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WC-Co composite made with doped binder: The effect of binder proportion on microstructure and mechanical properties

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ABSTRACT

Apart from hardness and density, the durability of cutting tools and other wear parts made of WC-Co composites depends on the homogeneity of the material. A homogeneous composite powder is obtained by mixing the carbide and the binder for long periods.

To shorten the homogenization time and improve the sustainability of these products, a new type of binder was created by incorporating the grain growth inhibitor into the cobalt binder. The presence of the inhibitor in the binder is supposed to improve the latter's distribution in the mixture and make the binder harder, therefore more easily incorporable into the mass of the tungsten carbide particles, reducing the homogenization time.

A WC powder with a particle size of about 0.5 μm was mixed with 6, 9 and 12% by weight of cobalt powder doped with Cr_3C_2 (doped binder). Classic mixtures (WC + Co + Cr_3C_2) were also prepared to assess the effect of the doped binder.

The mixtures were prepared by planetary ball milling for 10 h, with a speed of 600 rpm, using a balls/powder ratio of 4: 1, and 20 ml of ethanol as an anti-caking agent.

Samples were shaped and sintered by SPS technique at 1150 °C with a heating rate of 50 °C/min and a pressure of 50 MPa.

As expected, a more homogenous microstructure is obtained in the samples made with the doped binder. The composites with 6 and 9 wt% Co has superior densification thanks to the doped binder. The best hardness/toughness compromise is registered for composites with 9% Co (2100 HV_{30} and 9.1 MPa*$m^{1/2}$). Increasing the cobalt content to 12% decreases the hardness but does not improve toughness (9.5 MPa*$m^{1/2}$).

1. Introduction

Cemented carbides have a long tradition as working tool materials for numerous applications [1]. The durability of wear-resistant parts manufactured from WC-Co composites is related to the homogeneity of the material. In cemented carbides, cobalt plays a double role: (i) it is a binder for hard particles, and (ii) it provides the necessary toughness for the composite; thus, the hardness-toughness balance revolves around the proportion and distribution of cobalt in the composite. For composites intended for the manufacture of cutting tools, the proportion of cobalt lies between 6 and 15 wt%. Moreover, the toughness and hardness of the cemented carbides are influenced by the size of the WC hard particles [2].

In the 1990s, nanostructured WC-Co composites were introduced with the idea to increase the wear resistance of the cemented carbides and provide higher hardness without a decrease in toughness [3,4]. However, when the size of WC hard particles is reduced, the improvement of the properties of the cemented carbides is greatly limited by the *grain growth* that occurs during the sintering treatment [5]. In the case of nanostructured WC-Co composites the normal grain growth, may be accompanied by the appearance of a phenomenon known as “abnormal or exaggerated grain growth (AGG for Abnormal Grain Growth – one grain grows much more than any others around)”; the properties of liquid-phase sintered materials are often degraded by this phenomenon [6–9]. To prevent grain growth, the introduction into the hard metal composition of other phases with crystal structure different from the initial phases can be considered; those added phases play the role of diffusion barrier and grain growth inhibitors. In the case of the WC-Co system, the most appropriate additions are cubic carbides of transition metals [6,10].

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Moreover, the properties of cemented carbides are influenced by the binder. Choosing a binder with a suitable wettability towards WC hard particles leads to the elimination of pores during sintering, thereby improving the mechanical properties of the composite. By separating the hard particles with a thin and tenacious layer of binder, the propagation of cracks is slowed down, ensuring an increase in the toughness of the sintered alloy [11].

The use of cobalt as a binder in sintered hard composites is favoured by the fact that it allows total wettability of the carbide particles, which enables very good densification during sintering [12]. For a given size of WC particles, increasing the amount of binder has the effect of reducing the hardness. However, as it is the case for bending strength, the impact strength is strongly influenced by the content of the alloy binder. The impact resistance values increase exponentially with the increase in the cobalt content in the composite [13].

To summarise, hardness and toughness are influenced in opposite directions by the modification of the cobalt level content in the composition of the composite. The successful operation of a cemented carbide tool requires the simultaneous presence of both high hardness and very good toughness. Solving this problem remains a challenge in the cutting tool industry.

This article aims to study the influence of cobalt concentration on the mechanical properties (hardness and toughness) of the cemented carbides. The cobalt used as a binder is doped with grain growth inhibitor (a type of binder developed in our previous studies) [14,15].

