Manuscript refereed by Gian Pietro De Gaudenzi (F.I.L.M.S. S.p.A., Italy)

Impact Of The Amount Of Recycled Cemented Carbide Powder On The Sintering Behavior Of WC-Co Parts

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Key words: Cemented carbide, Recycled powder, Vacuum sintering

Abstract

Due to the high demand and use of raw cobalt in the field of batteries for electrical cars, it seems interesting to evaluate the use of recycled tungsten-cobalt carbide powder in the hard materials field. The studied material is made from two different powders: a powder composed of raw materials (WC and Co powders mixed together) and a recycled powder (crushed powder containing 7.5 wt% cobalt). The samples are densified by vacuum sintering. The influence of the ratio of recycled powder is discussed by analyzing the density, the phases and the mechanical properties (hardness and toughness) obtained after sintering.

Introduction

Since 2011, cobalt and tungsten are designated as "*critical raw materials"* (CRMs) by the European Commission [1]. The share of the worldwide production is mainly in Democratic Republic of Congo for cobalt and China for tungsten. That represents a risk of supply shortage which will have an impact on the EU economy. Moreover, the cobalt price has shown large fluctuations during the last 50 years due to different reasons. The most important ones are the cobalt crisis in DRC, the increasing demand in China and more recently, the massive use of cobalt for batteries in electric cars [2], [3]. The cobalt is also a by-product of copper and nickel mines, thus its price depends strongly on these two materials.

Cobalt and tungsten are essential materials in the cemented carbide field: indeed, cobalt, which is the most compatible metallic binder for tungsten carbide [4], [5], brings an excellent hardness to toughness ratio at the WC-Co parts. Recycling old tungsten carbide scraps is thus a solution to limit the use of raw cobalt and tungsten powders. The "Coldstream" process is a recycling technology used to pulverize hard materials [6]. The obtained powder contains agglomerations of tungsten carbide and cobalt with an average diameter of 45 µm. The cobalt content is 7.5 wt%.

In this paper, the influence of the amount of recycled powder contained in WC-Co parts on mechanical properties and densification will be studied.

Experimental methods

Two different powders have been used to prepare the different mixtures. The recycled powder was provided by Höganäs Belgium S.A. (PA2-40). The other one was prepared with WC powder (from Wolfram Bergbau und Hütten AG Austria) and cobalt prepared in the laboratory to form a WC-8wt%Co powder.

The powders have been milled with a Fritsch Pulverisette 7 Premium line ball mill, in two tungsten carbide bowls. The 10 mm diameter balls were made of tungsten carbide to avoid any contamination of the powder. The balls to powder ratio was 4:1 for each milling. The milling conditions were the following: rotation speed of 300 rpm, and 6 h milling time. Milling was carried out in wet conditions (20 ml ethanol in each grinding bowls) to prevent agglomeration of the powder [7].

Six different mixtures have been milled with different amount of recycled powder as shown in Table 1. XRD measurements have been carried out to evaluate the crystallite size (MAUD Software - Materials Analysis Using Diffraction [8]). The green bodies have been formed with a uniaxial press under 500 MPa before conventional liquid phase sintering [9], [10], [11], [12]. The sintering was undertaken in vacuum at 1400°C during 1 h. The heating rate is 4°C/min. The thermal cycle has two plateaux: the first at 350°C is a debinding step, used to remove the wax and lubricant employed during the forming stage. The second at 900°C is used to allow diffusion of the different elements and thus to improve the homogeneity.

Table 1 - Milling experiments

Sample name	Amount of recycled powder (%)	Amount of new powder (%)
M1	100	0
M2	80	20
M3	60	40
M4	40	60
M5	20	80
M6	0	100

The density of the samples was measured by Archimedes' principle. XRD experiments have been undertaken to verify that no disturbing phases such eta-phase and graphite have appeared during the sintering. The crystallite size was also determined, and a crystallite growth was calculated from the crystallite size of the powders. Mechanical properties have been analysed (Vickers hardness under a load of 30 kgf and toughness by Palmqvist law [13]).

Results and discussions

Figure 1 shows the XRD patterns and the main peaks of the four different phases seen in the sintered samples: tungsten carbide (WC) is the main phase present in the samples. Eta-phases (Co_3W_3C and Co_6W_6C) are seen, which is a sign of decarburization of the samples [14], [15], [16]. However, the amount of these phases is low in comparison to the tungsten carbide phase. The cubic cobalt phase is also observed.

