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Conventional sintering of WC with nano-sized Co binder: Characterization and mechanical behavior

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ABSTRACT

In this study, WC particles of 1–3 μm were blended with two different sizes of Co particles and sintered conventionally at two different temperatures. Compaction of initial powders was carried out using a relatively new dynamic compaction method called Magnetic Pulsed compaction (MPC). The maximum Vickers hardness for the samples found was around 1353 HV (13.27 GPa), while the maximum fracture toughness was observed at 4.6 MPa · $m^{1/2}$. The marked changes in density, hardness, fracture toughness and crack behavior observed in the samples indicate strong correlations among particle size, sintering process and mechanical properties of cemented carbides. In addition, the nature of crack initiation and propagation, which is indicative of the trend in fracture toughness of materials, was observed and analyzed.

1. Introduction

Cemented carbides have been used in industrial cutting and drilling applications for over a century. Out of all carbides, Tungsten Carbide (WC), with finely distributed Cobalt (Co) or other softer materials acting as binders, have been the most successful and used constituents, as they are known to display an excellent combination of hardness and wear resistance, toughness and stiffness [1–3]. A number of early studies on such carbides have focused on issues related to finding the right composition, consolidation temperature and ways to improve mechanical properties of the final products that were expected to be commercially used [4]. In recent years, however, the focus has shifted towards the study of approaching new ways and methods of powder processing altogether in an attempt to discover convenient and effective ways to manufacture these carbides. It has ranged from introducing different types of powders to incorporating multiple stages of processing to achieve better performance [5,6].

The fabrication of these carbides is considered to be quite difficult as opposed to many other composites that are aimed towards similar applications. While some of the modern techniques use simultaneous compaction and heating as the method for carbide bits production, the conventional route still uses them as separate processes [7]. Although conventional processing takes a longer time, it is still thought of as one of the stable processing routes for the manufacture of carbide products with economic incentives. Several attempts have been made to control the grain growth of these materials during the process by either incorporating commercial grain growth inhibitors, different sizes of initial powders—from coarse to fine, (micron to nanometer range), or just by making adjustments to the timing of the processing steps involved [8,9]. Since the binder within the composition of these carbides is primarily responsible for joining the particles at elevated temperature, attention has also been given in employing ultrafine and nanograde particles as an alternative, which can potentially help study the changes in grain growth and mechanical properties of these carbides.

Over the last few years, dynamic compaction has shown promising results for a wide range of metals and composites, aimed at reducing compaction time to even fractions of a second [5,10,11]. Magnetic pulse compaction (MPC) is one of the short-duration, high-impact compaction processes that are capable of manufacturing improved cemented carbide products in green compact form [12], with reasonably high initial density. Since pressure is one of the major factors affecting the quality of the products, the study of such dynamic compaction process is all the more critical in understanding how it behaves for carbides.

In this study, two sets of WC–7.5 wt.% Co powder mixtures having different sizes of Co particles were pressed using magnetic pulse compaction, followed by conventional sintering. This study will particularly help in understanding the contribution of fine and nano/ultrafine Co towards mechanical properties and microstructural behavior of WC–Co, as well as the contribution of temperature variation during sintering.

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2. Experimental procedure

WC particles of irregular hexagonal shape, sized at 1–3 μm, with 0.1 (wt.%) total oxygen, 0.06 (wt.%) free carbon and 6.10–6.18 (wt.%) carbon content were mixed with both 1–3 μm and 200–300 nm sized Co particles to prepare two different types of samples. The details of the samples are given in Table 1. Cobalt (Co) powders used in this study were prepared using Pulsed Wire Evaporation (PWE) equipment, and were sized at 200–300 nm and 1–3 μm range, which was controlled though changes made in input voltage. Powders were mixed using a high-energy ball mill. The process started by first placing the powders in a stainless steel container with WC inner lining and then mixing them with 10 mm diameter Ti coated stainless steel ball bearings with a ball to powder weight ratio of 5:1. The speed of rotation was set at 500 rpm and was used for 5 min to mix the powders under dry conditions. Powders were first compacted using a magnetic pulse compaction machine. Pressure was set at 1.5 GPa for all samples, while duration was observed at 0.3 s. A single action die was used for all compaction. The green compacts were then sent to TaeguTec Ltd* for conventional sintering. The samples were sintered at two different temperatures; 1400 and 1450 °C. The heating rate, cooling rate and holding time are not disclosed for this set of experiments.

