# Carbon-doped FeMn-based binders for tungsten carbide

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**Abstract**

The use of cobalt as binder for tungsten carbide raises more and more questions of environmental, health and societal ethics. The aim of this study is to find alternatives to cobalt as a binder for tungsten carbide.

The binders investigated for this study were FeMn-based binders. The latter were carbon-doped to prevent the presence of eta-phase. Expected results required $HV_{30}$ > 1600, and fracture toughness > 10 MPa·$m^{1/2}$.

The first aspect is to model the phases that were generated by the replacement of cobalt. Pseudo-binary phase diagrams have been performed. The second aspect was to process the alternative "WC – promising alternative binder" composites. The powder metallurgy method was chosen for this purpose. Vacuum sintering technology was used. The samples were then mechanically and morphologically characterized.

## 1. Introduction

### 1.1. Context

Tungsten carbide (WC) is a composite material made up of two phases: a carbide phase and a binder phase. The former gives hardness while the latter keeps the material cohesive and ensures fracture toughness. For performance reasons, the currently used binder for tungsten carbide is cobalt. However, the use of cobalt raises questions of environmental and societal ethics, since it is a critical raw material whose extraction and processing are highly polluting, and whose extraction does not respect human rights (forced child labour, source of funding for terrorist organizations in DRC, etc.) [1]. In addition, studies demonstrated the genotoxicity and carcinogenicity of this element [2]. Replacing cobalt as a binder is therefore a necessity. Nevertheless, undesirable phases may appear in the material if the alternative binder is too carburizing or too graphitizing. In the case of the use of a carburizing binder, η-phase is generated. The latter is known to weaken the composite material by dropping its fracture toughness.
The aim of this paper is to assess the compatibility of WC with a FeMn based binder, which presents a carburizing behavior, and to study the influence of carbon doping on the binder.
To this end, two aspects were addressed.

- The first was to thermodynamically model the phases that would be generated by the replacement of cobalt. ThermoCalc software was used to create pseudo-binary phase diagrams.
- The second aspect was to process the alternative WC-binder composites using the alternative binders that had been selected by the modelling stage.

The samples thus created were then characterized in terms of microstructure, Vickers hardness, fracture toughness and density.

### 1.2. Theoretical background

The first part of this study investigates the consequences of replacing cobalt as a binder for tungsten carbide on the phase's generation in the composite material. This implies the generation of pseudo-binary diagrams. The aim was to determine the present phases in function of the variation in carbon content, all in the presence of a defined binder composition and proportion. Diagrams of this type show the same trend as the one shown in Figure 1. In the case of this figure, the used binder is cobalt (10 wt. %), which is the reference in the field of tungsten carbide.

Several areas of interest can be noted.

- The first is the zone in which only tungsten carbide and binder will be generated (WC+FCC). This zone is referred to as the carbon window, since it is the zone in which the carbon content is appropriate to obtain the microstructure with the best properties represented in yellow on Figure 1.
- Areas on either side of the carbon window are prone to the appearance of undesirable phases. In the case of a carbon deficiency, the eta phase (M6C type) is generated. Its appearance can be facilitated when an excessively carburizing binder is used, and it greatly weakens the material, reducing its fracture toughness. This zone is represented in blue in Figure 1.
- Excessive carbon, on the other hand, can lead to the formation of graphite, resulting in a sharp drop in material properties. The use of an overly graphitizing binder can also lead to the same conclusion. This zone is represented in orange in Figure 1.