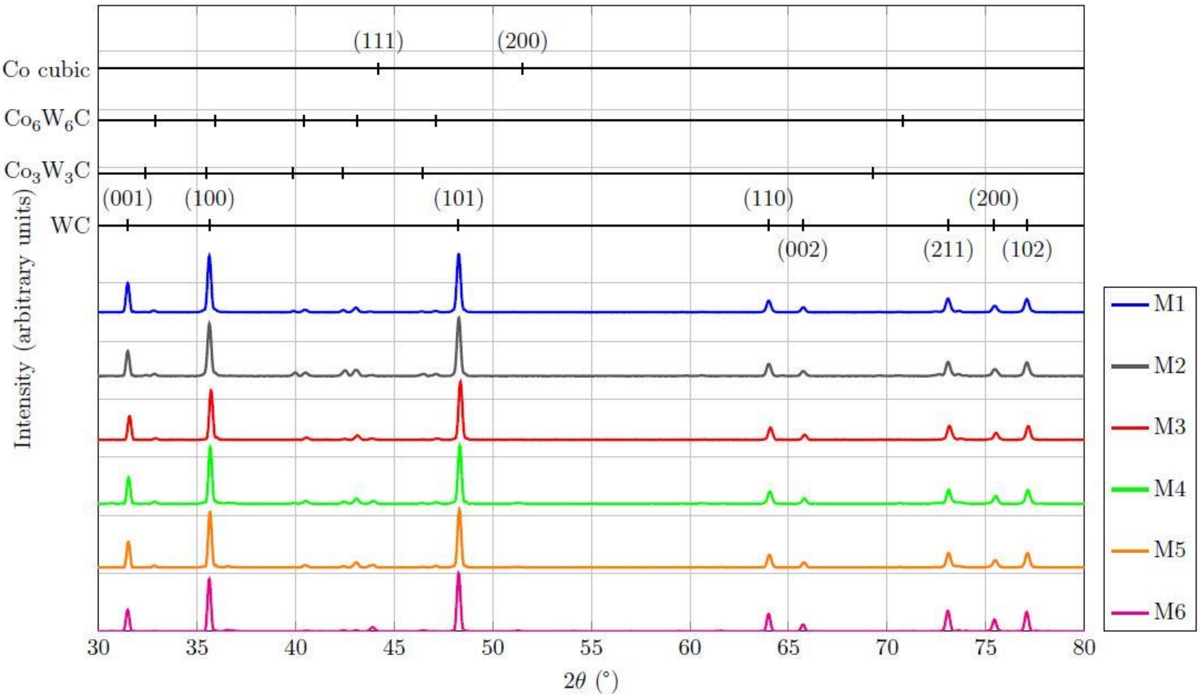

Figure 1 – XRD patterns of the sintered samples

The crystallite size was calculated by refining the parameters with MAUD software. Table 2 shows that the average crystallite size before sintering is around 27 nm except for the 100% new powder mixture (M6). The two mixtures containing more recycled powder (M1 and M2) show low average crystallite sizes after sintering (around 180 nm) while those of the other mixtures (M3 to M5) are coarser. The mixture M6 admits the larger post-sintering grain size. This could be explained by the absence of grain growth inhibitors (a small amount of Cr_3C_2 is contained in the recycled powder).
Although mixture M6 has the larger final crystallite size, it does not have the highest crystallite growth as shown in Table 2. The crystallite growth increases with the amount of new powder (M1 to M5).

Table 2 – Crystallite size (before and after sintering), crystallite growth and density of the samples

Sample	Before sintering [nm]	After sintering [nm]	Crystallite growth [%]	Density [g/cm³]
M1 (100 wt%)	27	177	556	14.81
M2 (80 wt%)	26	179	588	14.70
M3 (60 wt%)	27	239	785	14.69
M4 (40 wt%)	27	233	763	13.37
M5 (20 wt%)	27	248	819	14.35
M6 (0 wt%)	62	466	652	14.39

The mechanical properties of the sintered samples are shown in Figure 2: from hardness and toughness measurements, three different behaviours are seen. Without any recycled powder, the sample has a low hardness but a high toughness. On the opposite, the sample with 100 wt% recycled powder possesses the highest hardness with a reasonable toughness. A small amount of recycled powder (< 40 wt%) shows an increase in hardness for a toughness close to the 100% recycled powder sample. The hardness of samples containing 20 to 80 wt% of recycled powder varies between 1800 and 1850 HV_{30} while their toughness decreases until 9 MPa√m.

