DETERMINATION OF MICROSTRUCTURAL CHARACTERISTICS OF NANOSTRUCTURED CEMENTED CARBIDES

Danko Ćorić[1], **Tomislav Rodinger**[1], **Matija Sakoman**[1], **Mateja Šnajdar Musa**[2]

[1] Department of Materials, Faculty of Mechanical Engineering and Naval Architecture, University of Zagreb, Ivana Lučića 5, 10000 Zagreb, Croatia
[2] Department of Polytechnics, University of Rijeka, Sveučilišna avenija 4, 51000 Rijeka, Croatia

Original scientific paper / Izvorni znanstveni rad

Abstract

In recent times, the development of cemented carbides is based on the application of ultrafine and nano grain size powder particles. Sintering such powders significantly improves the properties of the final product and enables the use of tools at higher cutting speeds with a longer service life. Due to the high production cost of producing nanostructured cemented carbide tools and the complex sintering process in strictly controlled laboratory conditions, such tools are not yet comercially available. In this paper, sintering procedures for nanostuctured cemented carbide tools with 5, 10 and 15 wt. % Co were carried out. The characteristics of the initial powder mixturtes and the pre-sintering and sintering procedures are described. Nano-sized carbide grain formation was confirmed by field emission scanning electron microscopy (FESEM). By measuring the magnetic saturation it was confirmed that the samples don't contain unwanted microstructural defectes such as η-phase and unbound carbon and by measuring the coercitive forces it was also confirmed that the WC grains remained in the nano-sized area.

Keywords: *nanostructured cemented carbides; sinter-HIP, grain size*

Corresponding author: Tomislav Rodinger, tomislav.rodinger@fsb.hr

1. INTRODUCTION

Cemented carbides are metal composites obtained by a powder metallurgy process. Their application is continuously growing due to the increasingly complex requirements placed on cutting tools and favorable properties of cemented carbides such as high wear resistance, high hardness and flexural and compressive strength, high rigidity, thermal resistance, high corrosion resistance, etc. These properties are due to the structural constituents: hard and brittle tungsten carbide (WC), and softer and tougher cobalt matrix. In recent years, the development of cemented carbides is based on the application of ultrafine powders which achieve a significant improvement in properties and allows the use of tools at higher cutting speeds with a longer service life. Nano-sized powders simultaneously provide high hardness and high tool toughness. Therefore, the production of cemented carbide cutting tools is increasingly turning to nanoparticle powders and advanced consolidation processes. The tool is primarily required to withstand high temperature oxidation, dimensional stability, low coefficient of friction [1] and high strength and hardness [2] with high fracture toughness and high resistance to crack propagation [3]. The mentioned advantages of nanostructured cemented carbides can be used only if the carbide grain remains in the nano range even after consolidation [4]. Grain growth, which is unavoidable in the sintering process, can be mitigated by adding grain growth inhibitors such as vanadium, chromium, tantalum and niobium carbides [5] and by optimizing sintering time and temperature [6]. Previous researches have confirmed that cobalt particles do not have to be nano-sized because their primary function involves filling pores between carbides and allowing sintering at lower temperatures and shorter times.

Some of the leading powder metallurgy processes that achieve theoretical densities of cemented carbide products are the sinter-HIP process [7] and plasma sintering [8], but today they are still less present for commercial purposes and are mainly used in scientific research.

2. MATERIALS AND METHODS

For the purpose of conducting the planned experiments, the following starting powders were selected: nano powder of tungsten carbide (WC) (manufacturer: HC Starck, Germany), cobalt powder (Co) (manufacturer: Umicore, Canada) and grain growth inhibitors vanadium and chromium carbide (VC, Cr_3C_2). The characteristics of the selected powders are shown in the Table 1.

