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The use of niobium carbide as grain growth inhibitor in WC-10Co cemented carbides

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ABSTRACT

A key parameter in the processing of tungsten carbide materials is the control of the grain growth during the sintering stage. To limit the grain coarsening, grain growth inhibitors are added during the mixing of the powders. Those are transition metal carbides (vanadium, chromium, niobium, molybdenum) that are added in small amounts. Niobium carbide is an efficient GGI and can bring enhanced fracture toughness and reasonable hardness. The influence of niobium carbide (alone or with a combination of other inhibitors) on the grain growth was studied. To ensure a good homogeneity, a two-step ball milling was carried out: the first with cobalt and inhibitors, the second with WC and the doped-cobalt powder. The powders were sintered by vacuum sintering before the characterization of mechanical properties such as hardness and toughness. Niobium carbide is found to be an effective inhibitor since the mechanical properties are superior compared to the other inhibitors. Hardness and fracture toughness are 1858 ± 31 HV_{30} and 9.8 ± 0.2 MPa$\sqrt{m}$ for NbC alone and 1930 ± 22 HV_{30} and 9.4 ± 0.3 MPa$\sqrt{m}$ for the mixture NbC+Cr_3C_2 respectively.

1. Introduction

Cemented carbides are important materials in the engineering field: indeed, due to their unique set of properties (combination of high hardness, moderate toughness, good corrosion resistance), those materials are widely used in applications requiring abrasion resistance, such as cutting tools, mining tools or wear-resistant materials [1–3]. In these applications, the abrasion resistance is directly linked to the hardness of the cemented carbide. An important parameter in the processing of cemented carbide is thus the control of the mechanical properties.

Mechanical properties, and in particular hardness, are inversely proportional to the carbide grain size as shown by the Hall-Petch relationship [4]. The key parameter in the processing of tungsten carbide materials is the control of the grain growth during the sintering stage. To limit the grain coarsening, grain growth inhibitors are added during the mixing of the powders. These are typically cubic carbides from the transition metal groups IV to VI [5–8]. Vanadium carbides (VC) and chromium carbides (Cr_3C_2) are widely used due to their high efficiency. In a recent study, Liu et al. [9] has ranked different grain growth inhibitors regarding their performance towards mean grain size, hardness, toughness or transverse rupture strength. Although vanadium carbide (VC) provides the best inhibition and the highest hardness, niobium carbide (NbC) ensures medium hardness with high toughness and high transverse rupture strength. NbC is thus an efficient grain growth inhibitor for tungsten carbides.

Niobium carbide has been studied in numerous research [8,10–16]. Huang et al. [8,10] has studied the effect of NbC with the use of a non-conventional sintering technique: pulsed electric current sintering (PECS). Their conclusions show that presseless sintering (1 h at 1420 °C) is sufficient to reach full density. Solid-phase sintering, achieved by PECS, is possible but the densification is retarded compared to an inhibitor-free part. The addition of a small amount of NbC (around 5 wt % in WC-12Co) improves the combination of hardness and toughness. Zhou et al. [11] found that NbC enhances hardness but also transverse rupture strength with small additions (maximum 1 wt% in WC-10Co). The dominant fracture mode is intergranular. Xiao et al. [15] has made nanocrystalline WC-10Co with the use of VC and NbC. Both inhibitors decrease the average WC grain size and improve the mechanical properties.

However, very few studies have processed combinations of different inhibitors, including NbC. Its inhibition effect is the smallest, but the fracture toughness and transverse rupture strength are better compared to the other inhibitors. A mixture of NbC with VC and/or Cr_3C_2 could improve both inhibition effect (meaning the hardness of the part) and its

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fracture toughness. The paper proposes the study of NbC-containing inhibitor and its comparison with the conventional VC and Cr_3C_2.