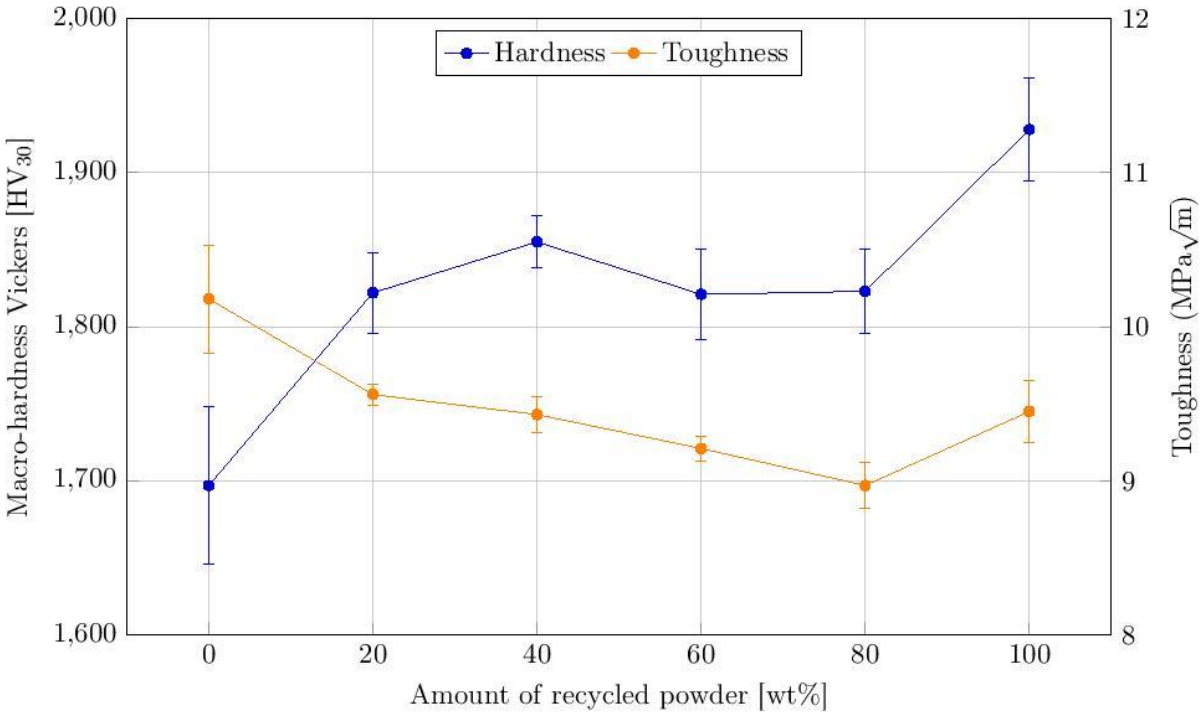

Figure 2 - Mechanical properties of the sintered samples (macro-hardness Vickers and Palmqvist toughness)

Figure 3 gives the microstructures of the samples as function of the amount of recycled powder. The figure shows that the samples with a higher amount of recycled powder contain more defects on their surface. These defects are not porosities as shown in Figure 4: the 3D image shows that only the area surrounded by the red line is a porosity. The other dark areas might be liquid phase concentration as suggested by Shi and co-workers [17] or the eta-phase.

The samples containing a higher amount of recycled powder admit also some area with no defects surrounded by high defects areas as shown in Figure 5. The cause of this effect might be a milling not long enough to ensure a good distribution of cobalt within the carbide phase or a concentration of the eta-phase.

Some samples also presented cracks on their cross section: these cracks might come from the hand-pressing step and explain the lowest density of the samples M4 to M6. Indeed, the cracks were encapsulated inside the sample and thus act as a huge close porosity. The longest crack was shown in the sample M4, and its density is the lowest.