Table 1. Characteristics of starting powders

Powder label	Grain size, µm	Specific surface area, m^2/g
WC DN 4-0	0.095	3.92
Co	0.640	2.96

A mixture of 10 wt. % Co with the addition of grain growth inhibitors: 0.5 wt. % VC and 0.75 wt. % Cr_2C_3, and the rest WC, was prepared.

The chemical composition of the starting WC DN 4-0 powder taken from the manufacturer's specification, including the proportions of unbound ($C_{unbound}$), bound (C_{bound}) and total carbon (C_{total}) is presented in Table 2.

Table 2. Chemical analysis of starting WC DN 4-0 powder

Element	Unit	Share	Element	Unit	Share
C_{total}	%	6.24	Cr	ppm	-
$C_{unbound}$	%	0.2	Fe	ppm	53
C_{bound}	%	6.04	Na	ppm	<1
O	%	0.37	Ni	ppm	4
Al	ppm	<3	Si	ppm	14
Ca	ppm	<3	S	ppm	13
Co	ppm	5	W	%	the rest

Consolidation of nanostructured cemented carbides was carried out at the Fraunhoffer Institute IKTS in Dresden, Germany. The powder metallurgy process began by mixing and milling the selected powders in a horizontal ball mill with the primary goal of homogenizing the mixture. For the test mixture, the carbon content in the sintering atmosphere was adjusted to 0.25 % C. A paraffinic plasticizer was added to the powder mixture for easier shaping. This was followed by granulation of the powder mixture by sieving and compaction by the uniaxial pressing in a mold. The last phase was pre-sintering to remove the binder and sintering which was carried out in a vacuum at 1350 °C with hot isostatic pressing in one cycle at pressure of 100 bar (sinter-HIP process, Figure 1). Sintering was performed in a furnace FCT Anlagenbau GmbH, type: FP W 280/600-3-2200-100-PS with the use of the inert gas argon to prevent the influence of the external environment.

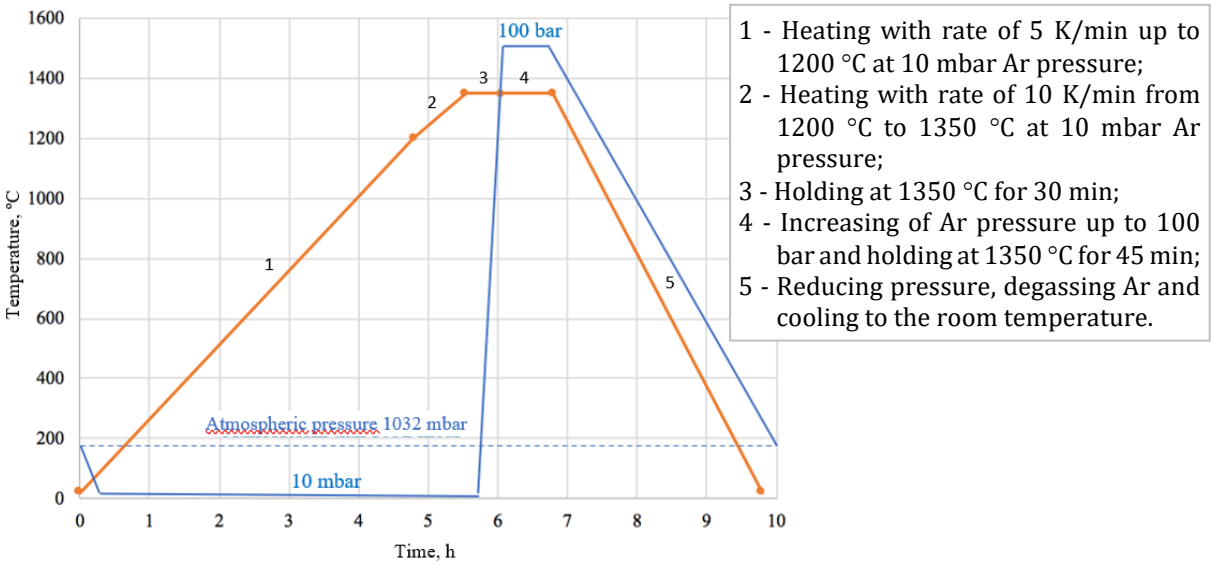


Figure 1. Scheme of sinter-HIP process [9]

Sintered sample with dimensions of 12.7 mm x 12.7 mm and thickness of 4.7 mm is shown in Figure 2.

