Cobalt-inhibitor mixtures for cemented carbides

V.I. Stanciu*, V. Vitry*, F. Delaunois*

* University of Mons, 7000 Mons, Belgium

Abstract

In cemented carbides based on ultrafine carbide powders the use of growth inhibitors is indispensable for the preservation of satisfactory mechanical properties of sintered product. The inhibitors manifest their effect by blocking tungsten carbide diffusion through the metal binder. Use of chromium carbide as inhibitor has proved very effective, especially by ensuring a high toughness for the alloys where it is used. Following some according to recent studies that have proved that the diffusion distance is very important in effective inhibition of carbide particles growth, there are limits which should not be exceeded. An homogeneous distribution and a lower inhibitor particle size are the premises to obtain a uniform microstructure. This study was aimed at obtaining homogeneous carbide-binder-inhibitor mixtures. To this end, four (4) Co + inhibitor compositions have been milled in a planetary mill under dry and wet conditions. Grinding effect on the homogeneity of the powder was studied by X-ray diffraction, optical and electron microscopy on polished samples. Subsequently, the optimal mixture will be mixed with nano tungsten carbide and sintered to verify effectiveness.

Keywords

Grain growth inhibitors, nanotungsten carbide, mixtures, high energy milling.

Introduction,

Inhibition of grain growth is usually observed in sintered materials systems with more than one solid phases: when two immiscible solid phases are mixed, a decrease of grain growth is observed [1, 2]. However, the production of nanoscale sintered carbides from tungsten carbide powders without the use of growth inhibitors is not possible because grain growth is reversely proportional to initial grain size. This is due to the fact that the WC grains form facets and therefore have a strong tendency to abnormal growth (AGG), where a few large grains will reach larger sizes than average. This is very detrimental for the mechanical properties because these abnormal grains act as starting points for cracks [3]. This abnormal growth can be decreased by the use of an inhibitor that works by reducing the transport of surface material during the dissolution and re-precipitation process. Cubic carbides such as Cr_3C_2, TaC, NbC or VC can thus be added to WC-Co mixtures to inhibit the growth of the tungsten carbide grains [4]. Increasing the quantity of inhibitor in the alloy causes refinement of the structure, leading to better densification [5]. Among the possible inhibitors, Vanadium carbide increases the hardness of WC-Co alloys [6] while Cr_3C_2

brings a better tensile strength [7]. The effectiveness of growth inhibition appears to be closely related to the carbon content of the alloy and to the sintering temperature. VC is effective at low temperatures but its effectiveness decreases if the alloy is saturated in carbon. Chromium carbide efficiency is not affected by the carbon balance of the alloy [8-10]. The carbon balance is very important for the alloy properties. In the case of low carbon, eta phase makes the alloy brittle; an excess of carbon leads to the apparition of free graphite in the microstructure. Moreover, a very recent study reveals that the solubility of the inhibitors in the binder is highly influenced by carbon balance [11]. The usual amount of inhibitor added to the sintered carbides is 5 to 10 wt.% of cobalt [12] and a uniform distribution of inhibitor in the matrix is required to ensure the uniformity of the inhibition. This good repartition of the hard phase in the matrix can be obtained by mechanical alloying. Mechanical Alloying (MA) is a technique for manufacturing powders in the solid state, involving the repeated welding, fracturing and re-welding of the powder particles in a high energy ball mill. This process, which is increasingly used for the manufacture of carbide powders [13 - 17], was developed by John Benjamin and colleagues [18, 19] in 1966. It is the result of extensive research in the development of nickel-based superalloys. The process was further developed in the 1980s and was used to produce metal nanocomposites [20, 21]. In the early 1990s, modeling has allowed understanding the mechanisms governing the process of mechanical alloying (MA) [22].

This article intends to study the possibility of obtaining a cobalt powder doped with uniformly dispersed chromium carbide by mechanical grinding. For this purpose, four mixtures Co- Cr_3C_2 mixtures will be milled in various liquid media and compared with a dry milled series that has been the subject of an earlier publication [23].

Experimental,

Various amounts (1, 5, 10 and 20 wt. %) of chromium carbide (Cr_3C_2) were added to cobalt, and the mixture was milled in a planetary ball (mill Fritsch Pulverisette 7 Premium line). A chromium carbide powder with 99.98% purity supplied by Inframat Advanced Material, having a particle size of about 3-5 μm (up to 10 microns based on SEM observation) was used. The cobalt powder used has particle size inferior to 90 micrometers and has been prepared by milling in our laboratory.The samples were compared with a batch of pure cobalt, milled under the same conditions, used as reference.

Milling was conducted at 600 rpm, the highest speed at which the planetary ball mill can be operated in safe condition. The milling time was 10 hours in steps of 2 hours with the following grinding cycle: 5 minutes milling + 5 minutes cooling, with reversal of the direction of rotation of the bowls (jars) after each stop. The balls / powder ratio was 4: 1, with 10 mm balls (100 times larger than the largest powder particles). Samples were taken every 2 hours of milling for analysis.

To prevent agglomeration of the powder which is observed during the dry grinding [(Stanciu et al. 2014)], we used a liquid medium. After a review of the literature [18], demineralized water and ethanol were chosen as grinding media. 20 ml of grinding medium was added to each jar, and fluid loss due to evaporation was compensated every 2 hours of grinding. The fluid loss was evaluated by weighing of the grinding bowls.

The powders were analyzed using a JEOL scanning electron microscope equipped with EDX analysis and WDX, which allowed observation of powder morphology and aggregation (agglomeration), particle size and distribution of chromium carbide in the cobalt matrix. Particle size analysis was conducted by wet

testing laser diffraction (Mastersizer 3000E Malvren) to determine the size distribution of the powder particles. X-ray diffraction experiments were conducted to identify crystalline species and measure the size of the WC grains. An X-ray diffractometer Siemens D5000, equipped with cobalt cathode (λ=1.78 nm) was used to identify the crystalline species and to measure the grain size of the obtained powder. The measurement of crystallite size was carried out using MAUDE software, as an average value for all the peaks present on the XRD pattern.