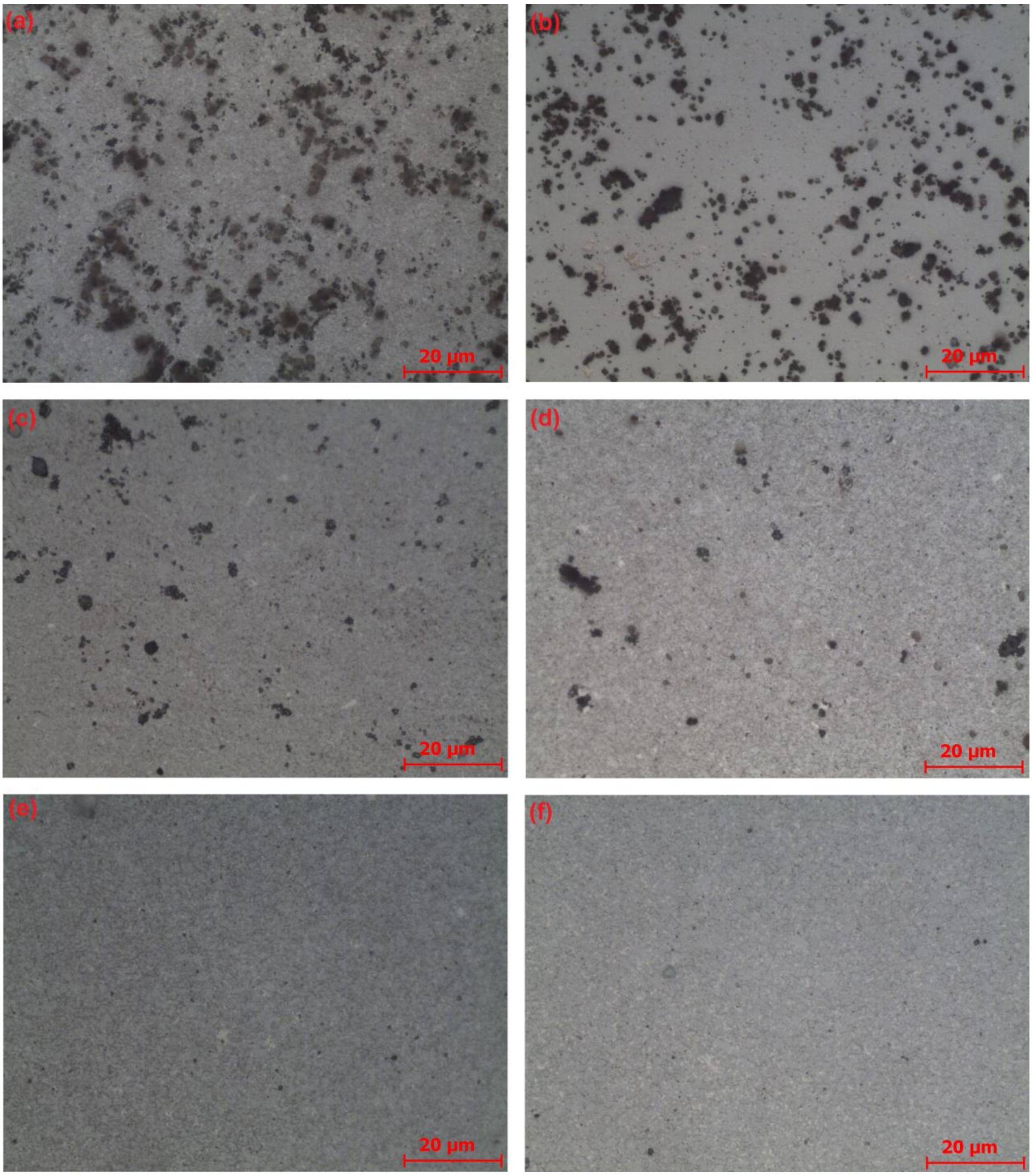

Figure 3 - Microstructures as function of the amount of recycled powder: (a) 100%, (b) 80%, (c) 60%, (d) 40%, (e) 20%, (f) 0%; etched by Murakami reagent (x 500)

