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Study HTHP Sintered WC/Co Hardmetal

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WC/Co is widely used as cutting tools, because has a unique combination of high strength, hardness, toughness, and moderate stiffness, especially with fine grained WC and finely distributed cobalt. WC/Co powder mixture sinters by different methods such as vacuum sintering, microwave sintering and SPS. High pressure high temperature (HPHT) sintering is a proposed method that can result in better distribution of cobalt and avoid undesirable phases by using high pressure, high temperature and very short sintering time. In this study, a powder mixture of WC- 10 wt% Co was sintered by HPHT at 1500 to 1900ºC under a pressure of 7.7 GPa for 2 minutes. Microstructural/structural analyses were performed by SEM/EDS. Hardness and compression test were also done to obtain the effect of sintering parameters. It was found that HPHT sintering method can be used to produce WC/Co hardmetal with low sintering time and high production rate. It was realized that increasing sintering temperature in HTHP sintering method results in increasing density but hardness and compression strength increase by increasing sintering temperature up to 1800 ºC and then decrease.

Keywords: *Hardmetals, High pressure high temperature, HPHT, WC*

1. Introduction

WC–Co cemented carbides are widely used as cutting, machining and rock drilling tools in due to their high hardness and strength, good fracture toughness and wear resistance over a wide range of temperatures[1]. In its simplest form the cemented carbide consists of WC as hard phase and Co as cementing binder phase due to its excellent wetting, adhesion and adequate mechanical properties, however, there are some reasons to substitute it with other metalic binder[2]. The conventional production route is through powder metallurgy, where the main steps are: ball milling mixtures of WC and Co powder in proper media; drying, pressing, debinding and liquid phase sintering in the temperature range 1400–1500 °C[3,4].

Drifting Co between parts of carbide particles has an important rule during the sintering and can affect on gradient of cobalt content and make inhomogeneous properties in produced cemented carbides. Co drifts between parts of carbide were reported in literature with respect to the possibility of fabrication of functionally graded cemented carbides[5-8].

WC grain growth is a common problem in sintering cemented carbide that can affect the mechanical properties. It were studied in various works some including carbides as grain growth inhibitors to suppress the growth[9-12]. During sintering the average carbide grain size increases by means of coarsening or Ostwald ripening, i.e. large grains grow and small grains dissolve, leading to an increase in average grain size. Abnormal grain growth may also occur, i.e. a few large grains consume all small grains, leading to an abnormally large grain size. In cemented carbides, where normal WC grain size is of the order of μm or less, abnormal grain growth can sometimes lead to grain sizes of several hundred μm. In the case of cemented carbides the diffusion distances are very short and the common faceted shape of the WC particles indicates that the difficulty in forming new atomic layers rather than long-range diffusion is the rate controlling mechanism[13].

In the present work, a WC/Co powder mixture prepared and sintered via high pressure high temperature sintering method at higher temperature than conventional sintering method. High pressure and high temperature allow decreasing sintering time to avoid WC grain growth, increasing production rate and improving some properties such as achieving to 100% relative density.

2. Experimental procedure

2.1. Preparation and sintering of powders

Commercial Co powder and WC powders were used as the starting materials. WC powder had an average particle size of 12.8 μm and Co powder had an average particle size of 11.45 μm. Figure 1 shows corresponding morphologies of powders. Co and WC powders were weighted with the

