the crystallite size of the samples increase under higher sintering temperature. The milled samples show the formation of CoFe phases (binder) due to Fe contamination during processing. Although it is known that Fe decreases the coarsening rate of WC, it is probable that the joint action between the milling process and the Fe impurities generated by this process develops a favorable configuration that leads to preferential grain growth, which would explain the abnormal grain growth in the samples with the presence of the CoFe binder. Peaks corresponding to the Co_3W_3C phase (η phase) in the WC-10CoCr mixed and milled samples are observed. The formation of this phase is directly related to the addition of Cr, since it was only detected in samples modified with such element. Yu B et al. [11] reported a similar behavior, increasing the Cr content increased the formation of η-phase. For both cases the formation of η-phase is associated with the C deficiency in the Co-rich phase.

3.3. Analysis of crystallite size, density, and microhardness

In the case of a nanostructured material, the crystallite size of the material is the most predominant factor which influences the physical and chemical properties. X-ray diffraction is the most convenient method for determination of crystallite size. Fig. 3 shows the crystallite size of WC-10Co and WC-10Co-1Cr systems mixed and milled in the form of powders, pre-sintered samples, and HIP sintered samples at 1300 and 1400 °C. The crystallite size of WC has been reduced approximately by half after milling in both systems, WC-10Co from ~32 to ~18 nm and WC-10Co-1Cr from ~34 to ~19 nm. For the sequence of stages: mixed-milled → pre-sintering → HIP (1300 °C), gradual growth in the crystallite size with close values between both systems, WC-10Co and WC-10Co-1Cr, is observed. The crystallite size increase with the sintering treatments can be attributed to the fact that higher temperatures enhance the diffusion process. During sintering by HIP at 1400 °C a smaller value in the crystallite size in the WC-10Co-1Cr samples compared to the WC-10Co samples is obtained. The difference between mixed and milled samples is ~13.7 and ~27%, respectively. From the mentioned results it can be inferred that the Cr addition as grain growth inhibitory agent, and possibly the presence of Fe impurities due milling media wear, change the nature of binder and have a positive effect not only in the grain size but also in the crystallite size at high temperatures (1400 °C).

Fig. 4 shows the density obtained of WC-10Co and WC-10Co-1Cr systems mixed and milled corresponding to pre-sintered samples

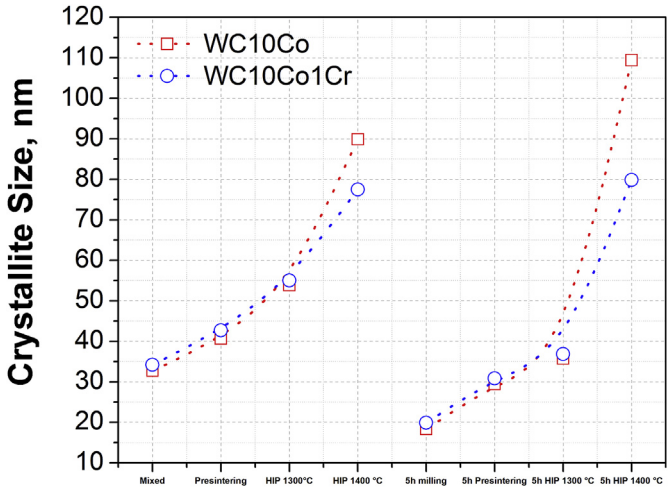

Fig. 3. Crystallite size of WC-10Co and WC-10Co-1Cr systems mixed and milled corresponding to powders, pre-sintered samples at 1200 °C and HIP sintered samples at 1300 and 1400 °C.

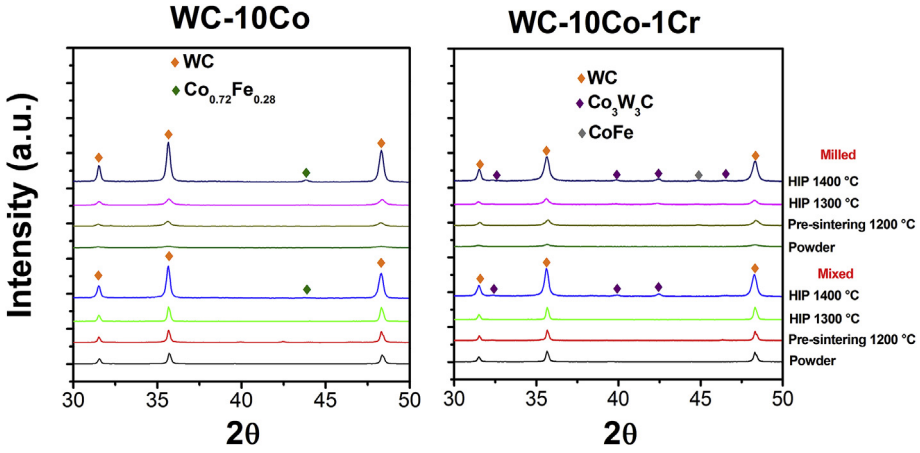

Fig. 2. XRD diffractograms of WC-10Co and WC-10Co-1Cr systems mixed and milled corresponding to powders, pre-sintered samples at 1200 °C and HIP sintered samples at 1300 and 1400 °C.