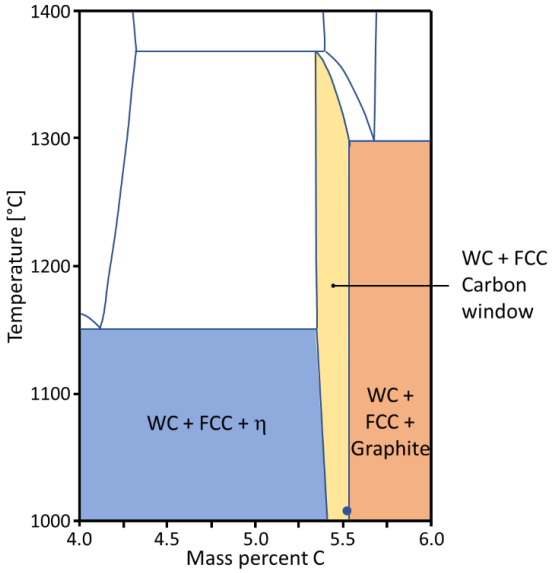


**Figure 1 - WC - 10Co pseudo-binary phase diagram**

The stoichiometric point is also represented in Figure 1. It corresponds to the mass percentage of carbon required to stoichiometrically create WC in the blend. For 100% of WC (no added binder), 6.13 wt.% of carbon are required to reach the equilibrium. If a binder is integrated in the material, the stoichiometric point x-coordinate varies, according to the following law.

$$Abs_{stoichio} = (1 - wt\%_{binder}).6.13$$

Since the wanted phases are WC and FCC phases, the carbon window corresponds to the region where the stoichiometric point should be.
However, if this point appears in the “graphite” or in the eta-phase zone, it becomes important to adjust the binder composition or the amount of added carbon.
In the case of an excessively carburizing binder, it may be interesting to study the influence of carbon addition (doping of the binder). Indeed, in view of the theoretical aspects detailed above, the latter could prevent eta phase generation during sintering, and thus preserve a two-phase microstructure as desired.

Iron-manganese binders have been shown to offer comparable performance to cobalt binders, particularly in terms of densification and hardness. They are also less expensive and have a lower environmental impact than cobalt while being nontoxic.
More abundant and cheaper than cobalt, Fe-Mn binders have already been investigated in the past and some compositions showed promising results as alternative binders [3][4]. However, the composition of the binder is carburizing, leading to eta phase formation during sintering. This significantly reduces the material's fracture toughness.
The formation of eta-phase can theoretically be prevented by carbon addition before the milling step. This possibility makes it worthwhile to study the doping of FeMn binders with carbon doping, as this could lead to an improvement in the microstructure of the alloys concerned.

## 2. Materials and Methods

### 2.1. Simulations

The first part of this study requires the modeling of pseudo-binary diagrams. ThermoCalc was used to create these diagrams. This software is a CalPhaD-type program, based on the principles of Gibbs' free energy minimization to generate equilibrium curves and diagrams. The pseudo-binary diagrams created were all the same type. The TCFE11: Stells/Fe-alloys v.11.0 database is used for their generation. Those diagrams represent the evolution of the proportion of carbon as a function of that of tungsten, all in the presence of a fixed quantity of binder. The diagrams focus mainly on temperature variations between 1000 and 1400°C (interval where phase transformations take place), for a carbon content varying from 4 to 6 wt. %. The aim is to represent the variation in carbon content as a function of tungsten content, all in the presence of a fixed proportion and composition of binder.

### 2.2. Material processing

Once the most interesting alternative binder compositions are selected by ThermoCalc, it is necessary to create them in the laboratory. Indeed, the fact that the modeled materials are comprised of the required phases is no indication of the quality of their mechanical properties. Powder metallurgy is the chosen method.

The tungsten carbide powder used has a granulometry < 1 µm, supplied by ThermoScientific. The iron powder is < 10 µm, supplied by Merck. The manganese powder is supplied by Sigma Aldrich and has a particle size of less than 100 µm.
Initially, iron and manganese mixtures are created in a first milling cycle. The used planetary mill is a Fritsch Pulverisette 7 Premium line. The grinding jars for these cycles are made of hardened stainless steel. 10 mm hardened stainless steel milling balls were used. The mass ratio of balls to powder was 4. This milling cycle is carried out in a wet environment (ethanol), at a rotation speed of 500 rpm, for 10 effective hours. It is also during this stage that black carbon powder is added for doping.
A second milling and mixing cycle then takes place, to blend the tungsten carbide with the binder. During this cycle, the same planetary mill is used, but the grinding jars and balls are made of tungsten carbide. In addition, the mill rotation speed is lower (300 rpm) for 5 effective hours of grinding in ethanol medium. After grinding, the powders are oven-dried and compacted in a cold uniaxial press system.