Results and Discussion

Dry milling: Co + chromium carbide

Agglomeration of the powder is observed during dry milling, along with sticking on the walls of the grinding chamber. The accumulation of ground material on the milling balls is low and is only observed in the first hours of grinding. The addition of chromium carbide significantly reduces the particle size compared to pure cobalt, as can be seen on the size distribution curves shown in Figure 1. The granulometric distribution shows two maxima, the second peak demonstrate the presence of agglomerates in the powder composition. The second peak is assumed to decrease with increasing chromium carbide content in the composition of the alloy. Agglomeration of the powder was studied on embedded powder samples after polishing and etching with Murakami's reagent. Micrographs of two samples are shown in figures 2 and 3 (optical microscope). They show that the increase of the proportion of chromium carbide powder influences the particles agglomeration. At high chromium carbide content, the dimensions of the largest particles did not exceed 200 µm, while lower chromium carbide content and pure cobalt lead to maximum particle size around 700 µm.
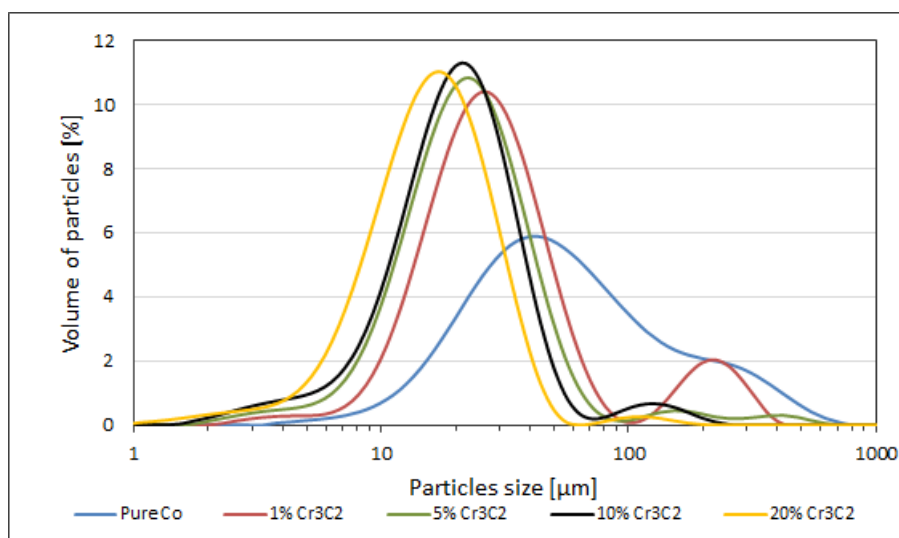

Figure 1. Size distribution of the powders after 10 hours of dry milling.

The lamellar structure obtained by mechanical alloying is easily observable in Figures 2a and 2b. The large particles have a composite structure obtained by assembling a number of small particles, along with the presence of chromium carbide particles at their interfaces. The mixture containing 10% Cr_3C_2 (Fig. 2a) presents, in the largest particle, islands where cobalt has not been homogenized with chromium carbide (light gray). The effectiveness of grinding is limited because the proportion of hard phase was insufficient, which allowed ground powder to stick to walls of the bowl due to the malleability of cobalt.
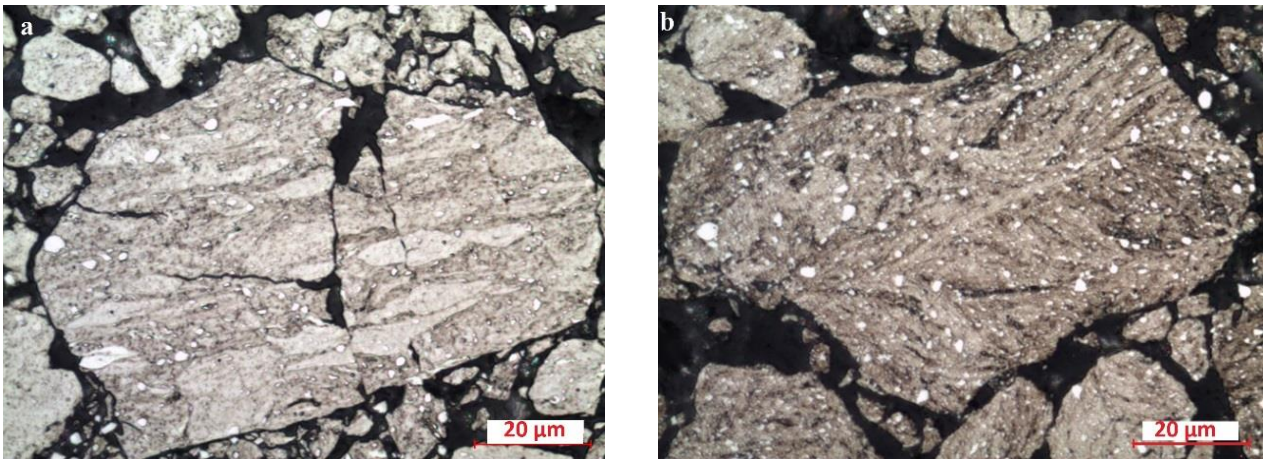
Figure 2. Microstructure of Co+10% Cr$_3$C$_2$ (a) and Co+20% Cr$_3$C$_2$ (b) after 10 hours of dry milling. Nital etchant, MO 1000X