2. Experimentation

The powders were prepared by mechanical alloying using a Fritch Pulverisette 7 Premium line planetary ball mill, equipped with two tungsten carbide bowls of 80 ml capacity. For each grinding cycle, the first bowl was loaded with a mixture of WC and doped cobalt (cobalt mixed with 10 wt% Cr_3C_2 in a separate cycle, named "doped mixture") and the second bowl with a mixture of WC, cobalt, and chromium carbide, named "classic mixture", of identical average composition. The WC powder with an average particle size of 0.52 μm was supplied by Wolfram Bergbau- und Hütten AG Austria. The chromium carbide powder with an average particle size of 3–5 μm was delivered by Alfa Aesar. The cobalt powder with a purity of 99% (the rest is iron and manganese) was prepared in the laboratory by milling; the fraction <90 μm was used for the preparation of doped cobalt. The milling speed was set at 600 rpm, and each bowl contained 200 g of WC-Co 10 mm diameter balls. The ball-powder ratio was 4: 1, thus obtaining 50 g of the mixture in each bowl. The tests were carried out without a protective atmosphere (under air) using 20 ml of ethanol as a milling environment. The milling time was 10 h.

The samples were sintered by SPS (Spark Plasma Sintering) technique, using an SPS HPD10 machine from FCT System GmbH, Germany. The sintering parameters are presented in Table 1.

The density of samples was measured by Archimedes' method.

The samples were cut and mounted in a resin to be studied both on the surface and the cross-section. X-ray diffraction tests were carried out to identify the crystalline species and to measure the grain size obtained after sintering. The diffractometer was a Siemens D5000 with cobalt anticathode, and the crystallite size was calculated with the Rietveld method using MAUD software.

Samples microstructure was analysed using a Hitachi 8020 scanning electron microscope, equipped with EDX analysis, which allowed obtaining an overview of powders to check the grains size and to determine the local chemical compositions of the samples.

Hardness was measured by the Vickers method under a 30 kgf load with an EMCO instrument. The toughness of the samples was measured by the Palmqvist approach which consists of measuring the length of the cracks appearing at the apex of the Vickers imprints; the toughness is then calculated by the formula published by Shetty and Spliegler [16,17].

Table 1
SPS parameters.

Sintering temperature [°C]	Dwell time [min]	Pressure [MPa]	Heating speed [°C/min]	Sample diameter [mm]	Sample weight [g]
1150	15	50	50	20	~20

3. Results and discussion

The experiments aim to study the influence of the proportion of doped cobalt on the microstructure and the mechanical properties of WC-Co composites. A range of cobalt content from 6 to 12 wt% Co was chosen to stay in the industry standards. Composites containing a low amount of Co are mainly used for metal cutting applications, while those containing a higher Co content are used in applications requiring higher toughness, but also offering good wear resistance.

The density of the composites after SPS sintering is presented in Fig. 1 as a function of the cobalt content in the doped and the classic mixtures. At low cobalt content (6 wt%), the doped mixture has better densification compared to the classic mixture, in agreement with its microstructure (Fig. 2a). Increasing the cobalt content to 9 wt% allows increasing density, reaching almost 100% for the doped mixture. At higher Co content (12 wt%), the density decreases for both types of mixture. The best density is therefore obtained for the mixture doped with 9 wt% of Co. The unsatisfactory densification observed in some cases could be linked to the intense grinding, as suggested by Poetschke and al [18]. However, this phenomenon should (and will in further work) be investigated in more details because, unlike Poetschke, we used a pressure-assisted sintering method.

As seen in Fig. 1, after sintering the densification of doped mixtures is higher than those of classic mixture, except for high Co content. An explanation could be the temperature of SPS sintering, fixed at 1150 °C in this work. Normally, for a composite containing only 6 wt% of cobalt, the sintering temperature would be closer to 1200 °C [19]. The use of a doped binder thus allows lowering the sintering temperature compared to the classic mixture. A possible cause for the decrease of densification in the case of the mixture with 12 wt% Co is the presence in a greater proportion of the inhibitor (Cr_3C_2) which seems to reduce the densification [20].