Finally, a sintering cycle is applied. This consists of conventional vacuum sintering in an argon/hydrogen atmosphere (95-5). The final temperature of this cycle is 1400°C. This temperature is the ideal compromise to densify samples while limiting grain growth, which is detrimental to the hardness of sintered materials.

### 2.3. Characterizations

The sintered samples are cut, mounted into resin, and polished. This metallographic preparation makes the observation of the microstructure possible using a Leica optical microscope. To quantify the sintering efficiency, the porosity rate is measured. For this purpose, the image processing software "ImageJ" is used. This enables porosities to be isolated and their percentage calculated. In addition, the morphology and size of porosities can be studied.
The material can then be color-etched using Murakami reagent. This reveals the microstructure of the samples, which can therefore be observed under an optical microscope. The aim is to detect the presence of undesirable phases, such as eta or graphite. Tungsten carbide grains coated with binder are however not visible under an optical microscope, as the latter's magnification is insufficient. The use of a scanning electron microscope (SEM, Hitachi SU8020, equipped with EDX chemical analysis) is then a necessity. This SEM observation allows us to see the morphology of the carbide grains, a sign of sintering quality, as well as the homogeneity of the microstructure, a sign of milling quality.

The mechanical properties of the samples were also measured. Vickers hardness ($HV_{30}$) is measured with an EMCO device. The average of 8 prints has been made per sample. This property is by far the most important for tungsten carbide, in view of its industrial applications. The material's fracture toughness is also of vital importance since it enables the material to be impact-resistant, which is essential for cutting and machining tools, for example. The fracture toughness of the material can be

determined using the Palmqvist method. The latter requires the measure of the cracks generated by the Vickers hardness indentation. By linking the length of these cracks to the hardness footprint via the formula below, it is possible to determine the fracture toughness.

$$K_{1c} = A\sqrt{\frac{HV_{30}}{\sum l}}$$

with $K_{1c}$ as the stress intensity factor (MPa√m), $A$ as constant, $HV_{30}$ as Vickers macro-hardness under 30 kg load ($HV_{30}$) and $\Sigma l$ as the sum of the cracks (mm) that appeared at the corners of the indentation prints.

## 3. Results and discussion

### 3.1. Samples creation

The first step in this study was to draw up pseudo-binary diagrams. The aim was to reveal which FeMn-based binders' compositions could substitute cobalt the best. Observation of the carbon window and its position relative to the stoichiometric point was the most important parameter to consider. A proportion of 10 wt. % of binder is chosen. As a result, the stoichiometric point is 5.51 wt. % C. The binders that showed the best possible compatibility with tungsten carbide were those containing at least 60 wt. % iron. Indeed, composites whose binders contained higher levels of manganese were subject to much smaller carbon windows. The case of a reduced carbon window is an issue, as the carbon doping operation becomes very difficult. Therefore, binders that were accepted are 6Fe4Mn, and 9Fe1Mn (Figure 2). To observe the effect of the presence of manganese in the binder, a sample containing a 100% iron binder was also created (Figure 3).