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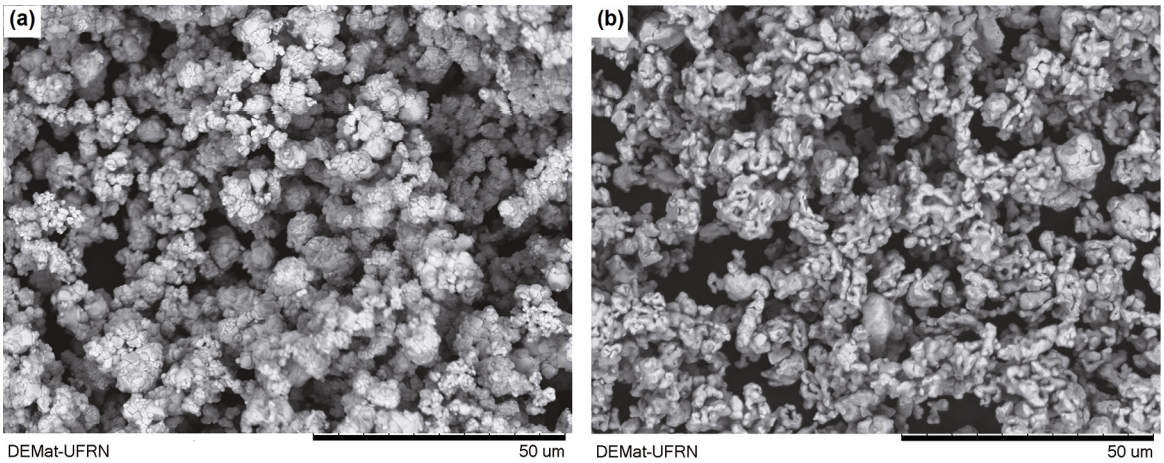

Figure 1: SEM morphologies of as-received powders. (a) WC and (b) Co.

nominal composition of WC–10Co powder, and mixed via ball milling in cychlohexane media. Milling speed and time were 200 rpm and 2 hours respectively. The ball to powder ratio was 10 to 1 and hardmetal balls and vessel were used to prepare the powders. Finally, WC–10Co ball milled powder mixture was obtained after drying under vacuum. Figure 2 shows SEM photograph of mixed powder.

Prepared powder then capsulated in a cylindrical graphite capsule with 5 mm in diameter and closed with graphite cap. Sintering was done using an industrial high pressure high temperature (HPHT) machine. To study the effect of sintering temperature and morphology evaluation, compacted capsule were subjected to 5 different temperatures of 1500, 1600, 1700, 1800 and 1900 °C. Sintering machine parameters lined up to apply 7.7 GPa pressure for 2 minutes and heating was applied when the pressure reached to 7.7 GPa.

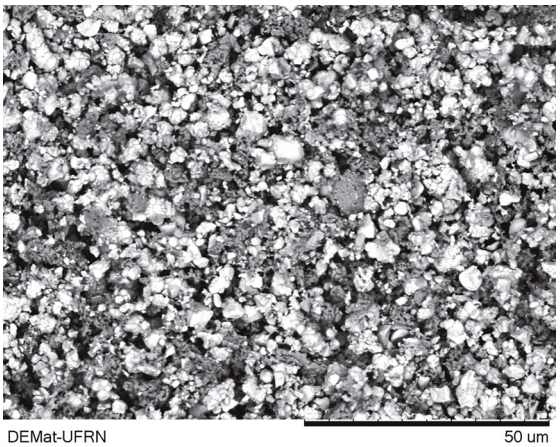

Figure 2: SEM morphologies of WC–10 Co powders.

2.2. Material characterizations

The morphologies of WC, Co and WC – 10Co powders and sintered samples were discerned by a scanning electron microscope (Hitachi Tm3000 desktop SEM). The samples were ultrasonically cleaned for 30 minutes and then were sectioned, ground, and polished. Microstructures were observed in the mode of backscattered electron. The densities of sintered composites were measured by the Archimedes method according to ASTM B962. Hardness was measured with a 10 kgf load according to ISO 3878. Compression test was also done according to ISO 4506 in order to find the yield strength and compression strength.

3. Results and Discussion

Figure 3 shows the micrograph of sintered samples in different temperature. As it was found in SEM images, the samples sintered at 1500 ºC had some porosities (Figure 3-a). Other samples were almost free of porosity however some small porosity also found in the samples sintered at 1600 ºC (Figure 3-b). It seems that short sintering time at lower temperature even at high pressure is not enough to rearrangement the powder particle and diminishes the free space between particles. The binder (Co) acts as a viscous mass spreading over WC surfaces giving rise to Laplace forces and rearrangement of the carbide particles into clusters. The first stage of WC–Co sintering is limited by the rate of binder spreading, which in turn is governed by intrinsic properties of the binder and the microscopic character of the carbide–binder composite [14]. At low temperature, spreading of liquid Co between WC particles is slower in compared with higher temperature because of lower viscosity. In the diffusion point of view, at lower temperature the diffusion rate is lower than higher temperature, then, the rearrangement and solving the porosity during sintering is easier at higher temperature especially at very short sintering time. For these two reasons the higher porosity in samples sintered at lower temperature can be explained.