The microstructures of the composites obtained by optical microscopy after polishing and etching with Murakami reagent are presented in Fig. 2. The microstructures of the samples made with the doped binder (doped mixture, Fig. 2a, b, and c) are more homogeneous, with more uniformly distributed phases. For samples made with the classical binder (classic mixture, Fig. 2d, e and f), the existence of light areas

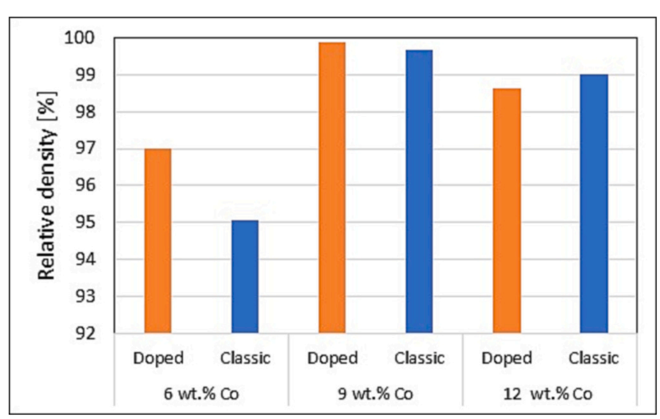


Fig. 1. The density of composites with different Co contents obtained from doped and classic mixtures after SPS sintering.

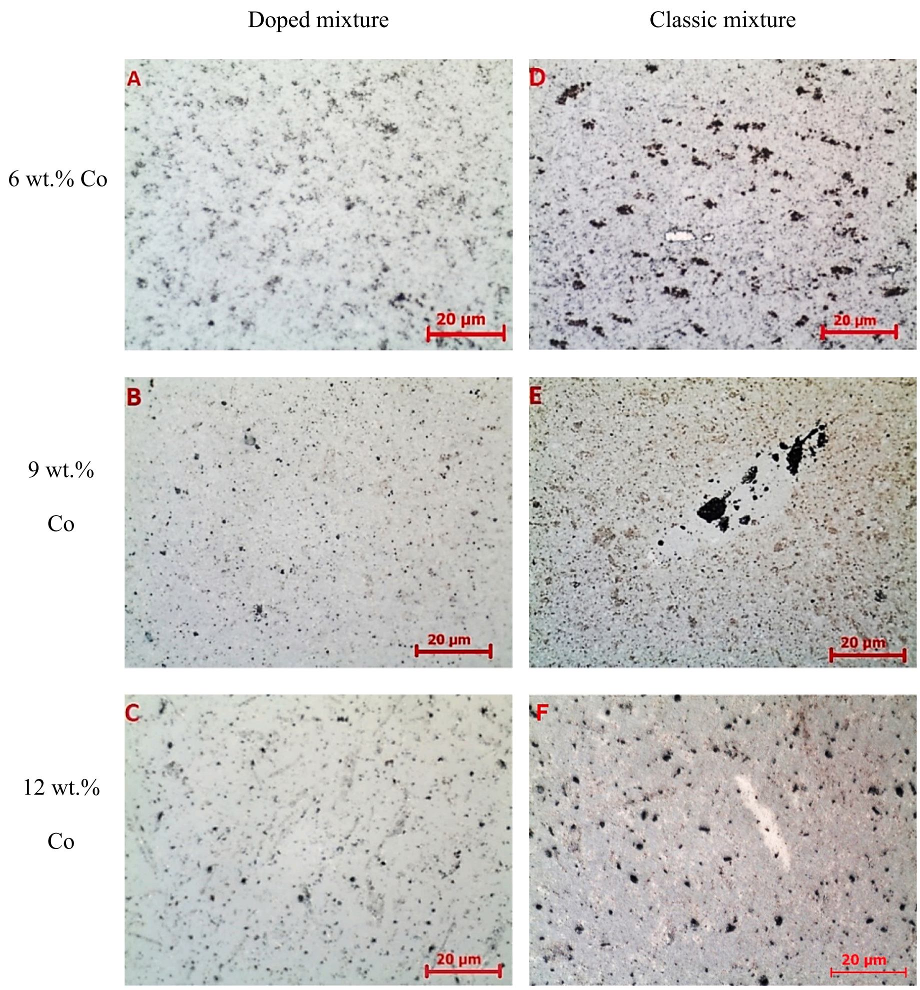


Fig. 2. Sample microstructures as a function of cobalt content and binder type: a, b and c, samples with the doped binder (doped mixture); d, e and f, samples with the classical binder (classic mixture). 1000×, Murakami etching.

made of pure cobalt that did not perfectly homogenize with tungsten carbide after 10 h of mixing can be observed.