2. Materials and methods

Tungsten carbide powder from Wolfram Bergbau und Hütten, Austria with an average size of 1 μm has been used (FSSS 1.03 μm, BET 1.02 m^2/g, C_{tot} 6.13 %, C_{free} 0.01 %). Cobalt powder is constituted from ring-milled pellets of the lab (99 %, average size 45 μm). Grain growth inhibitors (chromium (99.5 %, average size 45 μm), vanadium (99 %, average size 45 μm) and niobium carbides (99 %, average size 10 μm)) have been purchased from VWR. The preparation of the powders has been achieved in a two-step ball milling process [17]. First, inhibitors-doped cobalt powders were milled at 600 rpm for 10 h (effective milling time). Then, the doped Co powders were mixed with tungsten carbide powder at 300 rpm for 6 h (effective milling time). For each milling, the ball-to-powder ratio was 4:1 and ethanol was chosen as the milling medium to reduce the agglomeration of the particles. The powders have been dried in an oven at 100 °C for 12 h. According to Hayashi and analyzed by Farag et al. [6], grain growth inhibitors are effective between 0.5 and 2.5 wt%. The samples contain 10 wt% binder with around 2 wt% grain growth inhibitors. The powders were formed with a uniaxial press under 500 MPa and then sintered in a tubular vacuum ThermConcept furnace at two different temperatures depending on the inhibitor (1400 and 1450 °C) for 1 h. The difference in sintering temperature is chosen to reach a sufficiently high density to compare mechanical properties with a minimized effect of the densification. As some authors indeed suggested that VC requires higher sintering temperature to reach high density [6,18–21], grades containing VC have been sintered at 1450 °C. A summary of the grain growth inhibitors used in the samples is listed in Table 1.

Physical properties have been measured in terms of density, porosity, microstructure, phases and grain size distributions. Microstructures and porosity are measured with a LEICA optical microscope. Porosity has been measured by treatment of the black and white image before etching of the samples coupled with ASTM B276 standard. Density has been evaluated by Archimedes' principle. X-ray diffraction (XRD) is used to characterize phases (Malvern Panalytical Empyrean device, θ-θ configuration, copper anti-cathode $\lambda = 1.54$ Å). Scanning electron microscope (SEM-HITACHI SU8020) was used to characterize microstructure and grain size distributions. Mechanical properties have been characterized in terms of hardness (EMCO device) under 30 kgf and fracture toughness (Palmqvist method). An average of ten measurements has been made for the two latter properties.

3. Results and discussion

Table 2 shows the porosity of the samples after polishing and before etching for the two sintering temperatures. The sample containing NbC as grain growth inhibitor exhibits a lower porosity than the reference. The sample containing VC as grain growth inhibitor has a low porosity but was sintered at higher temperature. The Cr_3C_2 and mixed inhibitors have porosity contents similar or higher to the reference. Those results are in good agreement with the traditional measures of densities by Archimedes' principle. Fig. 1 depicts the porosity distributions of the samples. Reference shows many large pores, between 25 and 100 μm. Parts N and V show very small porosities (A04B00C00) while the other parts have larger porosities (A08B02C00 for C and NC, and A02B04C00 for NV). Reference sample shows a porosity of A02B06C00. Fig. 2 depicts the XRD graphs of the samples after sintering. Three phases are observed: tungsten carbide (WC), cubic cobalt (fcc-Co) and eta-phase (Co_3W_3C). The amount of the latter is very small.

Table 1
Amount of grain growth inhibitors added in the cobalt binder.

Sample label		NbC (wt %)	Cr_3C_2 (wt %)	VC (wt %)	Sintering temperature (°C)
R	(Reference)	0	0	0	1400
N	(NbC)	2	0	0	1400
C	(Cr_3C_2)	0	2	0	1400
V	(VC)	0	0	2	1450
NC	(NbC+Cr_3C_2)	1	1	0	1400
NV	(NbC+VC)	1	0	1	1450

Table 2
Density and porosity characterizations of sintered parts.