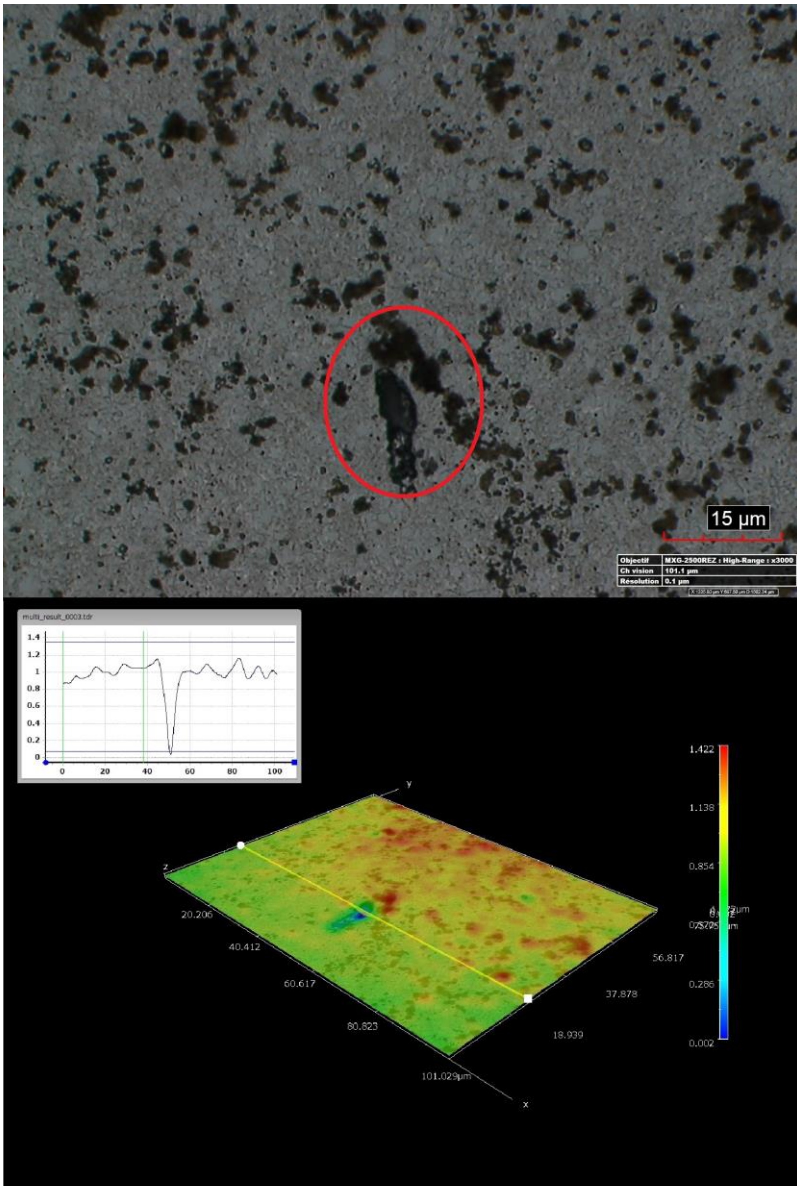

Figure 4 - Microstructure and 3D imaging of the 100 wt% recycled powder (M1)

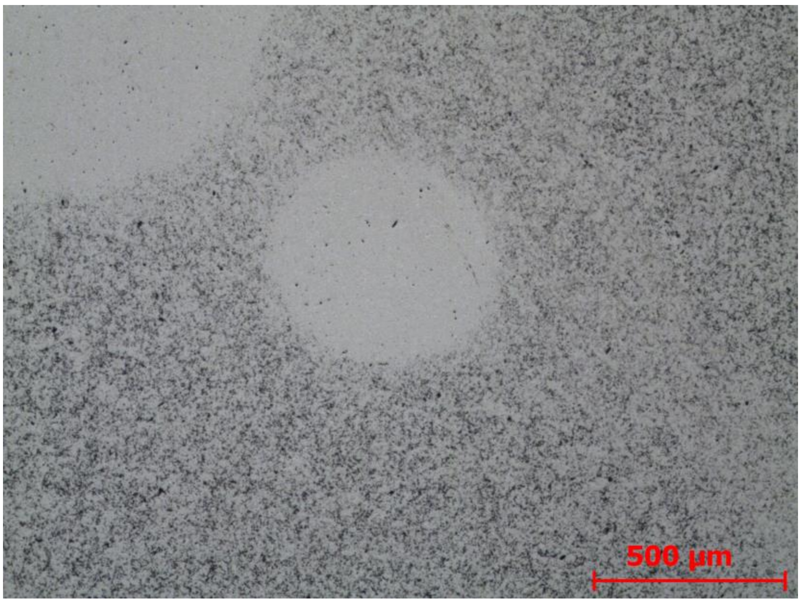

Figure 5 - Sample M1 (100 wt% recycled powder): presence of areas without defects

Conclusions and perspectives

The experiments show that the use of recycled tungsten carbide-cobalt powder modifies the mechanical properties of WC-Co parts: hardness is increased while toughness is slightly decreased. Vickers hardness values between 1800 and 1950 HV_{30} are typical for ultrafine grains while toughness values are rather higher for 7.5 wt% cobalt parts. Recycled WC-Co powder, obtained from the Coldstream process, can be definitely used in the cemented carbide field and can replace the use of raw powders.
The perspectives of this work are the elimination of the decarburization of the samples. Addition of black carbon to equilibrate the carbon balance and other sintering technologies are the main solutions. The crystallite growth of the 0 wt% recycled powder must be reduced, thus grain growth inhibitors (Cr_3C_2, VC, NbC for example) will be added to the mixture.