This does not happen in the case of 20% Cr$_3$C$_2$ mixture (Fig. 2b) where the mixture is well mixed, with a uniform distribution of chromium carbide (light gray) in the Co matrix (dark gray). A significant reduction in the size of chromium carbide particles is observed: they do not exceed 2-3 microns after grinding (Fig. 2b), which is much smaller than the original size (up to 10 microns). For the mixture with 1% Cr$_3$C$_2$, two chromium carbide particles (indicated by white arrows in Fig. 3a) are inlaid in a cobalt particle, and a thin cobalt layer is detected by EDX analysis on the free surface of these chromium carbide particles. A large number of free carbide particles is observed in the mixture containing the higher amount of chromium carbide (Fig. 3b).
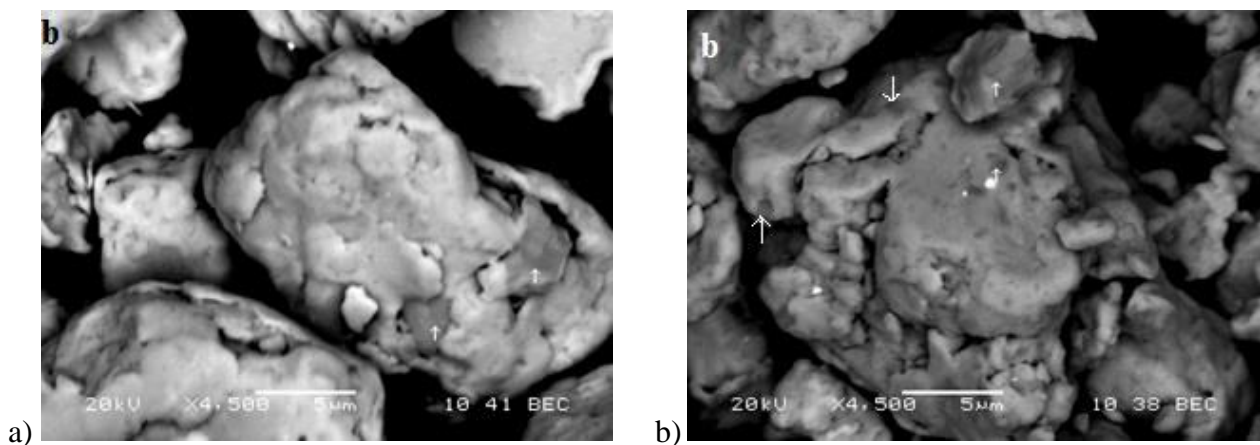

Figure 3. The particles morphology of a) Co + 1% Cr$_3$C$_2$ et b) Co + 10% Cr$_3$C$_2$. The white arrows indicate the chromium carbide particles. SEM BSE 4500X

Milling in liquid: Co + chromium carbide

Given that dry milling allows the powder to stick to the wall of the grinding bowl very quickly after the start of grinding cycle, liquid has been added to act as an anti-caking agent. Water and ethanol have been chosen for this. The effects that these two grinding media have on the powder are discussed hereafter. The grinding conditions in water are identical to those of dry milling, except the addition of 20 ml of water to each mixture. The use of water as milling medium allowed obtaining a more homogeneous powder, as

can be seen in figures 4a and 4b. However, at higher magnification (Fig. 5), the presence of cobalt hydroxide platelets on the surface of the particles can be observed.
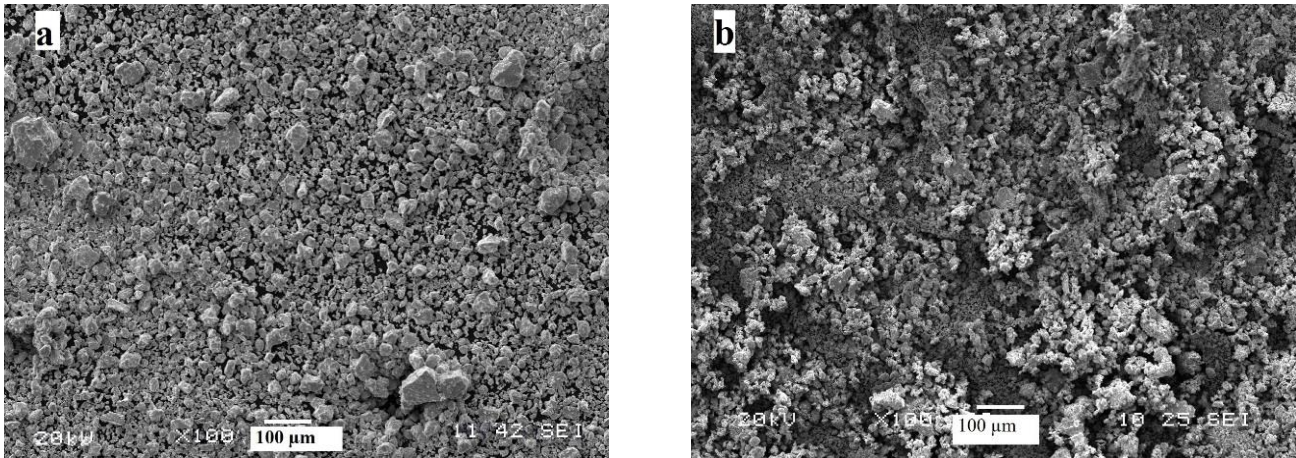

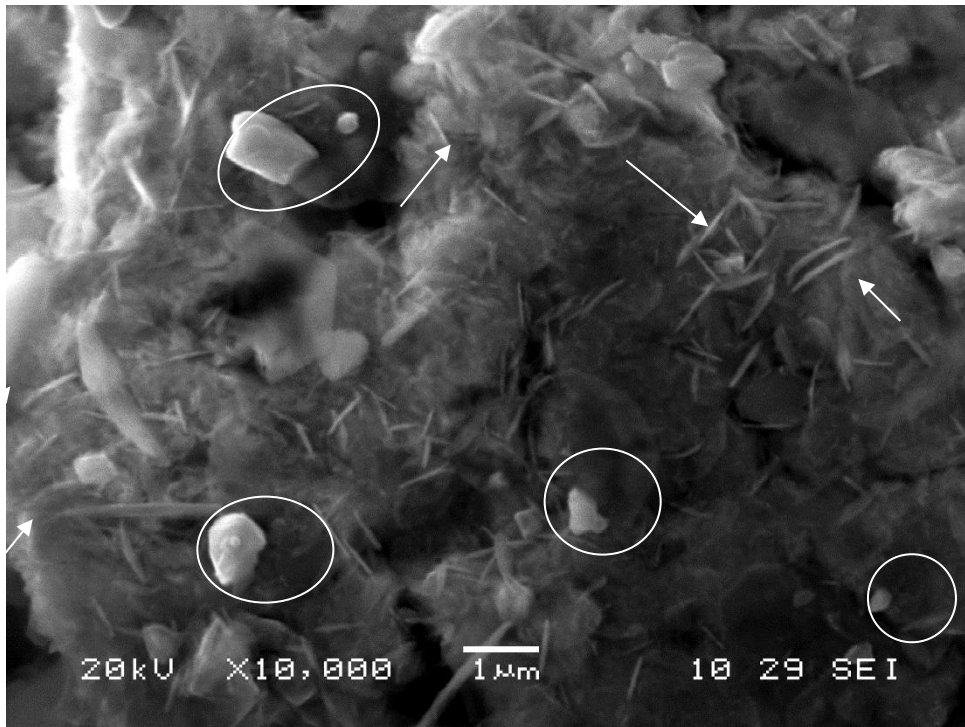Figure 4. Morphology of Co + 10% Cr_3C_2 particles after 10 hours of dry milling a) and water milling b). SEM SEI 100X