Sample	Density (g/cm^3)	Theoretical density (g/cm^3)	Densification (%)	Porosity (vol%)	Porosity according to B276 Standard
R	14.1	14.5	97.0	2.3 ± 0.6	A02B06C00
N	14.2	14.4	98.6	0.5 ± 0.0	A04B00C00
C	13.4	14.4	93.4	3.1 ± 0.1	A08B02C00
V	14.2	14.3	99.3	0.4 ± 0.1	A04B00C00
NC	13.6	14.2	95.6	2.4 ± 0.1	A08B02C00
NV	13.9	14.2	98.1	2.9 ± 0.1	A02B04C00

Mechanical properties (hardness and fracture toughness) are shown in Fig. 3. To compare the samples together, dashed lines have been drawn. As hardness and toughness must be optimized to reach excellent mechanical properties, those lines represent the multiplication of hardness times fracture toughness. The samples can thus be classified into three categories. niobium containing parts (N and NC samples) are located on the second line, meaning that they possess equivalent properties. Then VC and Cr_3C_2 alone are found one line below: their mechanical properties are thus lower than Nb-containing parts. Finally, the part NV is the worst in terms of mechanical properties, probably due to the large porosities observed in its microstructure. The SEM microstructures and the corresponding grain size distributions are shown in Fig. 4. Without grain growth inhibitor, the average WC grain is the largest, around 720 nm. It implies a good fracture toughness (around 12 $MPa\sqrt{m}$) with a moderate hardness (around 1450 HV_{30}). As shown by literature, NbC has the least efficient inhibition effect. The average WC grain is around 575 nm while the other inhibitors or mixtures of inhibitors are between 500 and 530 nm. The best inhibition effect is the combination of NbC and VC with an average WC grain around 480 nm. In addition,

Fig. 3 shows comparison with literature samples sintered by conventional vacuum sintering and containing inhibitors (Cr_2C_3 and VC for Schubert et al. [22] and NbC for Farag et al. [6]). The results of Schubert et al. show that their hardness to toughness ratios are in the same order of magnitude as the parts of this paper. The part of Farag et al., containing NbC as grain growth inhibitor admits lower hardness but high fracture toughness than the parts of this work.

The combination of niobium carbide with chromium carbide leads to interesting properties. Cr_3C_2 provides an inhibition effect of the WC growth. The average WC grain since is indeed of the same order of magnitude as those of VC and Cr_3C_2 inhibitors alone. But thanks to its excellent strength properties, the reduction of fracture toughness is limited compared to NbC inhibitor. It results an excellent combination of mechanical properties with high hardness (around 1930 HV_{30}) and a moderate fracture toughness (around 9.3 $MPa\sqrt{m}$) whereas VC and Cr_3C_2 admit fracture toughness below 9 $MPa\sqrt{m}$.

4. Conclusion

Used alone as grain growth inhibitor, niobium carbide provides the third highest hardness value (around 1860 HV_{30}) and the best toughness value (around 9.8 $MPa\sqrt{m}$) of all GGI for the WC-10Co parts. The disadvantage of NbC is its high price due to the location of the mineral reserves almost exclusively in Brazil. Vanadium and chromium carbides are highly efficient but provide lower toughness after sintering.