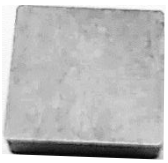


Figure 2. Sintered sample of cemented carbide

The density of the sample after consolidation, which indirectly provides information on the degree of porosity, is the basis for assessment of the sintering quality. Density values were determined by the comparative method by weighing the sample in air and in liquid in accordance with the standard HRN EN ISO 3369:2011 [10]. These measurements were performed at a temperature of 23.6 °C on the Metler Toledo device.

To examine the presence of η-phase and unbound carbon, magnetic saturation (M_S) measurements were carried out. Low M_S values indicate the formation of unwanted W_6Co_6C or W_3Co_3C (η-phase) metallic carbides due to the dissolution of W in Co matrix, while high values are characterized by the appearance of graphite induced by excessive C content in the binder. These tests were performed on the sigmameter, manufactured by Setaram Instrumentation, France, type: D6025.

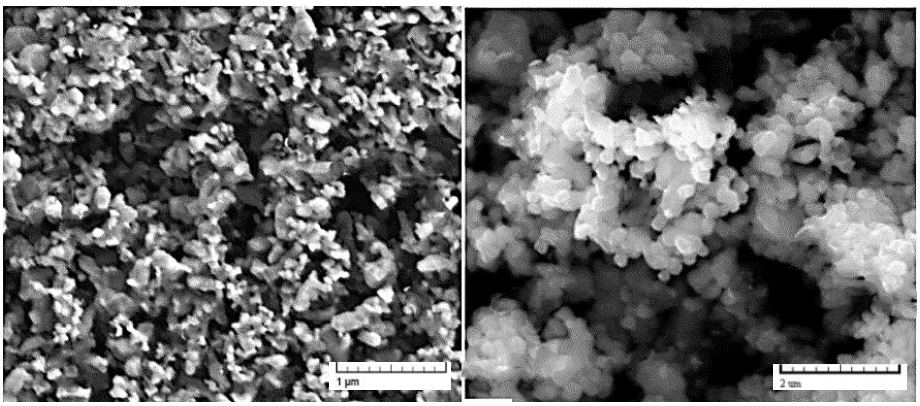
The carbide grain size was determined by measuring the coercivity (H_C) on a koerzimat 1.096, manufactured by Förster, Germany. The H_C value is significantly affected by the volume of Co binder and these two quantities are inversely proportional. Thus, the presence of larger WC grains results in lower values of coercivity due to the appearance of larger areas of cobalt binder.

Polished surface was analyzed by the light microscopy to determine pores, cracks and unbound carbon. For this purpose, grinding, polishing and subsequent ion polishing were performed and the surface was analyzed at 200x and 500x magnification with an Olympus GX51F-5M microscope (Olympus Europa SE & Co., Germany). The degree of porosity and unbound carbon was determined by comparing the polished surface with the photomicrographs in ISO 4505:2011 [11].

The homogeneity of the microstructure was analyzed by the electron microscopy on a field emission scanning electron microscope (FESEM, Ultra 55, Carl Zeiss AG, Germany) at 5000x and 20000x magnifications. Carbide grain size was determined by the Average Grain Intercept (AGI) method using the *Image J* software.