Figure 5. Morphology of Co + 10% Cr_3C_2 particles. The white arrows indicate the cobalt hydroxide particles and the white circles the chromium carbide particles. SEM SEI 10000X

Average particle size is shown in Figure 6 for various chromium carbide contents after water milling for 10h. The average particle size was close to 20 microns for all samples, with a slightly smaller size for the mixture containing 5 wt. % and 20 wt. % of chromium carbide. The primary effect of using water as a grinding medium is the total elimination of adhesion to the wall of the grinding bowl. This is demonstrated by the fact powder particles greater than 50 micrometers are present in the composition as we can see on Figure 4b.
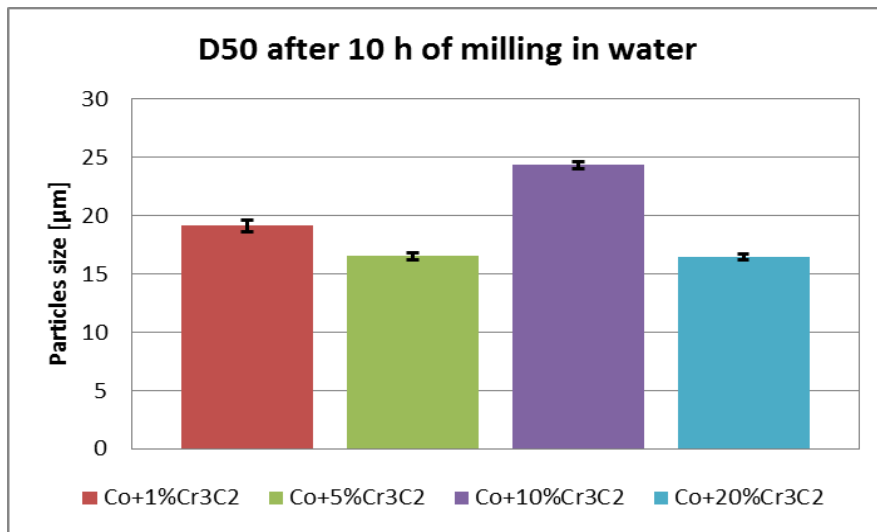
Figure 6. Average particle diameter for the series milled in water.

In conclusion, the grinding of cobalt-inhibitor mixtures in liquid medium is recommendable from the viewpoint of the particles size but water is not the ideal medium for grinding because it causes oxidation of the powder.

Grinding in ethanol was carried out in identical conditions as in water. Given the higher volatility of ethanol relative to water, there are more fluid losses during milling but complete drying of the mixture is never reached. In this way the viscosity on the powder-liquid mixture increase. This fact results in a reduction in effectiveness of the milling by changing (disturbing) the movement of the balls and of the powder inside the bowls during planetary movement.

Average particle diameter values are presented in Figure 7. A significant decrease in particle size is observed when the amount of chromium carbide increases.
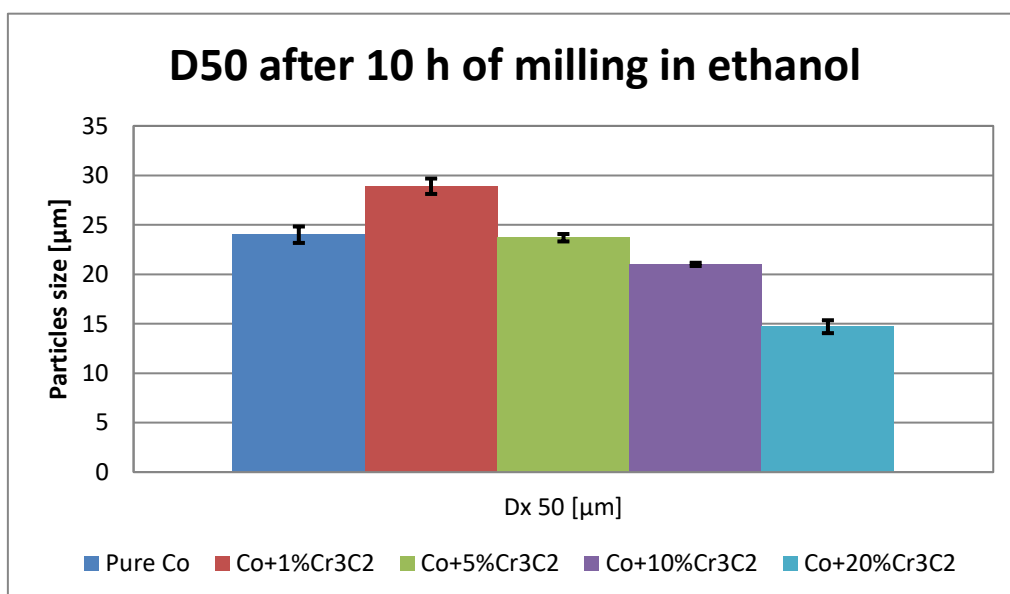

Figure 7. Average particle diameter for series milled in ethanol.