A solution to enhance the toughness properties of WC-Co parts at

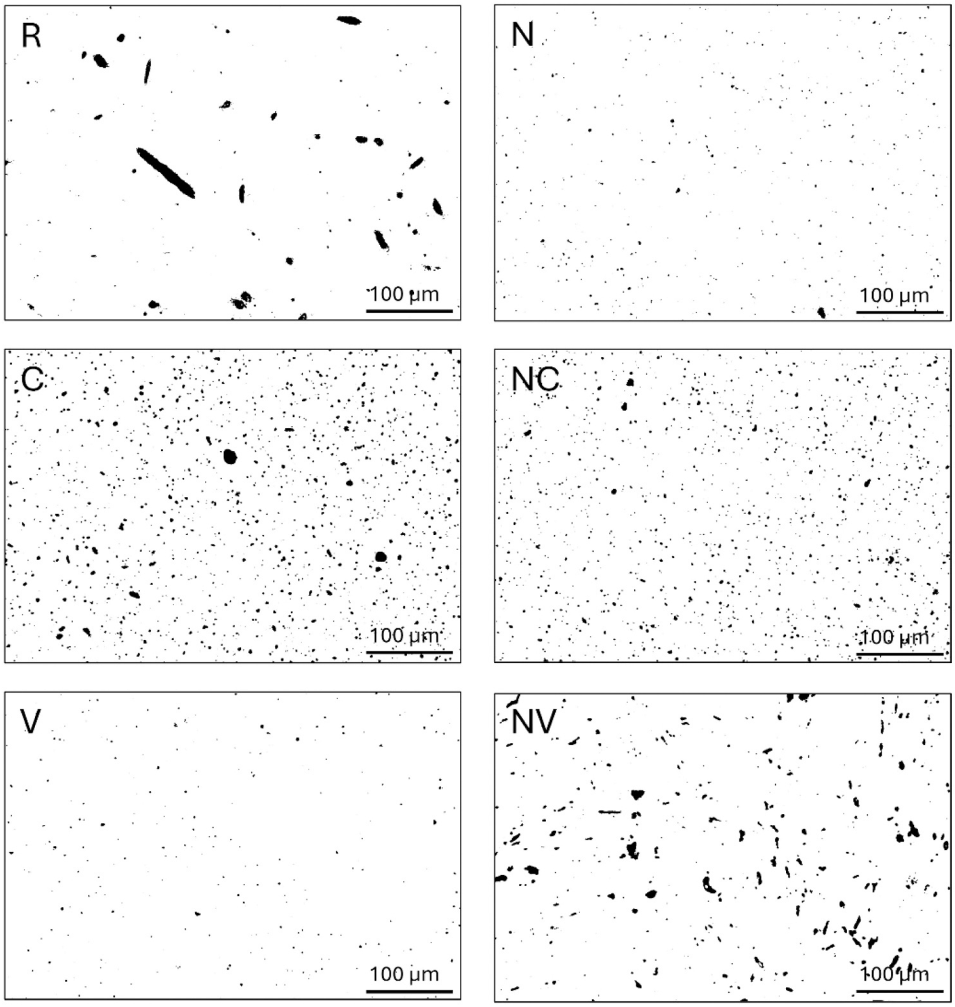

Fig. 1. Porosity measured by optical microscopy of the samples R, N, C, NC, V, NV (200x).

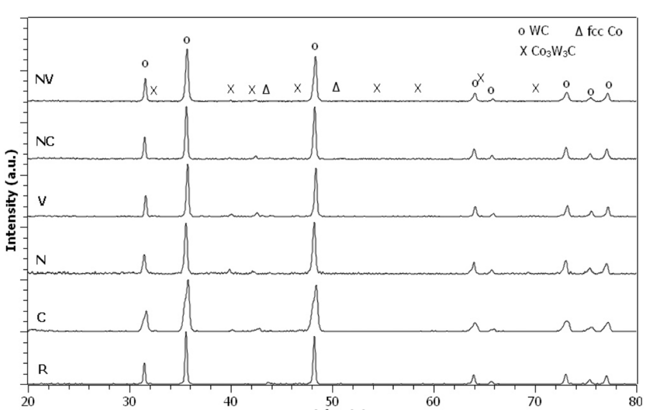

Fig. 2. X-rays diffraction of the samples R, N, C, NC, V, NV.

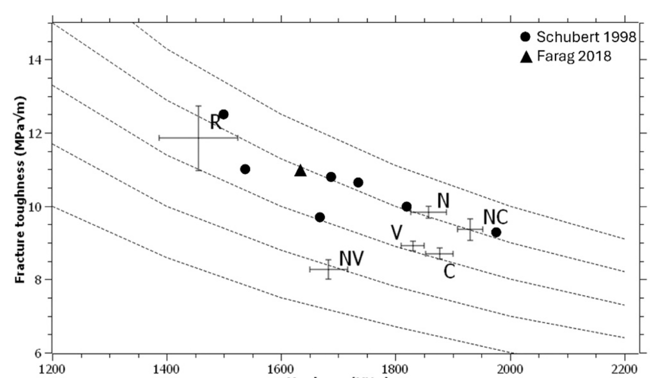

Fig. 3. Hardness as a function of the fracture toughness of the different parts [6,22].

lower cost, is to combine NbC with Cr_3C_2: hardness (around 1930 HV_{30}) and toughness (around 9.3 $MPa\sqrt{m}$) are interesting for applications demanding higher hardness such as cutting tools or wear tools not subjected to impact loads.