This situation is explained by the high toughness of pure cobalt: its deformation and fragmentation to be evenly distributed in the mass of WC particles thus require much longer homogenization times [21,22]. On the contrary, doped cobalt, due to the presence of finely dispersed chromium carbide particles, has a high hardness and is more easily dispersed in the WC powder. The lack of homogeneity observed for the classic mixtures can also explain their insufficient densification after SPS sintering; the adaptation of the homogenization time would be the most suitable solution to solve this problem. Increasing the pressure applied during sintering don't seems to be a solution to improve the densification or mechanical properties [23].

The detailed microstructures obtained by scanning electron microscopy are shown in Figs. 3, 4 and 5, together with the distribution of chromium and cobalt obtained by EDX.

Fig. 3 shows the microstructures of the samples containing 6% Co by weight. For the classic mixture, the presence of abnormal grain growth (AGG) is observed (marked with a red circle). The EDX maps show a more uneven distribution of chromium and cobalt in the sample made with the classic binder.

Fig. 4 shows two details of the microstructure of the samples with 9 wt% cobalt: areas with a lack of homogenization were selected to observe the distribution of cobalt and that of chromium carbide. On the classic binder sample, an example of abnormal grain growth (AGG) is observed even in the vicinity of a chromium-rich zone. Although the cobalt seems to present a good distribution, the chromium is not at all well distributed. In the case of the sample made with doped cobalt, there is no AGG and the chromium and cobalt are distributed much more homogeneously.

The details of the samples made with 12 wt% cobalt are presented in Fig. 5. For the sample with doped cobalt (doped mixture), a higher but more evenly distributed porosity is observed in the form of smaller but more numerous pores. In the case of the sample with a conventional binder, the presence of large pores is noticed.

The effect of the proportion of binder on the hardness and toughness of WC-Co composites is illustrated in Fig. 6. For the composites containing 6 wt% cobalt, hardness greater exceeds 2000 HV_{30} for the doped mixture while the classic mixture presents a hardness lower than 1800 HV_{30}. On the other hand, those samples present similar toughness values (7.9 $MPa{*}m^{1/2}$). Consequently, the doped mixture seems to be the optimum composite because an increase in the hardness of the composite is obtained without decreasing the toughness.

For both mixtures - doped and classic - the increase in cobalt content up to 9 wt% (with 1 wt% of grain growth inhibitor in the doped mixture) allows obtaining hardness values around 2100 HV_{30}, with improved toughness values compared to the 6 wt% cobalt composition (Fig. 6). As hardness values exceeding 2000 HV_{30} are only recorded for low Co (4–6 wt%) composites using VC as grain growth inhibitor [2] that generally present a toughness in the range of 8.1–8.9 $MPa{*}m^{1/2}$, the results obtained in this work (high hardness and higher toughness) are of notable achievement.

A decrease in hardness is observed for composites containing 12 wt% Co compared to composites containing 9 wt% Co (Fig. 6). On the other