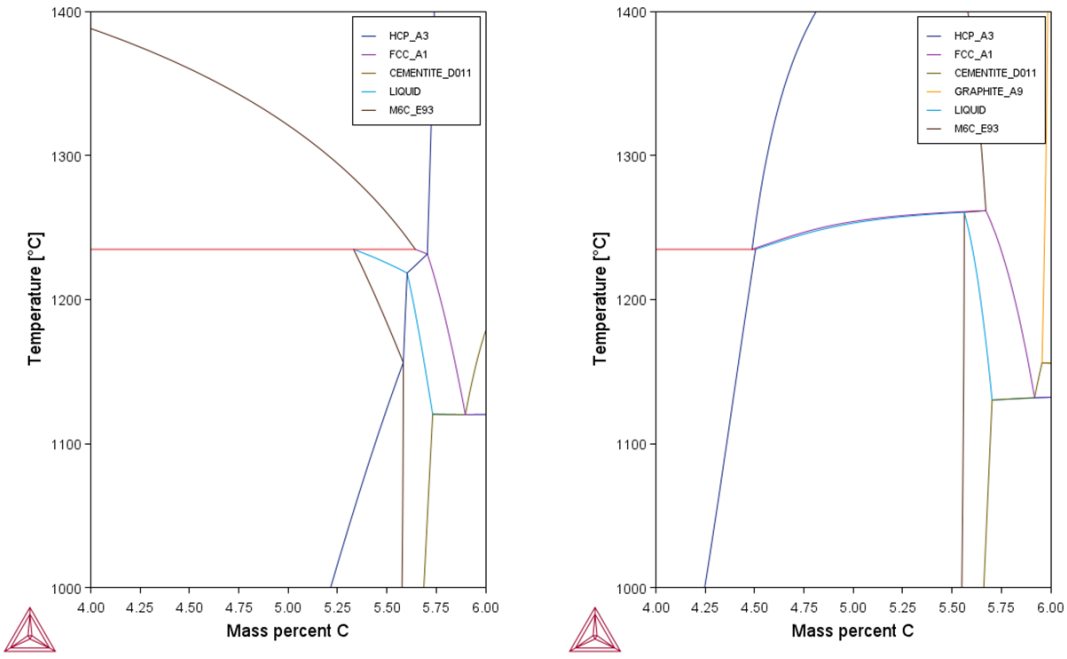


**Figure 2 - WC - 9Fe1Mn phase diagrams (a) and WC - 6Fe4Mn phase diagram (b).**

For each selected binder, an undoped and a doped version were processed. The binder was carbon-doped before the first milling cycle, simply by adding black carbon powder to the iron and manganese powders. The amount of carbon added systematically corresponded to what was needed to bring the stoichiometric point to the centre of the carbon window. In theory, this amount would prevent the generation of both eta phase and graphite. After binder doping, the binder was mixed with tungsten carbide in a second milling cycle.

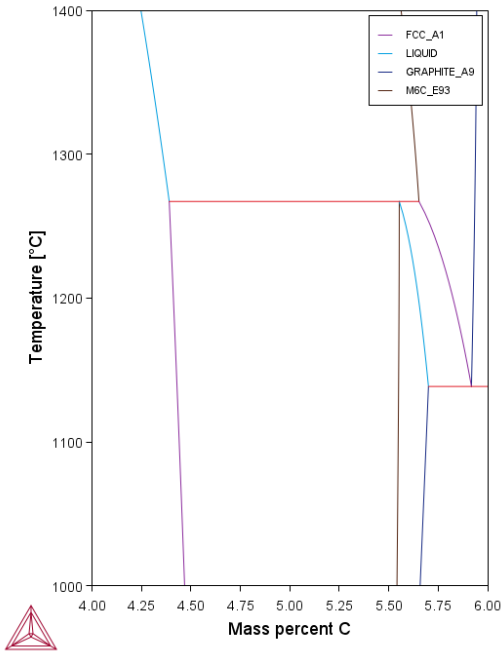


**Figure 3 - WC - 10Fe phase diagram**

### 3.2. Samples characterization

Firstly, the relative densities (complementary to the porosity rate) of the samples were determined by image processing of the samples' microstructure prior to etching. The results are shown in Table 1.

**Table 1 - Densification rate of the sintered samples**

| Sample composition | Image treatment densification rate |
|---|---|
| WC-10Fe | 75.8 ± 5.3 % |
| WC-10Fe+C | 86.4 ± 6.7 % |
| WC-9Fe1Mn | 94.2 ± 6.1 % |
| WC-9Fe1Mn+C | 95.9 ± 7.5 % |
| WC-6Fe4Mn | 69.8 ± 2.7 % |
| WC-6Fe4Mn+C | 86.5 ± 2.8 % |

Doping plays a key role in the densification process. Indeed, each doped composition admits a lower porosity rate than its undoped counterpart. One hypothesis could be that the addition of carbon, which reduces the proportion of eta phase, improves sinterability. A second hypothesis is that the behaviour of the carbon-doped binder (iron in particular) improves the wettability of carbide grains during sintering. These two hypotheses need to be investigated in a future study.

The microstructure of the samples has then been studied, on the one hand using an optical microscope after etching with Murakami's reagent, and on the other hand using a SEM. SEM images (Figure 4) clearly show that the carbon doping of the binder plays a key role in the microstructure of the samples. Indeed, the eta phase, a consequence of carbon deficiency, is very present in Figure 4a (WC - 9Fe 1 Mn) and much less so in Figure 4b (WC - 9Fe 1Mn + C).