The samples were sectioned after sintering, mounted and conventionally prepared (down to 1 μm diamond paste) for metallographic analysis. For etching, a batch of Murakami reagent was prepared. Density of the WC–Co samples was measured by Archimedes method, weighing them in water and air. Hardness measurements were performed on a Vickers Micro Hardness tester, with 1 kgf load. For microstructural analysis including crack length measurements, a TESCAN MIRA LMH FE-SEM was used. Since the sintered samples were quite small in size, fracture toughness values were calculated using the following equation [13]:

$$K_{1c} = 0.016\sqrt{(E \div H)}\left(P \div c^{3/2}\right) \quad (1)$$

where E is Young's modulus [14–16], H is the hardness of the material measured using a Vickers Micro Hardness tester, P is the indentation load, and c is half of the average indentation crack length. The crack lengths are measured from the initiation points, which are along the edges of the indentation marks, till the end of the propagation.

3. Results and discussion

For hard-to-consolidate materials, it is of great importance that the composition or mixture is homogeneous in nature; which not only ensures greater chances of displaying the desired mechanical properties, but also reduces the probability of the green compacts and sintered carbides of failing through surface and/or edge cracking. Fig. 1 shows the SEM micrographs and EDS analysis of both WC–7.5 Co and WC–7.5 nano-Co. While both powders illustrate a homogeneous mixture (c and d) of WC and Co, it can also be noticed that WC–7.5 nano-Co powders are slightly more irregularly shaped than the other sample. The difference in nature in Fig. 1(b) can be attributed to the difference in size between both particles, which may have caused WC particles to collide more during the milling process, resulting them to break in an uneven manner, slightly more than what can be seen in Fig. 1(a), where both WC and Co particles are of the same initial size. In addition, the binder content within the composition is quite low, and is only present to facilitate the bonding between particles in the presence of a liquid phase, usually observed at elevated temperatures. The size of the particles in general however does not suggest that they have gone through much agglomeration within the short duration of mechanical milling, carried out at a relatively low speed. It is also understood that most mechanical mixing processes [17,18] can potentially result in the particles being slightly unevenly shaped, except where spray conversion was used [2,19].

Fig. 2 shows the XRD patterns of both samples, sintered at two different temperatures. The WC peaks are quite prominent in all samples, which confirm the concentration. Co peaks were found to be difficult to detect due to its low concentration in the samples. It is understood that the liquid phase transformation of Co at high temperature in carbides may also be one of the reasons for displaying such low intensity. Furthermore, the presence of α-Co (fcc structured phase), which is usually visible after short duration milling [3], seemed to have disappeared after high temperature sintering. The identified peaks were detected to be of hcp structure. Traces of Co peaks are usually identified at 44 (fcc α-Co and hcp ε-Co), 52 (fcc α-Co), 65, 77 (fcc α-Co and hcp ε-Co) and 92 (fcc α-Co and hcp ε-Co) 2θ angles. In addition to the XRD traces in this study, reports, including our previous work, suggest that there is not much peak broadening observed after sintering, which is indicative of similar grain or crystalline size within the microstructure [5,20].

Fig. 3 shows the changes in density (a) and hardness (b) with respect to sintering temperature and Co particle size within the composition. It can be quite clearly interpreted that both density and hardness are illustrating incremental patterns with decreasing particle size from micron to nanolevel. However when it comes to sintering temperature, there isn't such a shift noticed for the samples. It is safe to assume that slight changes in temperature do not reflect on these properties of sintered cemented carbides. In addition, the fact that both temperatures are below the melting point of the primary binding constituent of the composition can also be related to the absence of change in density and hardness profiles. It can also be said that the change in interfacial energy between solid and liquid phase is not sufficient within this temperature range to instill a difference in wettability status between the phases. In other words, the first stage of liquid phase sintering, which is a dominant step for rearrangement of particles, has not varied enough to affect the solubility behavior of the constituents of the phases; which otherwise could contribute to a change in density, and therefore, hardness, through further microstructural evolution [4]. On the other hand, when temperature is kept constant, there seems to be an increasing pattern in both density and hardness with respect to the decrease in Co particle size. While several factors can be involved here, one possible explanation includes the idea that nanoparticles tend to impart faster diffusion between grains, promptly initiate necking behavior between constituents, as opposed to how coarse or fine grained phases would behave under such sintering conditions. It is also expected the nano-Co particles occupy WC interparticle spaces and thus increase density while this is not the case for micron size Co particles. During hardness test, indentations were generated on the surface and along the cross section of the sintered samples, which resulted in the initiation and propagation of cracks along the edges of the indentations, as shown in

Table 1
Mixing and processing conditions of WC–Co powders.

Sample number	Composition	Size of WC particle	Size of Co particle	Milling time (min)	Weight of mixed powder (g)	Compaction pressure (GPa)	Sintering temperature (°C)	Con size (μm)
1	WC–7.5 Co	1–3 μm	1–3 μm	5	2.0	1.5	1400	204.7
2	WC–7.5 Co	1–3 μm	200–300 nm	5	2.0	1.5	1400	202.2
3	WC–7.5 Co	1–3 μm	1–3 μm	5	2.0	1.5	1450	203.6
4	WC–7.5 Co	1–3 μm	200–300 nm	5	2.0	1.5	1450	204.1