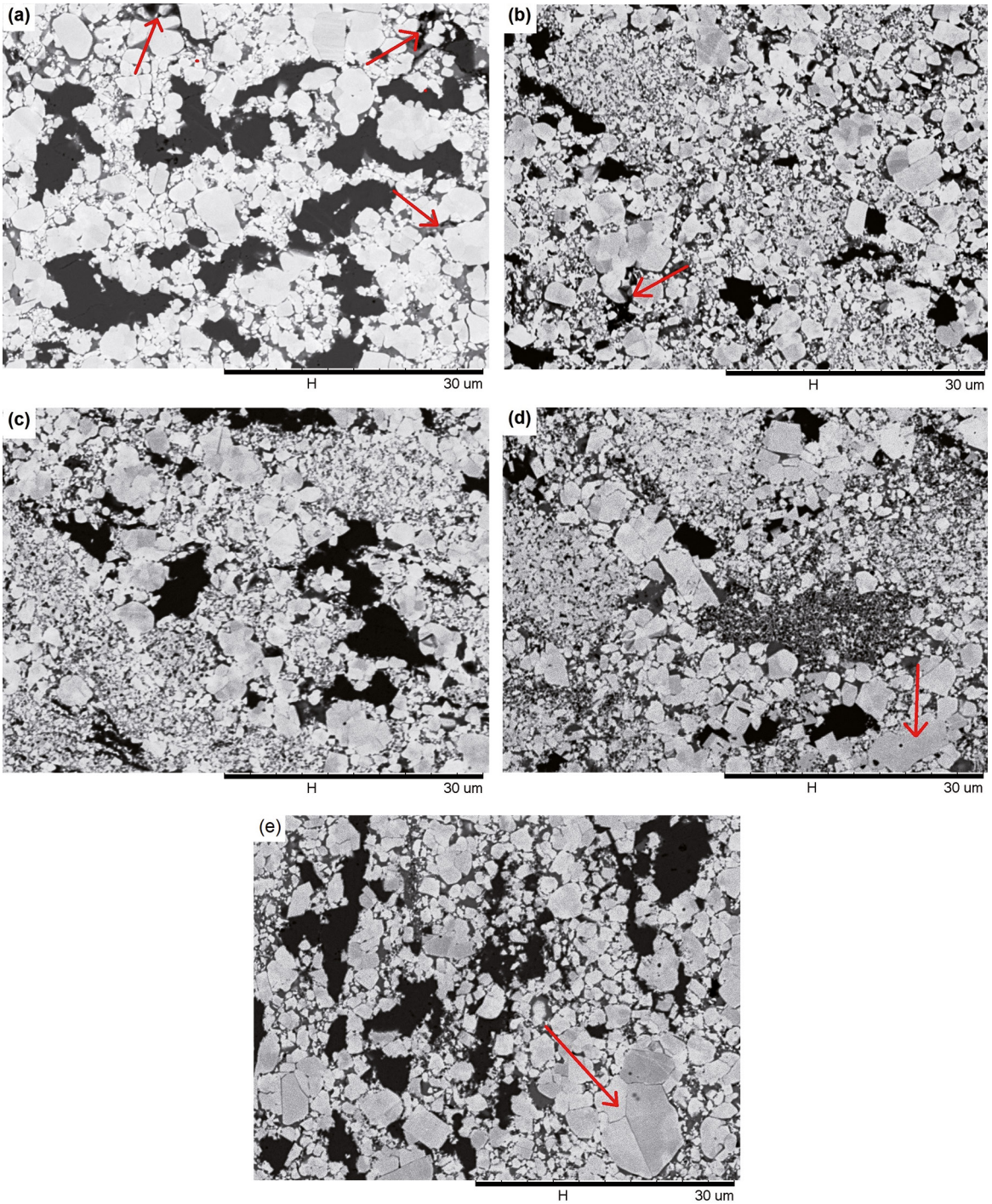

Figure 3: SEM metallographic images of sintered WC-10Co at different temperature. 1500ºC (a), 1600ºC (b), 1700ºC (c), 1800ºC (d), and 1900 ºC (e). Porosity in lower temperature and abnormal grain growth in higher temperature.