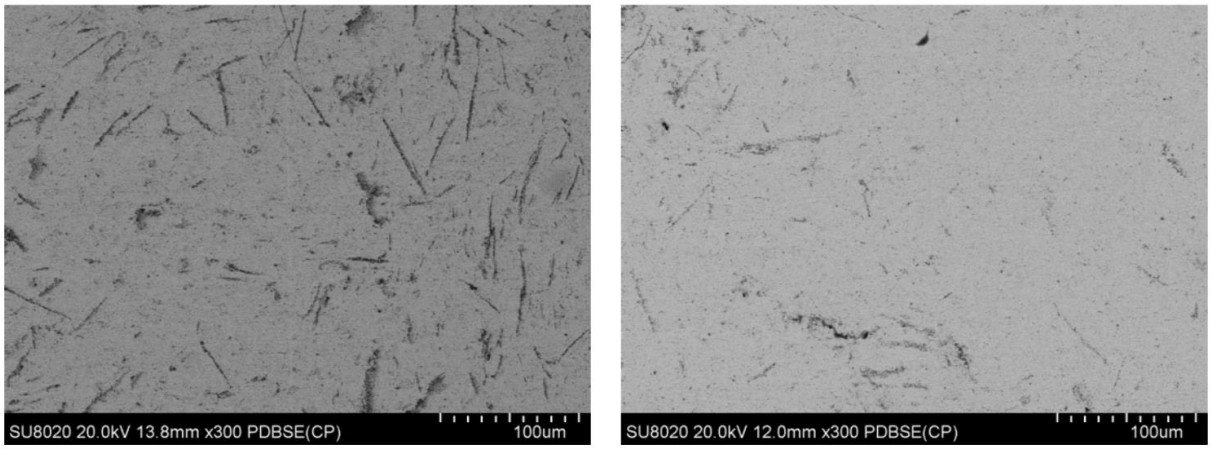


**Figure 4 - SEM images of WC - 9Fe1Mn (a) and WC - 9Fe1Mn + C (b). The eta phase is visible in these images as the darker lamellar phase.**

The eta phase ratio is reduced by the carbon doping of the binder. However, the entire eta phase has not disappeared, as vacuum sintering is highly prone to decarburization.

These decreases in eta and porosity levels both had a very positive impact on the mechanical properties of the samples. Figure 5 and Figure 6 show hardness and fracture toughness respectively. It can be seen that:

- Carbon doping of binders slightly reduces hardness in the case of FeMn binders. This correlates with the reduction in eta phase, which is harder than the tungsten carbide phase.
- The fracture toughness of these samples, on the other hand, is improved by doping. This is due to the reduced levels of the brittle eta phase and porosity rates.
- The 9Fe1Mn binders, both doped and undoped, led by far the way in hardness, offering properties comparable to those offered by the cobalt binder. In terms of hardness, the origin of the failure of the other three alternative binders is the high porosity of the sintered parts.
- In terms of fracture toughness, the binders show relatively similar trends, albeit less than what can be achieved with cobalt.
- This lower fracture toughness may be due to heterogeneities in the microstructure (Figure 7). For example, the presence of binder pools may lead to a binder deficit elsewhere in the material. Binder deficiency often leads to a reduction in toughness. Optimizing milling conditions could help remedy this problem.