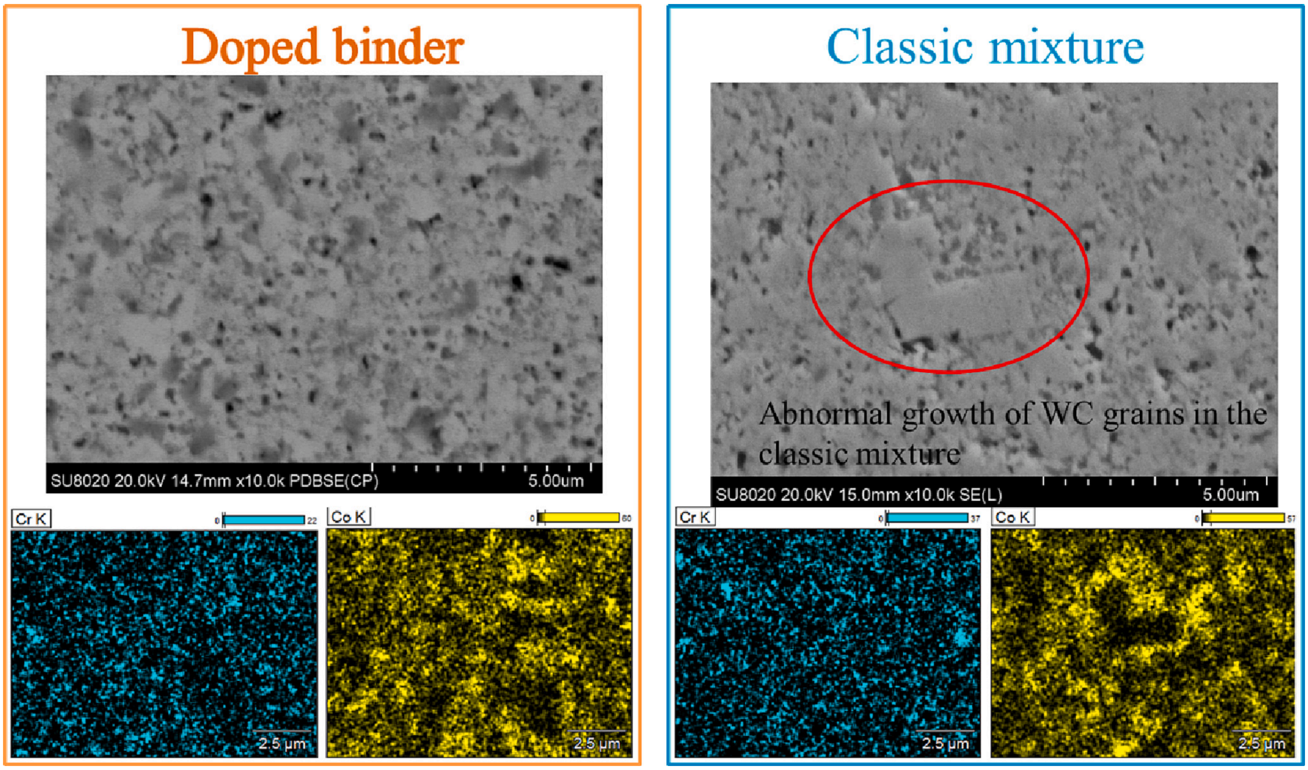


Fig. 3. Microstructure and chromium and cobalt distribution for samples with 6 wt% Co. SEM, 10000×, EDX.

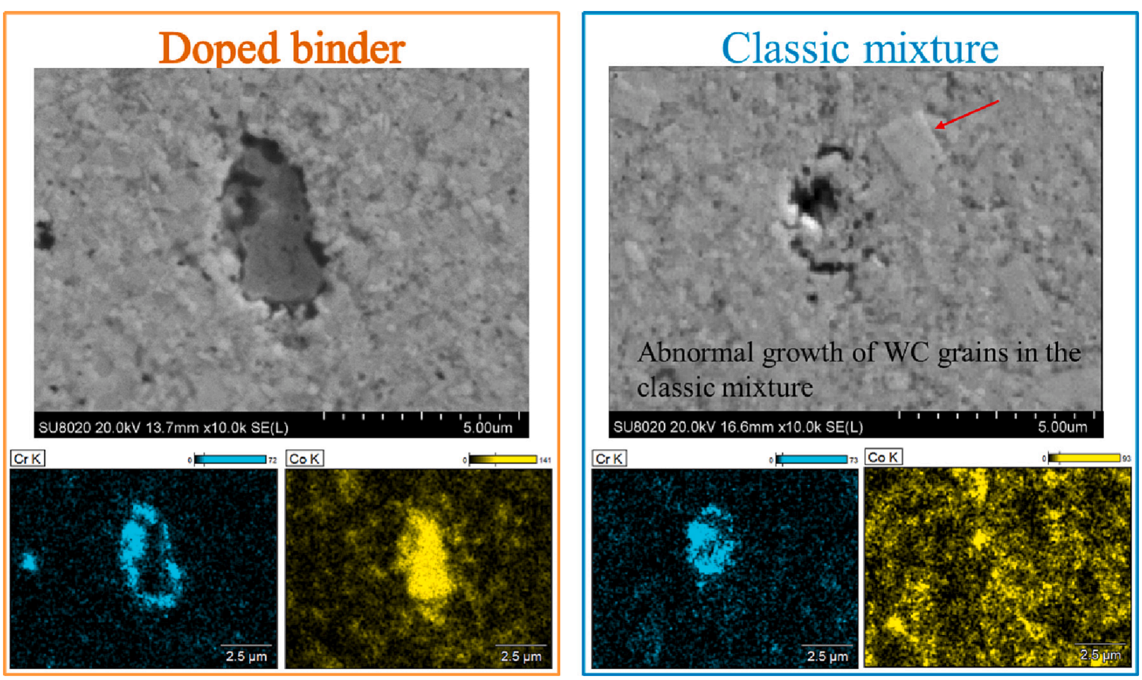


Fig. 4. Microstructure and chromium and cobalt distribution for samples with 9 wt% Co. SEM, 10000×, EDX.

hand, the toughness remains similar for the doped mixture. A slight increase is found for the classic mixture but with a very large standard deviation. This situation is due to the presence of relatively small but numerous (usually 2–3 μm, some of them up to 20 μm) pure cobalt grains in the microstructure of the classic composite due to the insufficient homogenization of the powder (Fig. 2e). These grains block the propagation of some cracks, while others, located in areas less rich in cobalt, can propagate over longer distances. The hardness values are higher than others encountered in the literature (1590 HV_{30}) for similar compositions, instead of toughness values which are lower (10.9–12.1 MPa*$m^{1/2}$ [24]). The use of a higher cobalt content doesn't provide the expected advantage in terms of toughness and densification.