Figures 8a and 8b present samples milled in water and in ethanol containing 10% by weight chromium carbide were analyzed by EDX. On the sample milled in water, cobalt hydroxide quickly appeared. Figure

10a shows a sample milled in and the 3 points where the EDX analyses were performed. The oxygen rate recorded by EDX is very high in the places where the presence of the cobalt hydroxide platelets is observed (Fig. 9a). The chemical compositions for all the points analyzed in figure 8a are presented in Table1.

For mixtures milled in ethanol, the situation is different. Figure 8b shows the aspect of a Co sample with 10% chromium carbide which does not present cobalt hydroxide platelets. Oxygen is present in small amounts, due to the surface oxidation generated by the contact of the powder with air, as can be seen in Figure 9b. The chemical compositions for the points analyzed in Figure 8b are presented in Table 2.
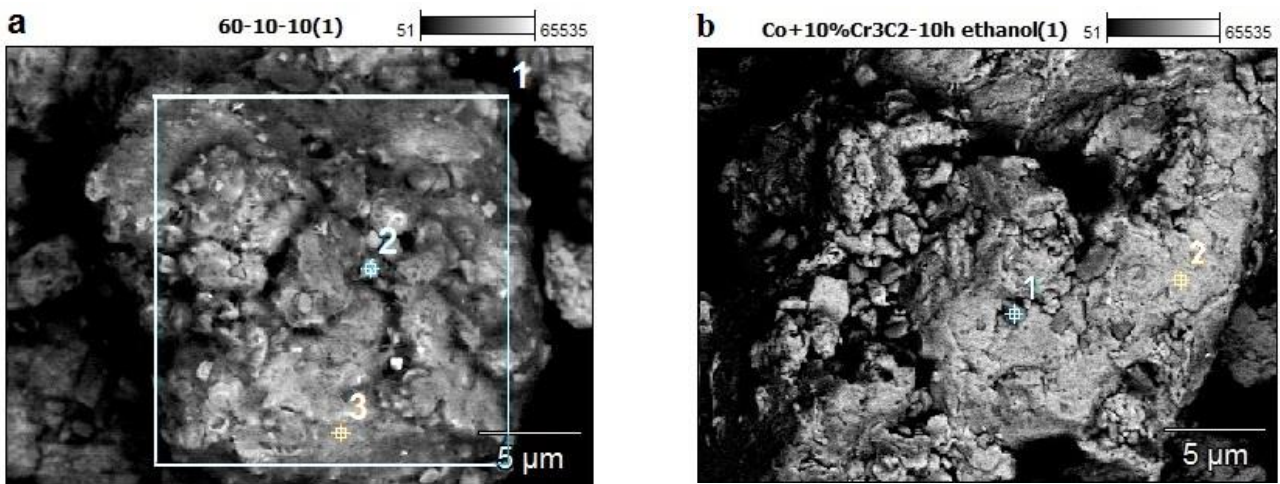

Figure 8. a) Sample milled in water. The chemical compositions for the analyzed points are presented in table 1; b) Sample milled for 10 hours in ethanol. The chemical compositions for the analyzed points are presented in table 2.
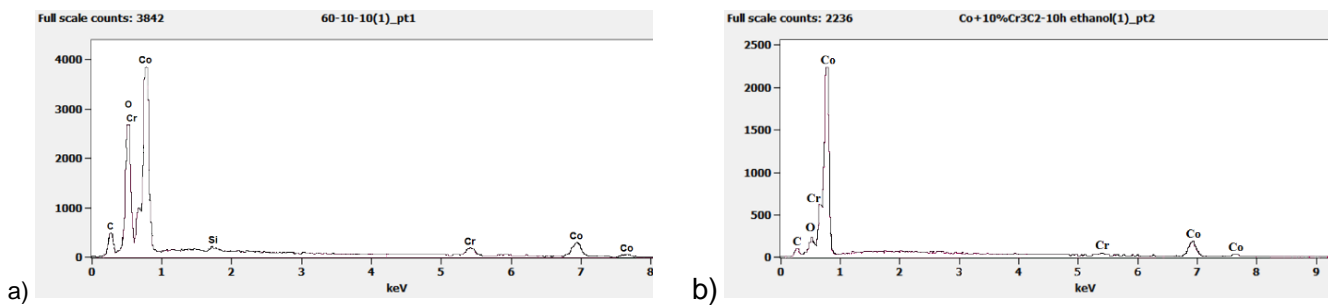

Figure 9. a) EDX analysis spectrum corresponding to point 3 on figure 8a, and b); EDX analysis spectrum corresponding to point 2 on figure 8b

Table 1. Chemical composition for figure 8a.

	Chemical composition [%, wt.]				
	C	O	Cr	Co	Si
pt1	2.6	14.3	8.8	73.7	0.6
pt2	6.6	5.2	66.4	21.8	
pt3	3.8	16.0	18.1	62.1	

Table 2. Chemical composition for figure 8a.

	Chemical composition [%, wt.]			
	C	O	Cr	Co
pt1	1.17	2.23	5.14	91.44
pt2	1.88	1.26	2.75	94.21