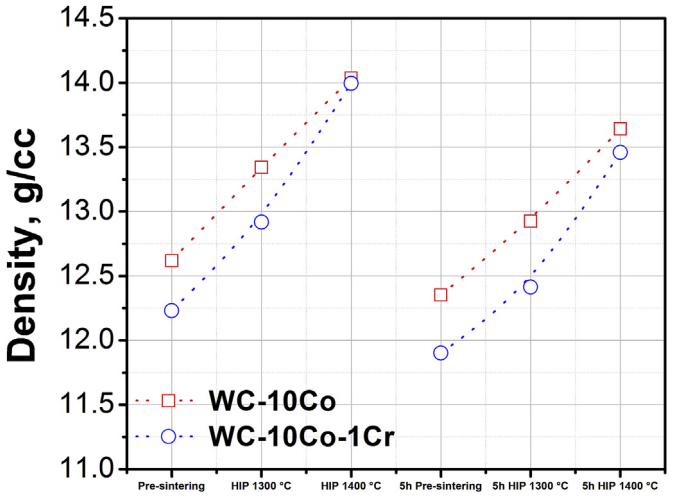

Fig. 4. Density of WC-10Co and WC-10Co-1Cr systems mixed and milled corresponding to pre-sintered samples at 1200 °C and HIP sintered samples at 1300 and 1400 °C.

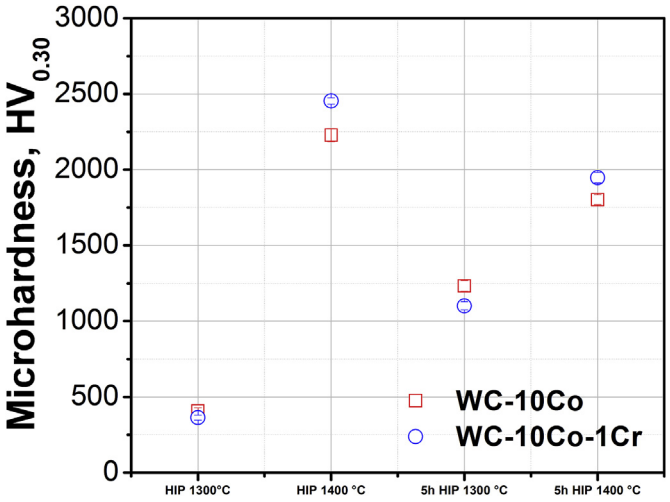

Fig. 5. Vickers microhardness ($HV_{0.30}$) of WC-10Co and WC-10Co-1Cr systems mixed and milled corresponding to HIP sintered samples at 1300 and 1400 °C.

and HIP sintered samples at 1300 and 1400 °C. Based on density measurements we found that the milled samples have lower density compared to the mixed samples: WC-10Co 12.61 (mixed) and 12.23 g/cc (milled), WC-10Co-1Cr 12.35 (mixed) and 11.90 g/cc (milled). These results are somehow expected due to the internal deformation and low compressibility of the particles caused by the high energy milling process [16,18]. Also, lower density values in WC-10Co-1Cr mixed and milled samples compared to WC-10Co mixed and milled samples during all sintering processes were obtained. Such behavior is predictable since the primary function of the inhibitors is to maintain the grain size of the starting powders in the sintered product by means the slowing down of solution/reprecipitation reactions at WC–Co interfaces and acts to interfere with the overall grain growth [8,32]. For all systems, the highest density values are observed in HIP sintered samples at 1400 °C due to liquid sintering promotes better densification, this is because cobalt tends to spread over the WC particles to reduce the surface energy, increasing the overall density of the sample. However, the formation of the liquid phase will inevitably lead to the growth of WC grains due to Ostwald ripening.

Fig. 5 shows Vickers microhardness ($HV_{0.30}$) values obtained of WC-10Co and WC-10Co-1Cr systems mixed and milled corresponding to HIP sintered samples at 1300 and 1400 °C. The HIP sintered samples at 1300 °C show a higher value with WC-10Co samples (mixed ~408 and milled ~1234 HV) compared with WC-10Co-1Cr samples (mixed ~363 and milled ~1101 HV), such results can be associated with the obtained density values, where a substantial difference in density is evident, a direct impact on the hardness value can be inferred due to porosity presence. Besides, the milled samples showed higher values compared to the mixed samples (~67%), this behavior is associated to sintering process in the solid state, and is expected that micro deformations and defects generated during mechanical milling are still present. Samples HIP sintered at 1400 °C showed a higher value in WC-10Co-1Cr samples (mixed ~2453 and milled ~1947 HV) compared to the WC-10Co samples (mixed ~2227 and milled ~1802 HV), these results can be associated with grain size, since a smaller grain size in the samples with Cr additions was obtained (Fig. 3) and density values between both samples were very close (Fig. 4). Furthermore, the mixed samples showed higher values compared to the milled samples (~20%), which is associated with the densification rate and mainly with the microstructure homogeneity.

4. Conclusions

The effect of both, the impurities of Fe and the addition of Cr, on WC-10Co nanostructured cemented carbides has been studied; the main conclusions are listed below.

- The iron impurities generate a change in the array of binder (Co→CoFe) that produces an abnormal grain growth.
- The effect of pure Cr as grain growth inhibitor is evident based on the generation of a bimodal grain size distribution for samples with this element.
- The presence of the η-phase is associated with Cr addition and the C deficiency in the Co-rich phase.
- The crystallite size and density also were affected by Cr addition generating changes in the Vickers microhardness.

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