The X-ray diffractograms of the sintered samples are shown in Fig. 7. The presence of three phases is noted: tungsten carbide, cobalt and Co_3W_3C (eta phase, type M_6C). The corresponding peaks for cobalt and the eta phase are very weak in intensity. This situation is due to the

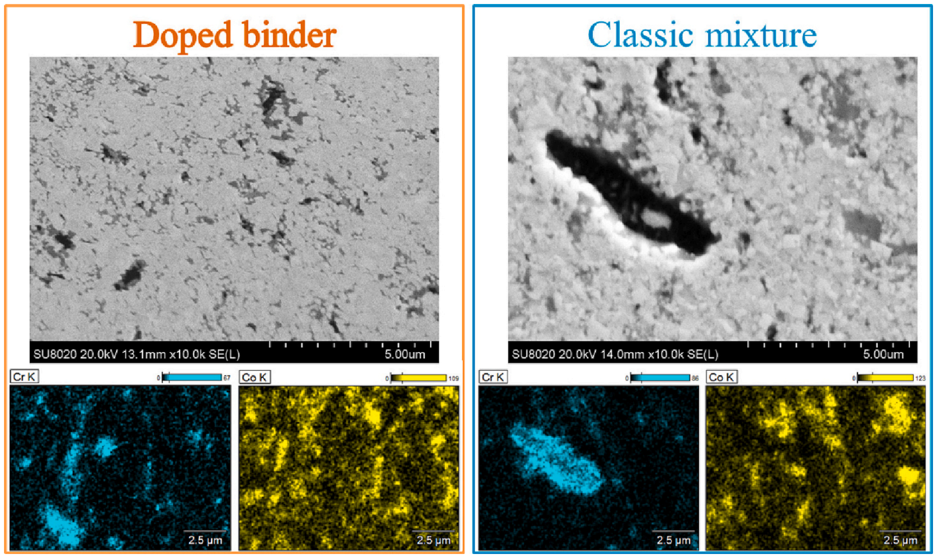


Fig. 5. Microstructure and chromium and cobalt distribution for samples with 12 wt% Co. SEM, 10000×, EDX.

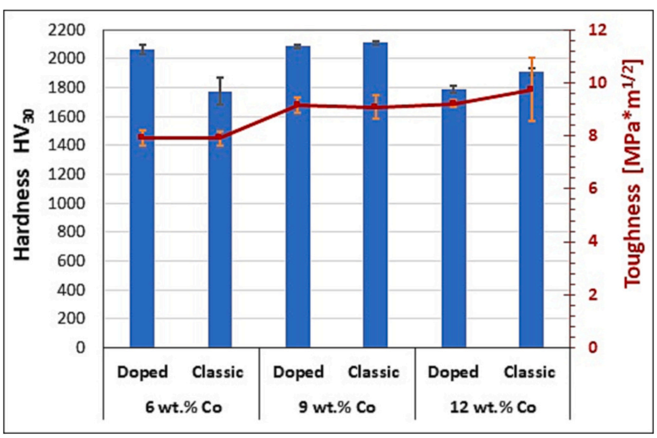


Fig. 6. Influence of the cobalt content on the hardness and toughness of the composites obtained from doped and classic mixtures after SPS sintering.

limited quantity of these phases but also to the atomic mass of the tungsten carbide, being known that the heavy elements are “shading” the lighter elements [25].

For mixtures with 6 wt% of Co, the peaks for metallic cobalt do not appear on the diffractogram, but they appear for higher cobalt content, demonstrating the presence of crystalline cobalt.

The type of binder (doped or classic) does not seem to have an effect on type and quantity of phases observed in the microstructure. The appearance of the eta phase in the microstructure of the samples with 6 wt% of Co may be due to an increased deformation of the cobalt during the mechanical alloying, a fact which may lead to easier formation of new phases [26].

The peaks linked to eta phase (type M_6C) present an inverse effect to cobalt and their intensity decreases with increasing cobalt proportion.