CRediT authorship contribution statement

Mégret Alexandre: Writing – review & editing, Writing – original draft, Methodology, Investigation, Data curation, Conceptualization. **Vitry Véronique:** Writing – review & editing, Validation, Supervision, Methodology. **Delaunois Fabienne:** Writing – review & editing, Validation, Supervision, Methodology.

Declaration of Competing Interest

The authors declare that they have no known competing financial

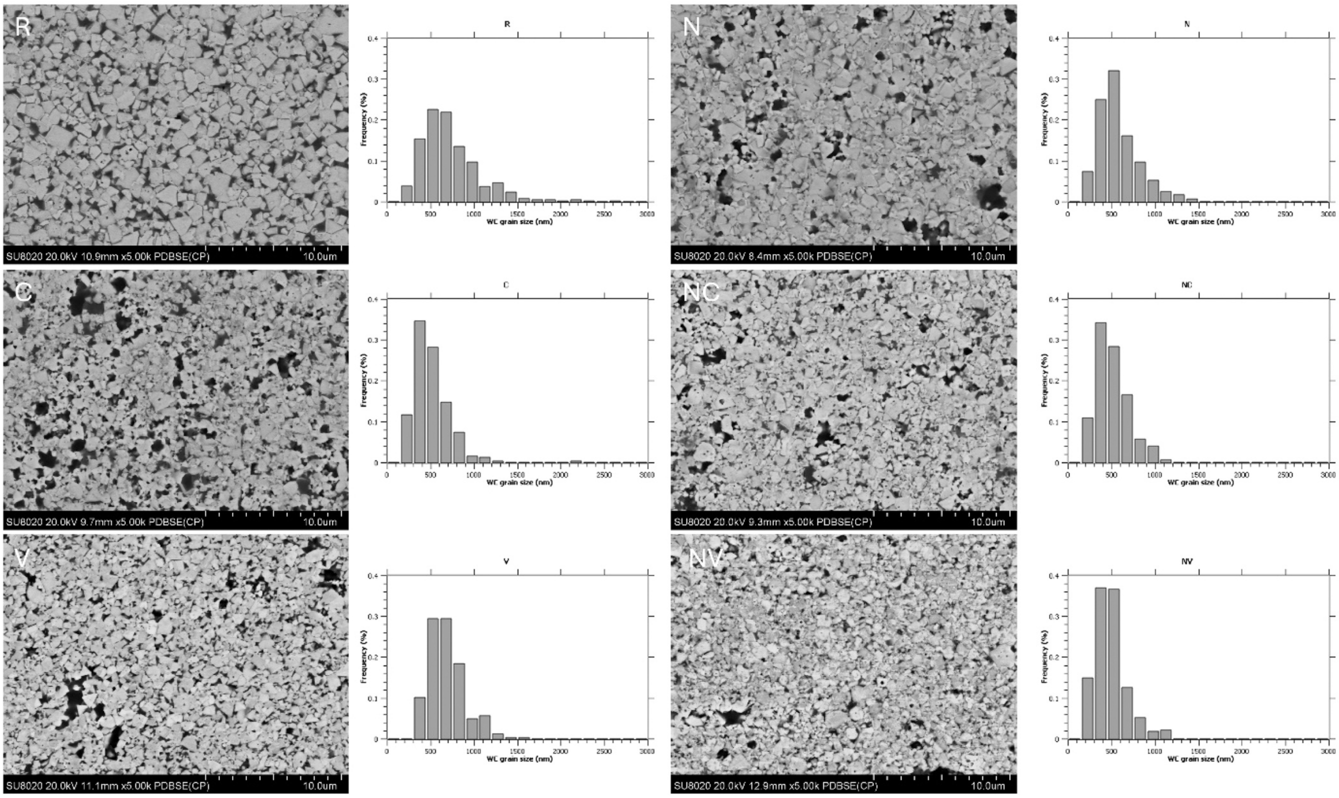

Fig. 4. SEM microstructures of the different parts showing the WC grain size and corresponding grain size distributions.

interests or personal relationships that could have appeared to influence the work reported in this paper.

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