3. RESULTS AND DISCUSSION

Figure 3 shows the WC and Co starting powders. WC powder particles are below 0.1 μm which corresponds to the manufacturer's specifications (0.095 μm). The grains are rounded in shape, as a result of the atomization process applied and form agglomerates that were impossible to avoid with the available sieving techniques. Slightly larger Co particles have also spherical shape and a few tenths of a μm in diameter. According to the manufacturer's certificate, the size of Co powder is 0.64 μm.



a) b)

Figure 3. FESEM micrographs: a) WC powder; b) Co powder

The porosity of the sintered sample was determined by a comparative method, i.e. by comparing the theoretical and measured density.

Table 3. Starting powder density

Constituent	WC	Co	VC	Cr_2C_3
Density, g/cm³	15.65	8.95	5.77	6.43

According to the content of different powders in the mixture and their densities, presented in Table 3, the theoretical density ρ_{th} follows from the equation:

$$\rho_{th} = \frac{1}{\sum \frac{x_i}{\rho_i}} \quad (1)$$

where x_i is the fraction of the i-th component ($\sum x_i = 1$), and ρ_i is the density of the i-th component, g/cm³. The density values of the sintered sample indicating the degree of porosity are presented in Table 4.

Table 4. Sintered sample densities

Theoretical density, g/cm³	Measured density, g/cm³	Relative density, %	Standard deviation, g/cm³
14.30	14.318	100.124	0.010

Since the real density is higher than the theoretical one, this indicates the formation of a non-porous structure. The value of relative density slightly above 100 % can be attributed to the possible occurrence of η-carbides (W_6Co_6C or W_3Co_3C) which have a somewhat higher density than the two-phase constituents of the WC-Co system [12]. Also, within the two-phase region of the WC-Co phase diagram the density values can vary which is also one of the possible reasons for higher density.

By measuring the magnetic saturation, M_S, the presence of η-phase and unbound carbon was examined. From three repeated measurements performed in accordance with ISO 3326 [13], a mean value of 14.47 μTm^3/kg was calculated, which is shown in Figure 4.

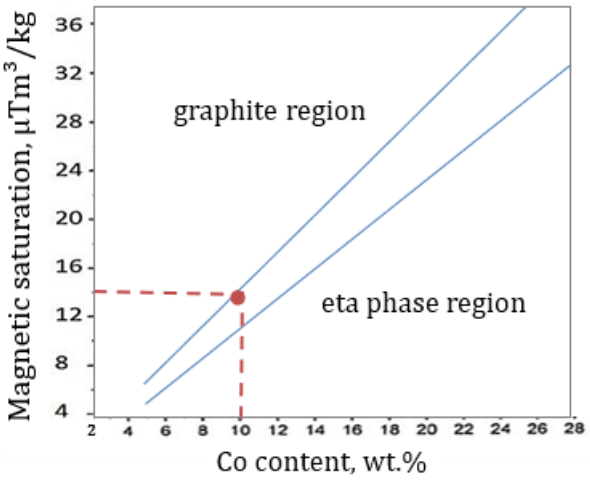


Figure 4. Influence of magnetic saturation and Co content on graphite and η-phase occurrence [9]

From the Figure 4 it is obvious that the proper adjustment of the sintering atmosphere did not create microstructural defects such as η-phase and unbound carbon in the form of graphite.

By measuring the coercivity, H_C, the approximate size of the WC grain after sintering was determined. The mean value of the three measurements of the coercive force in the amount of 41.73 kA/m indicates the presence of nano-sized carbide grains (<0.2 nm) [9], which can be seen from the diagram in Figure 5.