The size of the WC crystalline grains is shown in Fig. 8. In a previous study, we noticed that homogenization parameters have a very large influence on the size of WC grains [27]. The cobalt content in the composite also has a significant effect. After milling, the size of the WC grains decreased drastically from 68 nm to 18 nm for the mixture containing 6 wt% of Co, and to 21 nm for a content of 9 wt% of Co. For 12 wt % of Co, the decrease in the size of the WC grains was more modest, the final value being limited to 33 nm. This evolution is due to the toughness of cobalt which acts as a shock absorber, consuming part of the grinding energy by plastic deformation.

The degree of reduction of the crystalline grains size during homogenization has an important influence on their growth during sintering. The more the grain size has been reduced during homogenization, the more the grains will grow during sintering. It is observed in Fig. 7 that the grain growth extent also increases with the decrease of cobalt content in the composite.

After sintering, for samples containing 9 wt% of Co, there was an increase in the grain size of the WC grains, with an average size of 50 nm for the doped mixture and 51.4 nm for the classic mixture. Those results, added to the very high density obtained after sintering (almost 100%), explain the very high hardness obtained for these samples.

The largest size of WC grains is recorded for a mixture containing 12 wt% of Co. However, the grain growth increases are the lowest. Moreover, the final size of the WC grains exceeded the initial size of the same grains (size before milling). This observation, correlated with the higher content of cobalt, explains the lower hardness values observed for these samples.

The differences in grain growth between the two types of binder stay generally within the limits of the standard deviation. However, the smallest increase of WC grains size was observed for the mixtures with 9 wt% of Co.

Finally, the study concerns the effect of the type of binder (classic and doped) on the microstructure and the mechanical properties of WC-Co composites. Under the test conditions, the cobalt content has a marked influence on the densification, but there's no significant differences between types of binders except at a low cobalt content. Obviously, it is possible to modify the experimental conditions to obtain optimal densifications for each composition, but the purpose of this specific experiment was to determine if doping the cobalt before mixing it with the tungsten carbide can bring advantages. This experiment showed that at equal mixing time, the doped cobalt ensures a much more homogeneous distribution of cobalt and grain growth inhibitor, a fact reflected by the absence of abnormal growth of WC grains (AGG).

4. Conclusions

In the present study, a new way of introducing the grain growth inhibitor (GGI) in WC-Co composites has been studied (doped cobalt) in opposition to the classic variant. Three WC-Co composites with an increasing cobalt content (6, 9 and 12% by weight) were analysed in terms of densification, microstructure, and mechanical properties.

After powders preparation, the following conclusions can be drawn:

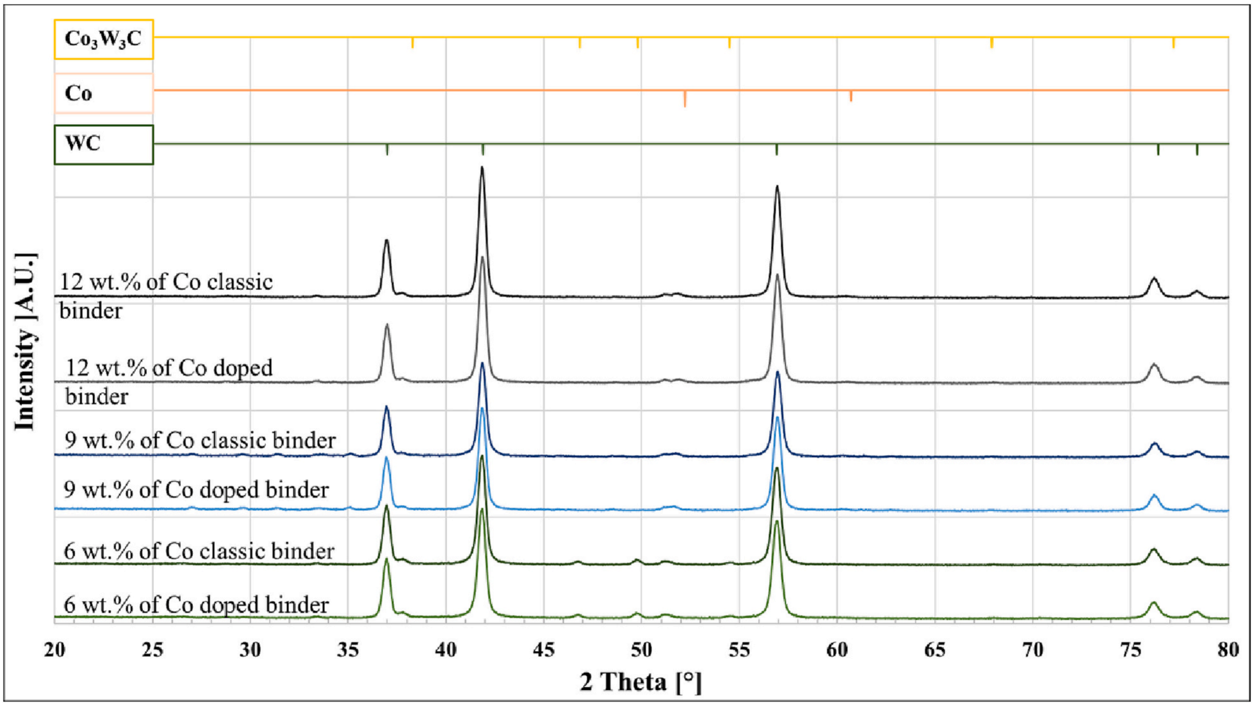
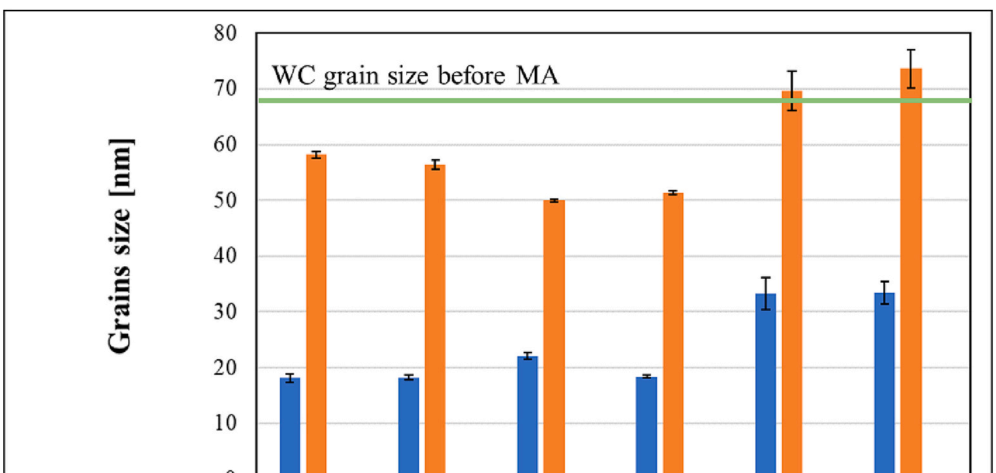


Fig. 7. XRD patterns for sintered samples.



	Doped	Classic	Doped	Classic	Doped	Classic
	6 wt.% Co		9 wt. Co		12 wt.% Co	
Before SPS	18.1	18.2	22.1	18.4	33.3	33.4
After SPS	58.2	56.4	50	51.4	69.7	73.6
Grains growth [%]	222	210	126	179	109	120

Fig. 8. Grains size evolution with cobalt content for doped and classic mixtures.

- Very significant decrease in WC grains size after milling/homogenization but with a strong dependence on the cobalt content.
- Decrease in mix homogeneity with the increase in Co content: interest to increase the duration of powder homogenization.

After SPS

- Increase in WC grains size after SPS: WC grains size values remain under 80 nm, but a higher level of cobalt generates a more pronounced growth.
- Influence of the initial WC grains size on the grains after SPS: the finer is the initial grain size, greater is the grains size growth.
- The sintered product has better homogeneity when a doped binder is used compared to the classic blend.
- The abnormal WC grains growth is observed for classic blends.
- The best compromise is obtained for a mixture containing 9 wt% of Co.

Authorship contributions

All persons who meet authorship criteria are listed as authors of the article "WC-Co composite made with doped binder: the effect binder proportion on microstructure and mechanical properties".

Their contribution is detailed like this:

Victor Ioan Stanciu.

Conception and design of the study, collected data and drafting the manuscript

Jean-Pierre Erauw.

SPS samples sintering supervision, density measurement, approval of the version of the manuscript to be published

Laurent Boilet,

SPS samples sintering, density measurement.

Véronique Vitry.

Revising the manuscript critically for important intellectual content,

Fabienne Delaunois.

Research supervisor, revising the manuscript and approval of the final version of the manuscript to be published.

Declaration of Competing Interest

None.

Data availability

Data will be made available on request.

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