The samples analyzed in figures 8a and 8b are presented as SEM pictures, in Figures 10a and 10b for better visibility. In figure 10a showing a sample milled in water, the cobalt hydroxide platelets are clearly visible, compared to the sample milled in ethanol (Fig. 10b) where there are no cobalt hydroxide platelets. This situation is characteristic for all samples milled in water and ethanol.
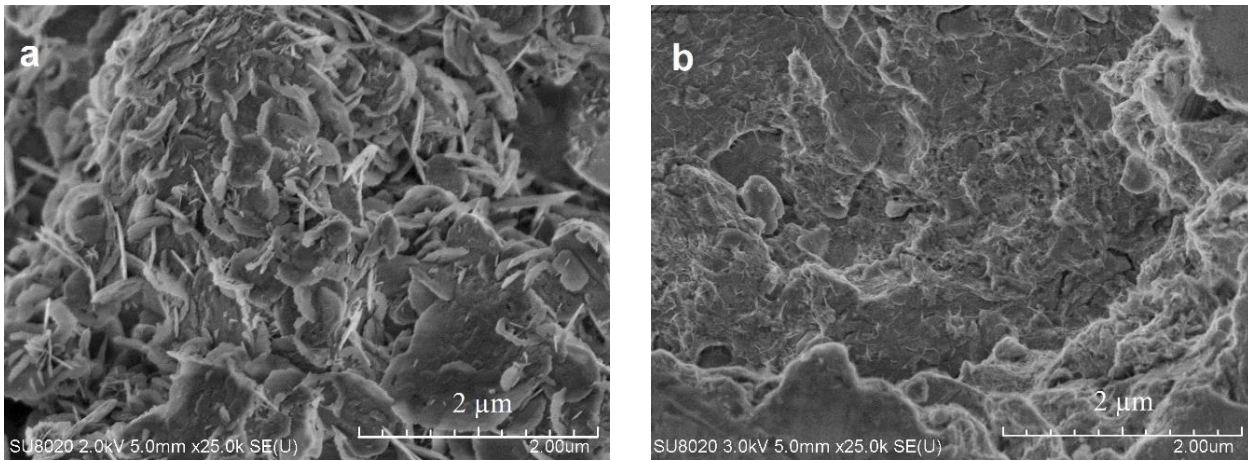

Figure 10. Co+10% Cr_3C_2 powders appearance after 10 hours of milling: a) in water et b) in ethanol. SEM 25000X

Figures 11a and 11b present the microstructure of two samples milled in different liquid environments, obtained by backscattered electron microscopy.

After polishing end etching with Murakami reagent, no significant difference between two samples can be observed.

Both samples are made up of agglomerates formed by the welding of finer particles in which chromium carbide particles are disseminated. Carbide particle size (dark gray in Fig. 11a and 11b) decreased greatly compared to the initial size (3-5 µm), the largest particles being about 2 µm. This type of microstructure is typical for mechanical alloyed mixtures, and is similar with the microstructure obtained by dry milling. For liquid phase milling, no bulk cobalt zones were observed in the particles microstructure, contrary to dry milling.
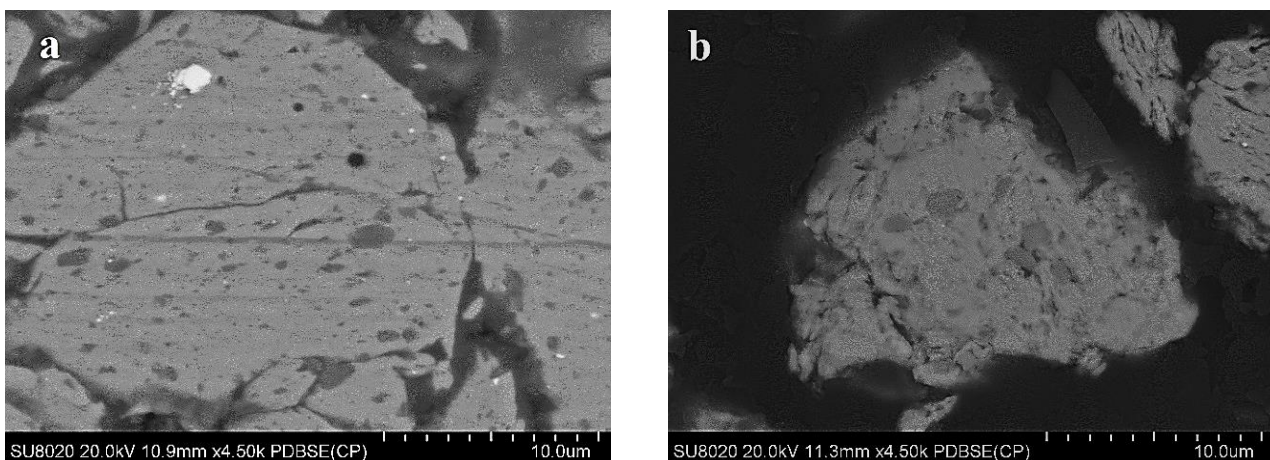

Figure 11. Co+5% Cr_3C_2 powder microstructure after 10 hours of milling: a) in water and b) in ethanol. SEM 4500X.

Comparison of particle size for all media is shown on Figure 12. An average particle size between 15 and 30 microns is observed for liquid grinding, depending on the composition of the mixture. It is also observed

that the ethanol grinding leads to the same particle size as the dry milling except for pure cobalt. This may be due to the high volatility of ethanol: evaporation during the milling process leads to significant increase of the viscosity of the suspension, which results in a reduction of grinding effectiveness at the end of the cycle.The use of water as a grinding medium provides much finer particle size in comparison with the dry grinding or in ethanol at lower chromium carbide content (less than 10 wt.%). With 20 wt.% chromium carbide content, a similar granulometry is found for all milling mediums.
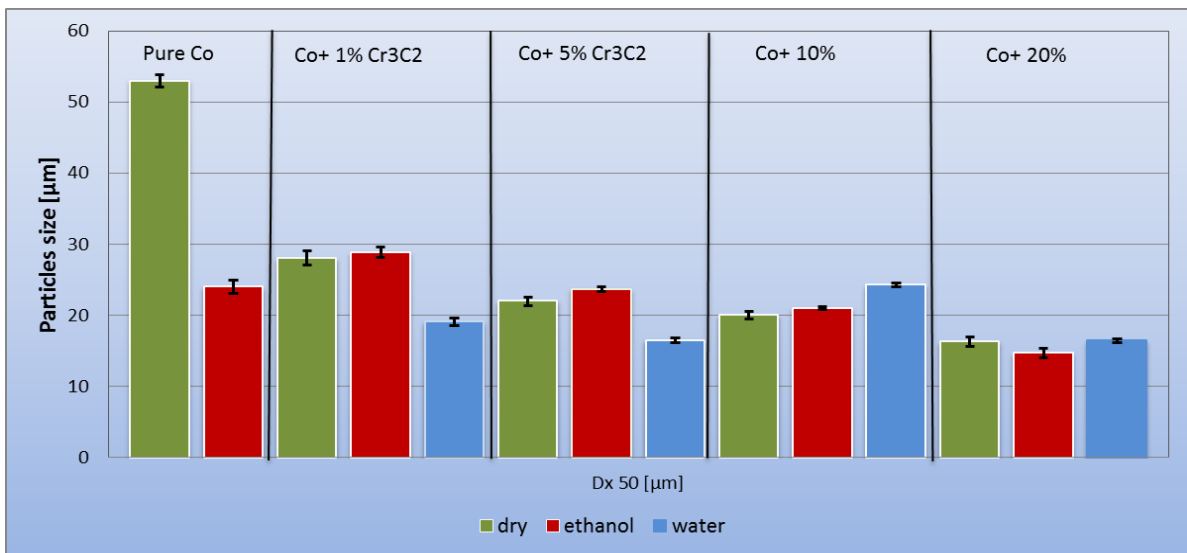