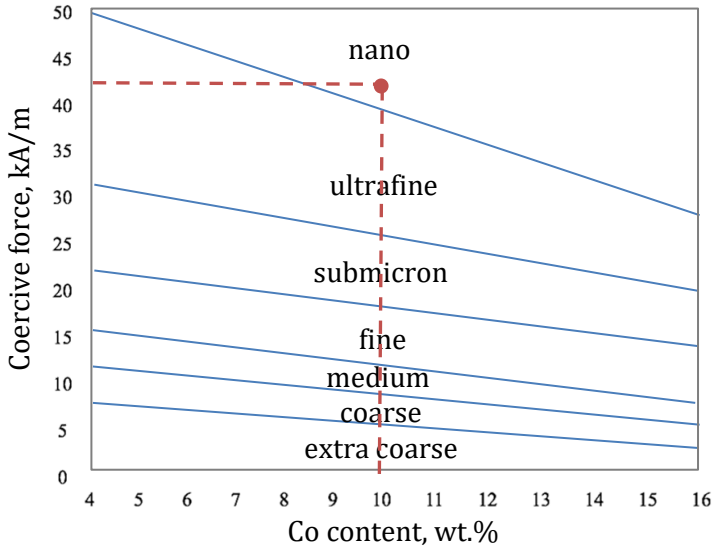


Figure 5. Influence of coercive force and Co content on WC grain size [9]

Polished surface of the cemented carbide sample is shown in Figure 6.

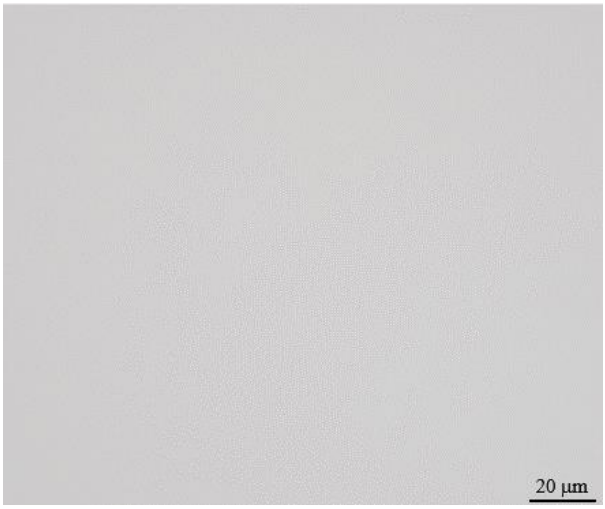


Figure 6. Polished surface of sintered sample

Analysis of the polished surface and its comparison with photomicrographs revealed the presence of porosity type A, which can be classified as A00, which indicates the absence of any, even the smallest pores, and it is also evident that there are no traces of unbound carbon (C00).

For the purpose of microstructural analysis, the surface was further etched in Murakami solution of the following content: $K_3Fe(CN)6$, 10 g NaOH or KOH and 100 ml water. The etching time was 5 seconds. Figure 7 shows the microstructure taken at 5000x magnification.

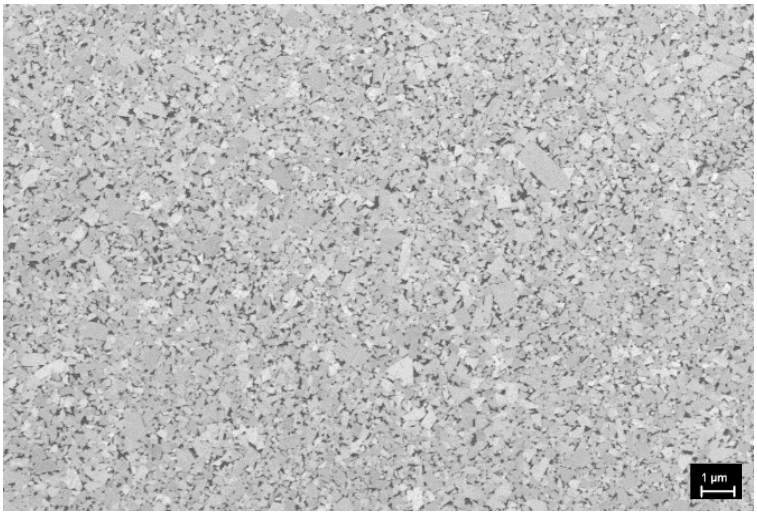


Figure 7. FESEM micrograph of sintered sample (5000x magnification)