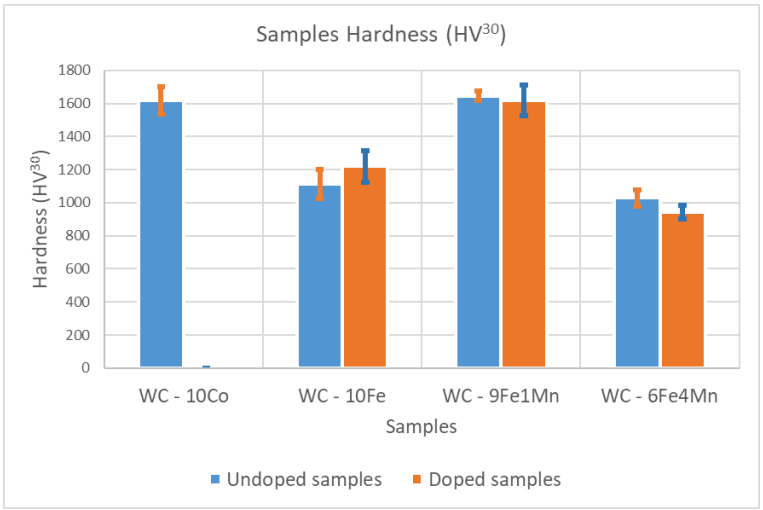


**Figure 5 - Vickers Hardness ($HV_{30}$) of the sintered samples.**

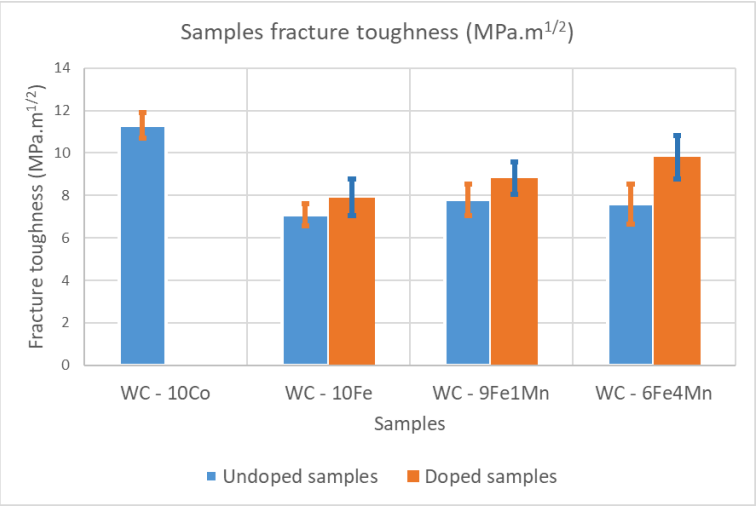


**Figure 6 - Fracture toughness (MPa.m$^{1/2}$) of the sintered samples.**

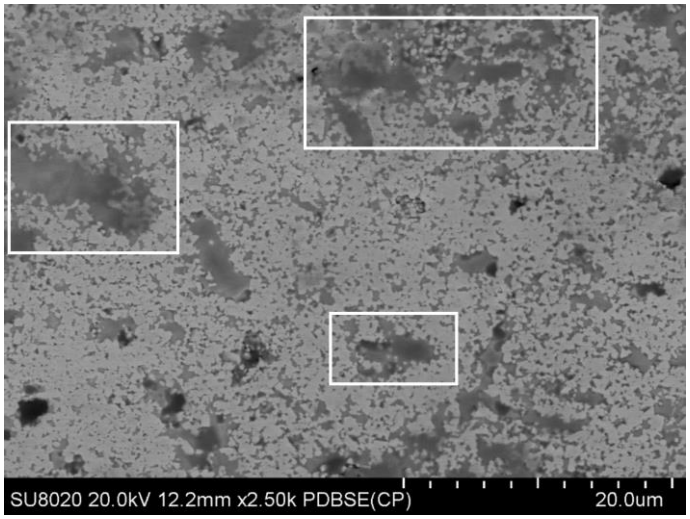


**Figure 7 - SEM image of WC - 10Fe microstructure. Some binder pools are underlined.**

## 4. Conclusion & perspectives

This study showed that carbon doping of FeMn alternative binders for tungsten carbides is very promising. This is true both in terms of microstructure and mechanical properties. Firstly, in terms of microstructure, the presence of eta phase is significantly reduced by the addition of carbon. In addition, doping has enabled better densification of the samples during sintering. On the other hand, in terms of mechanical properties, the hardness of the samples was only slightly modified by carbon doping, but fracture toughness increased significantly. This increase is also due to the lower eta phase content in the microstructure.

Further studies will provide a better understanding of the phenomena involved in carbon doping and establish the reasons for its involvement in reducing the porosity of sintered samples. Finally, another perspective lies in the search for optimum milling and sintering conditions, adapted to each alternative binder composition. This is likely to lead to a more homogeneous microstructure, smaller grains, and consistently better mechanical properties.

## 5. Acknowledgments

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