Figure 12. Average particle diameter for the series dry grinded or milled in ethanol or in water.

The XRD analyzes were performed to determine the size of crystallites and to identify the phases which are present in the powder. This was necessary because the highly deformed shape of the cobalt particles, the presence of partial welding of particles and of chromium particles at previous interfaces does not allow getting information about crystallite size by laser particle size measurement only.

The XRD analyzes demonstrated a transition from hexagonal close packing (HCP) cobalt to faced-centered cubic (FCC) cobalt and a significant decrease in the size of cobalt crystallites. This phase transformation appears to be influenced primarily by the proportion of chromium carbide, secondarily by the milling environment and by the milling time. Chromium carbide are very difficult to detect on the XRD patterns. On Figure 13, the patterns for mixtures with 10% chromium carbide milled in various media is compared with the raw cobalt powder pattern. After milling, peaks related to hexagonal cobalt undergo broadening and intensity decrease while other peaks that can only be associated with FCC cobalt (60.6°) and are not present in the initial cobalt powder appear.

 In the case of milling in ethanol, peaks related to chromium carbide present low intensity, proving that it has been very well blended in the matrix of cobalt. Calculation of crystallite size by the MAUDE software was carried out for all powder mixtures. Results are presented in Table 3.

The conversion from HC cobalt to FCC cobalt can be noticed, with a conversion rate of 95 to 100% at high chromium carbide content.

From Table 3, the cubic phase shows a crystallite size noticeably smaller than the hexagonal phase. The cobalt crystallite size decreases with the increase of the proportion of chromium carbide in the alloy. Wet

grinding ensures a very small crystallite size, inferior to 10 nm for mixtures with high chromium carbide content.
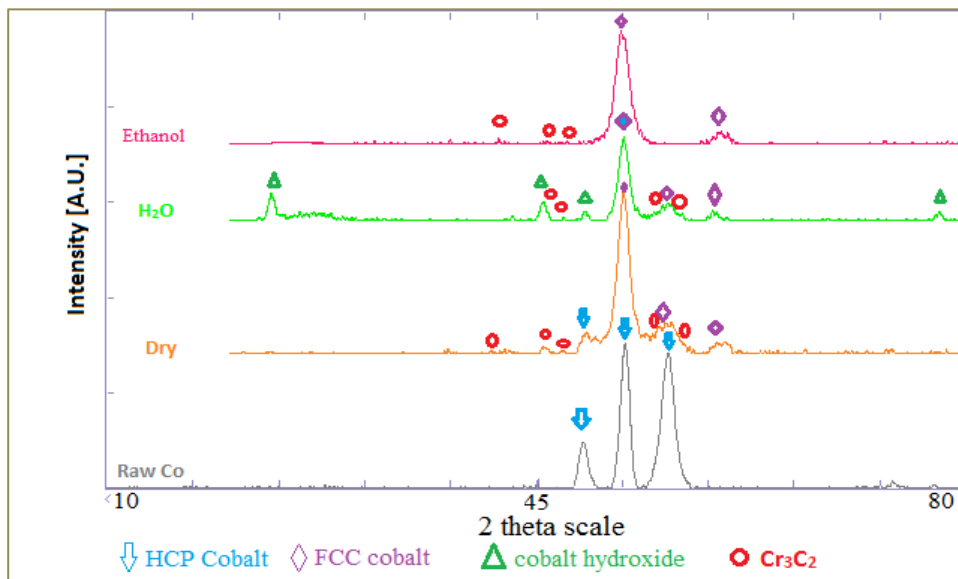

Figure 13. XRD patterns for mixtures of cobalt +10% Cr_3C_2 after 10 hours of milling.

Table 3. Cobalt crystallites size for the powders milled for 10 hours

Milling conditions	Inhibitor Cr_2C_3 content[%, by weight]			
	1	5	10	20
Dry	70% HC = 131 nm 30% FCC =67 nm	12% HC = 157 nm 88 % FCC = 12 nm	9% HC = 400nm 91% FCC =39nm	5% HC = 312 nm 95% FCC =34 nm
H_2O	100 % HC =132 nm	75 % HC = 119 nm 25 % FCC = 66 nm	1 % HC = 200 nm 99 % FCC =7.5 nm	100% FCC =6.3 nm
Ethanol	80% HC = 113 20% FCC =120	60 % HC 113 nm 40 % FCC 94 nm	3% HC =110 nm 97% FCC =5.4 nm	1% HC = 59nm 99% FCC =4.3 nm

*notes: HC= hexagonal compact; FCC=face-centered cubic;
The Phase proportion is expressed in % by volume.

HC to FCC conversion rate is lower in the case of dry milling because the powder is stuck to the walls of the bowls rather quickly, which limits the effectiveness of milling. Dry milling is also accompanied by significant heating due to friction, which will have an influence on the diffusion process inside the cobalt particles, and slows phase transformation from hexagonal to cubic.