The micrograph on Figure 7 indicates a homogeneous microstructure without the appearance of microstructural irregularities, such as carbide phase grouping and abnormal grain growth. The microstructure contains very fine WC grains uniformly dispersed in the Co matrix. The carbide grain size was determined by the AGI method in accordance with HRN EN ISO 4499-2:2011 [14]. For the purposes of measurement, a

FESEM micrograph of higher magnification was used, Figure 8. The image of the microstructure with 10 parallel lines was processed using the *Image J* software and the mean diameter of the carbide grain, d_{WC}, was determined according to the equation:

$$d_{WC} = \sum_{i=1}^{n_z} \frac{l_i}{n_z}, \text{nm} \quad (2)$$

where l_i is the total length of the individual cross-sections (nm), and n_z is the number of intersected WC grains (Table 5).

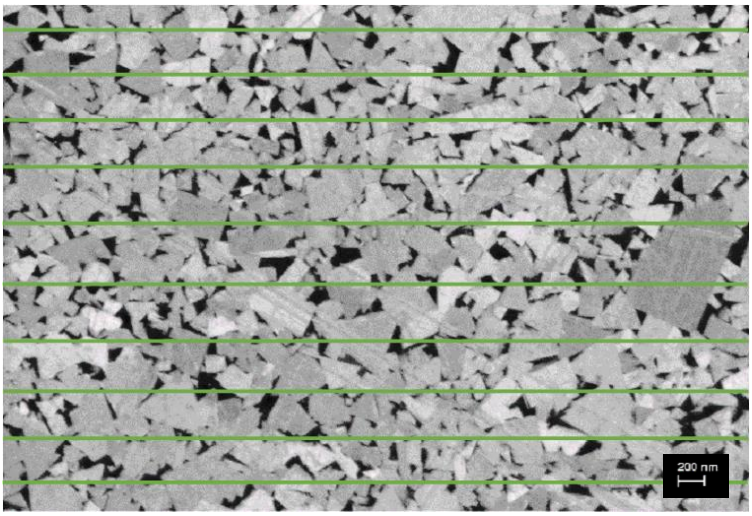


Figure 8. FESEM micrograph of sintered sample (magnification 20000x)

Table 5. Results of measuring of WC grains size

Line number	Total length of individual sections, nm	Number of intersected WC grains
1	5556.25	28
2		29
3		29
4		28
5		28
6		28
7		29
8		28
9		27
10		28
Mean value of intersected WC grains		28.2
Standard deviation		0.63
WC grain size, nm		197.03

4. CONCLUSION

Based on the obtained results, the following can be concluded:

By consolidating of nano-sized WC powder (95 nm), Co powder and grain growth inhibitors as vanadium and chromium carbides (VC, Cr_2C_3) using the sinter-HIP process, theoretical densities without porosity can be achieved.

By measuring the magnetic properties, the value of absolute magnetic saturation of 14.47 $\mu Tm^3/kg$ and relative magnetic saturation of 78.73 % was determined, which indicates any absence of defects in the form of unwanted metal carbides (η-phase) and unbound carbon.

Analysis of coercive properties performed for the purpose of indirect verification of grain size after sintering resulted in a mean value of 41.73 kA/m. Although these results cannot be taken with 100 % certainty, they indicate the WC grain size in the nano range as a result of proper content of grain growth inhibitors and the applied parameters of the sintering process.

Metallographic analysis of the polished surface of the cemented carbide sample confirmed the results of density measurements and the absence of both porosity and unbound carbon, as indicated by the results of magnetic properties.

Quantitative analysis of the microstructure after etching confirmed the absence of structural defects such as abnormal grain growth or WC grain grouping. The microstructure of the sintered sample contains very fine WC carbides evenly distributed in the Co matrix. The mean size of carbide grain determined by the AGI method was 197.03 nm and it is evident that the sintering did not affect on the particles size and the grains remained in the nano range.

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