Acknowledgements

The authors would like to thank *Höganäs Belgium S.A.* and *Wolfram Bergbau und Hütten AG Austria* for providing the different powders.

References

[1] European Commission, “Tackling the challenges in commodity markets and on raw materials,” 2011.
[2] K. B. Shedd, E. A. Mccullough, and D. I. Bleiwas, “Global trends affecting the supply security of cobalt,” *Min. Eng.*, vol. 69, no. 12, pp. 37–42, 2017.
[3] J. P. T. Kapusta, “Cobalt Production and Markets : A Brief Overview,” *J. Miner.*, vol. 58, no. 10, pp. 33–36, 2006.
[4] C. M. Fernandes and A. M. R. Senos, “Cemented carbide phase diagrams: A review,” *Int. J. Refract. Met. Hard Mater.*, vol. 29, no. 4, pp. 405–418, 2011.
[5] G. . Upadhyaya, “Materials science of cemented carbides — an overview,” *Mater. Des.*, vol. 22, no. 6, pp. 483–489, 2001.
[6] E. Lassner and W. D. Schubert, *Tungsten: Properties, Chemistry, Technology of the Element, Alloys, and Chemical Compounds*. New York, 1999.
[7] V. I. Stanciu, V. Vitry, and F. Delaunois, “Cobalt-inhibitor mixtures for cemented carbides,” in *19th Plansee Seminar*, 2017, pp. 1–12.
[8] L. Lutterotti, S. Matthies, and H. R. Wenk, “MAUD: a friendly Java program for Material Analysis Unsing Diffraction,” *Commision on powder diffraction*, pp. 14–15, 1999.
[9] L. E. Mccandllsh, B. H. Kear, and B. K. Kim, “Processing and Properties of Nanostructured WC-Co,” *Nanostructured Mater.*, vol. 1, pp. 119–124, 1992.
[10] Z. Z. Fang, X. Wang, T. Ryu, K. S. Hwang, and H. Y. Sohn, “Synthesis, sintering, and mechanical properties of nanocrystalline cemented tungsten carbide - A review,” *Int. J. Refract. Met. Hard Mater.*, vol. 27, no. 2, pp. 288–299, 2009.
[11] H.-O. Andren, “Microstructures of cemented carbides,” *Mater. Des.*, vol. 22, pp. 491–498, 2001.
[12] J. García, V. C. Ciprés, A. Blomqvist, and B. Kaplan, “Cemented carbide microstructures : a review,” *Int. J. Refract. Met. Hard Mater.*, vol. 80, pp. 40–68, 2019.
[13] D. K. Shetty, I. G. Wright, P. N. Nincer, and A. H. Clauer, “Indentation fracture of WC-Co cermets,” *J. Mater. Sci.*, vol. 20, pp. 1873–1882, 1985.
[14] A. Formisano, F. C. Minutolo, A. Caraviello, L. Carrino, M. Durante, and A. Langella, “Influence of Eta-Phase on Wear Behavior of WC-Co Carbides,” *Adv. Tribol.*, vol. 2016, pp. 1–6, 2016.
[15] L. Åkesson, “An Experimental and Thermodynamic Study of the Co-W-C System in the Temperature Range 1470–1700 K,” in *Science of Hard Materials*, 1983, pp. 71–82.
[16] O. Eso, Z. Z. Fang, and A. Griffo, “Kinetics of cobalt gradient formation during the liquid phase sintering of functionally graded WC – Co,” *Int. J. Refract. Met. Hard Mater.*, vol. 25, no. 4, pp. 286–292, 2007.
[17] K. Shi, K. Dong, and X. Zan, “Effect of Mo 2 C Addition on Properties of Non-bond Cemented Carbide,” in *Euro PM2018 Congress & Exhibition*, 2018, pp. 1–7.