Figure 3 also shows that the WC particle size distribution in all samples are almost the same specially for samples sintered at 1500 to 1700 ºC (Figure 3-a to 3-c). As it observed in samples sintered at 1800 and 1900 ºC, there is some abnormal grain growth in microstructure. It is clearer in samples sintered at 1900 ºC (Figure 3-d). It can be explained by the effect of higher temperature on diffusion rate. At higher temperature, because of the higher diffusion rate, it is easier for bigger particles to dissolve the smaller one and grows. Because of the short sintering time, these abnormal growths were found only in samples sintered at 1900 ºC however some evidence of starting the growth in samples sintered at

Table 1: Relative density of sintered sample at different sintering temperatures.

Sintering temperature (ºC)	1500	1600	1700	1800	1900
Relative density (%)	90-93	93-97	100	100	100

1800 ºC was also found but it seems that the sintering time was not sufficient for severe growth.

Table 1 shows the relative density of sintered samples to the theoretical density of WC-10Co at different sintering temperatures. The results are in agreement with the microstructure observation, as the samples sintered at 1500 ºC and 1600 ºC with some porosities (Figure 3-a and 3-b), did not achieve to the full density. All other three samples with no evidence of porosity (Figure 3-c to 3-e), have full density. As discussed before, achieving to the full density at higher temperatures can be related to higher diffusion rate at higher temperature. Also, as the temperature increases, porosities decreasing due to the higher liquid phase transaction during sintering could be a reason for increasing relative density [15].

The variation of Vickers hardness with sintering temperature is shown in Figure 4. The hardness of WC-10Co hardmetals was sensitively dependent on the sintering temperature. As can be seen in Figure 4, the hardness increases sharply by increasing the sintering temperature from 1500 to 1700 ºC and then increases slightly by increasing temperature up to 1800 ºC. After 1800 ºC, increasing sintering temperature causes a notable decrease in hardness.

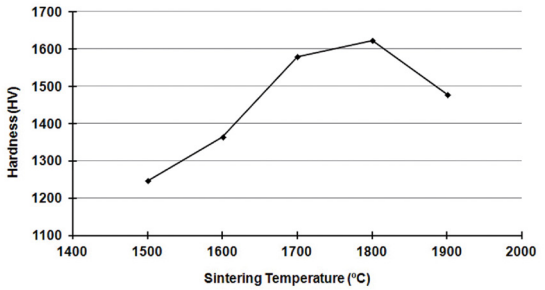

Figure 4: Vickers hardness as a function of sintering temperature.

Several studies reported hardness values for WC-Co hardmetals produced with different sintering methods. some of result listed in Table 2. As can be found, our results are in agreement with previous studies. Generally, hardness of the cemented carbides is affected by different parameters such as amount and type of the binder, size, distribution and the contiguity of the carbide phase, and porosity [15]. So, the rapid increase of hardness above 1500 ºC seems to occur due to the formation of a liquid phase during sintering which leads to sharply increase the relative density and decrease in porosity. Moreover, the hardness slightly decreases above 1800 ºC. It can be attributed to the fact that the sintered density reaches the saturated value, and the crystallite size of WC considerably increases at temperatures above as showed in Figure 3-d and 3-e for samples sintered at 1800 and 1900 ºC.

Figure 5 and 6 shows the effect of sintering temperature on yield strength and compressive strength respectively. Result values are all in same order of magnitude with result obtained by Santos[20] study of the mechanical properties of nanostructured WC-10Co hard metal, with and without grain growth inhibitors (VC and Cr3C2).

The trend in both graphs is almost the same as hardness results and the same explanation can be applied here as well. According to hardness and compression test results, it seems that the sintered density reached to saturated value at sintering temperature equal to 1700 ºC and after this temperature the WC particle size starts to grow that can have some effect on mechanical properties such as hardness and compression strength. This result is completely In compliance with the results achieved from density measurement (Table 1 and Figure 3).