It was not possible to obtain nanostructured mixtures at low chromium carbide content for any of the milling media after only 10 hours.

The liquid proportion during wet milling definitely has an influence on milling efficiency. The high volatility of ethanol compared with water produced an increase in powder viscosity, and a reduction in effectiveness by disturbing the movement of balls and powder.

Another possible option is to use a solid anti-caking agent to decrease the adherence of the powder and to determine the time needed for complete homogenization in order to optimize the dry grinding cycle.

Conclusion

Dry grinding of cobalt powder mixed with various proportions of chromium carbide generates a significant reduction in particle size relative to the pure cobalt powder; however, after 10 hours of grinding, the degree of agglomeration of the powder remains important.

- As the size distribution depends on the milling media and the composition of the mixtures, the use of liquid milling reduces the grain size.
- The degree of oxidation of the cobalt in water milled powder is considerable and cobalt hydroxide particles are formed. Water is thus not the most recommended grinding medium.
- The use of ethanol as a liquid milling medium allows obtaining a particle size of the powder similar to that obtained with water without oxidation of the cobalt powder.
- In terms of crystallite size, in dry milling conditions, a decrease in size with chromium carbide content was observed, from 130 nm at 1 wt. % Cr_3C_2 to 34 nm at 20 wt. % Cr_3C_2. A transition from HC cobalt to FCC was observed, going from 70 % vol. HC for Co-1wt. % Cr_3C_2 to only 5 % vol. HC for an alloy with 20 wt. % Cr_3C_2. This transformation is more evident in liquid medium. At low concentrations of chromium carbide, HC to FCC conversion is smaller than for dry grinding, however at high chromium carbide concentrations this transformation approaches 100%.

In light of these results, the use of ethanol as an anti-agglomerating agent permitted to obtain a homogeneous cobalt-chromium carbide mixture, having a crystallite size in the nanometer range. This allows the use of this mixture as a binder for the manufacture of nanostructured WC-Co alloys. The fine dispersion of chromium carbide in cobalt will greatly shorten the diffusion distance of grain growth inhibitor (chromium carbide).

In further work, chromium carbide doped cobalt powder will be mixed with nanoscale tungsten carbide, shaped and sintered to ascertain the effectiveness of the inhibitor.

References

1. D. F. Carroll, *International Journal of Refractory Metals and Hard Materials*, 10, 1-3, p. 123 (1999).

2. R. Porat, S. Berger, A. Rosen, Proceedings 14th International Plansee Seminar, v. 2, Cemented Carbides and Hard Materials, 1997, p. 582-595.

3. K. Mannesson, I. Borgh, A. Borgenstam, Ågren, *International Journal of Refractory Metals and Hard Materials*, 29, 4, p. 488 (2011).

4. T. Taniuchi, K. Okada, T. Tanase, Proceedings 14th International Plansee Seminar, v. 2, Cemented Carbides and Hard Materials, p. 644 (1997).

5. P. Seegopaul, L. E. McCandlish, L. Gao, Proceedings 14th International Plansee Seminar, v. 4, Cemented Carbides and Hard Materials, p. 304 (1997).

6. M.A. Xueming, J.I. Gang, Z. Ling, D. Yuanda, *Journal of Alloys and Compounds*, , no. 264, p. 267 (1998).

7. S.G. Huang, L. Li, K. Vanmeensel, O. Van Der Biest, J. Vleugels, *International Journal of Refractory Metals and Hard Materials,* , 25, p. 417 (2006).

8. C.W. Morton, D.J. Wills, K. Stjernberg, *International Journal of Refractory Metals and Hard Materials*, Volume 23, Issues 4–6, 287-293 (2005).

9. C. Buchegger, W. Lengauer, J. Bernardi, J. Gruber, T. Ntaflos, F. Kiraly, J. Langlade, *International Journal of Refractory Metals and Hard Materials*, Volume 49, , Pages 67-74 (2015).

10. Yingbiao Peng, C. Buchegger, W. Lengauer, Yong Du, Peng Zhou, *Int. Journal of Refractory Metals and Hard Materials* 61 121–127 (2016).

11. L. Lauter, R. Hochenauer, C. Buchegger, M. Bohn, W. Lengauer, *Journal of Alloys and Compounds*, Volume 675, pages 407-415, (2016).

12. S.Luyckx, M. Z. Alli, *Materials and Design*, 22, p. 507 (2001).

13. C.Suryanarayana, *Progress in Materials Science*, 46, p.0-184 (2001).

14. M. Naidoo, O. Johnson, I. Sigalas, M. Herrman, *International Journal of Refractory Metals and Hard Materials*, 37, p. 67-72 (2013).

15. F.L. Zang, M. Zhu, C.Y. Wang*, International Journal of Refractory Metals and Hard Materials*, Volume 26, p. 329 (2008).

16. M.H. Enayati, G.R. Aryanpour, A. Ebnonnasir*, International Journal of Refractory Metals and Hard Materials*, 27, 1, p. 159-163 (2009).

17. Y. Mahani, O. Radzali, H. Zuhailawati, *Materials & Design* Volume 32, Issue 6p. 3293-3298, (2011).

18. J.S. Benjamin, T.E. Vollin, *Metallurgical Transactions*, Volume 5, Issue 8, pp 1929–1934, (1974)

19. J.S. Benjamin, *Metal Powder Report*, 45, 2, p. 122-127 (1990).

20. Heinicke, G., Tribochemistry, Berlin, Germany: Akademie Verlag, 1984.

21. P.G. McCormick, *Mater Trans Japan Inst Metals*, 36, p.161-169 (1995).

22. D.R. Maurice, T.H. Courtney, *Metallurgical Transactions A*, A21, p. 289-303 (1990).

23. V.I. Stanciu, V. Vitry, F. Delaunois, Proceedings 23rd International Conference on Metallurgy and Materials METAL 2014, Brno, Czech Republic, 21 - 23 Mai 2014.