4. Conclusion

The following conclusions have been drawn from the study of high pressure high temperature sintering of WC-10Co cemented carbide:

1. HPHT sintering method can be successfully used in order to sinter cemented carbide with a high production rate.

2. Increasing sintering temperature up to 1900 °C via HPHT sintering makes it possible to decrease sintering time to 2 minutes.

3. Increasing sintering temperature causes in increasing relative density and to reach the 100% of relative density at 1700 °C.

4. Hardness, yield strength and compressive strength increase by increasing sintering temperature up to 1800 °C and then decrease. The increase at first part is related to improving sintering phenomenon by increasing temperature and the decrease in second part is related to WC particles growth at high sintering temperature.

5. Acknowledgment

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Table 2: Comparison of hardness obtained with different techniques.

Reference	Composition	Sintering method	Hardness (kgf/mm^2)	Sintering temperature (°C)	Holding time (min.)
[2]	WC-9.7Ni-0.3Al	CLPS	1064-1100	1460	60
[2]	WC-9.5Ni-0.5Al	CLPS	1263-1297	1460	60
[2]	WC-9.3Ni-0.7Al	CLPS	1376-1424	1460	60
[16]	WC-10Co-0.7VC	CLPS	1610	1370	60
[16]	WC-10Co-0.7VC	CLPS	1610	1410	60
[16]	WC-10Co	CLPS	1310	1370	60
[16]	WC-10Co	CLPS	1410	1410	60
[17]	WC-11Co	CLPS	1782	1390-1470	-
[17]	WC-17Co	CLPS	1591	1390-1470	-
[17]	WC-21Co	CLPS	1483	1390-1470	-
[17]	WC-12Co	CLPS	1748	1390-1470	-
[17]	WC-20Co	CLPS	1359	1390-1470	-
[17]	WC-14Co	CLPS	1426	1390-1470	-
[17]	WC-17Co	CLPS	1335	1390-1470	-
[17]	WC-21Co	CLPS	1264	1390-1470	-
[17]	WC-13Co	CLPS	1395	1390-1470	-
[18]	WC-12Co-0.4VC	HIP	1340–1381	1390	60
[18]	WC-10Co-2VC	HIP	1430	1260	30
[19]	WC-20Co	CLPS	1582	1350	1
[19]	WC-20Co-2.5VC	CLPS	1693	1350	1
[19]	WC-20Co-5VC	CLPS	1709	1350	1
[19]	WC-20Co-7.5VC	CLPS	1870	1350	1
[19]	WC-20Co	CLPS	1566	1400	1
[19]	WC-20Co-2.5VC	CLPS	1701	1400	1
[19]	WC-20Co-5VC	CLPS	1649	1400	1
[19]	WC-20Co-7.5VC	CLPS	1687	1400	1

CLPS – Conventional liquid phase sintering, HIP – Hot iso-static pressing.

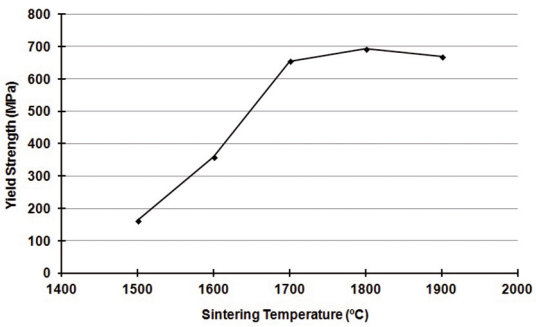

Figure 5: Yield Strength as a function of sintering temperature.

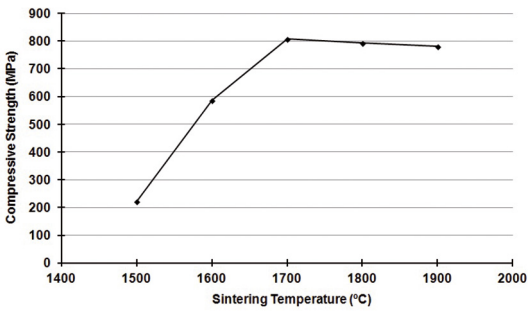

Figure 6: Compressive strength as a function of sintering temperature.

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