

POWDER METALLURGY PROCESSING OF HARDMETAL POWDER

M.A. Selamat, S.A. Manaf, N. M. Diah and T.R. Jaafar

*Structural Material Program, Advanced Materials Research Centre (AMREC),
SIRIM Berhad, Lot 34, Jalan Hi-Tech 2/3, Kulim Hi-Tech Park,
09000 Kulim, Kedah, Malaysia*

ABSTRACT

The microstructure and mechanical properties of sintered 94WC-6Co powders were investigated. In this work, sub-micron ($< 1\mu\text{m}$) of tungsten carbide (WC), cobalt (Co) and paraffin wax powders were wet mixing in a tubular mixer at a mixing speed of 50 rpm for 3 hours. Powders mixture were uniaxially pressed, cold isostatic pressing (CIPped) and sintered at 1200-1500°C for 1 hour in a nitrogen-based atmosphere using liquid phase sintering (LPS) mechanism. The fine WC particles were led to uniformity in microstructures at optimum sintering temperatures, 1450°C and showed a relative sintered density above 95% of theoretical. The sintered samples also obtained higher hardness and strength due to their fine microstructures, which are suitable for use in cutting tool application.

INTRODUCTION

The term hardmetal is used to describe alloys produced from metallic hard materials (primarily carbides) and tough binder metals of the iron group. In terms of microstructure, properties and performance, hardmetals can be divided into alloy types as shown in Table 1. Tungsten carbide (WC) is the main hard material used. Titanium carbide (TiC), tantalum carbide (TaC), and niobium carbide (NbC) are also important in metal cutting. Cobalt is the main binder used. The effects of the individual components on performance can be summarised as shows in Table 2.

To produce hardmetal components, grade powders are mixed and compacted or shaped into green compact. This is subsequently sintered to obtain its final shape and properties. Grinding or final shaping, and coating may follow. Figure 1 shows how hardmetal is produce through Powder Metallurgy routes [1]

Due to the great variety of shapes in which hardmetal is used, a number of shaping methods are employed. These can be divided into four groups: direct shaping by uniaxial pressing (die pressing), indirect shaping of cold isostatic pressed (CIP) powder blocks, extrusion and high and low pressure injection moulding [2,3]. The shaping process actually used depends mainly on the geometry of the part and the quantities involved. Common to all shaping methods is the low green density about 70-75% of the as-sintered density [4].

Table 1: The range of hard materials and their applications

Hard material	Grain size, μm	Binder content, wt-%	Range of applications
WC-Co	Ultra-fine: 0.2-0.5	2-4	Wood machining and wear parts
		6-9	Microdrills and micromills for PCBs; indexable inserts for metal cutting
		10-16	Shaft tools; paper cutting knives
	Sub-micron: 0.5-0.8	4-16	Indexable inserts for metal cutting; shaft tools
	Fine: 0.8-1.3	4-25	Indexable inserts for metal cutting; chipless shaping; wear parts
	Medium: 1.3-2.5	4-25	Heavy duty machining; chipless metal forming
WC-Ni,(Cr),(Co)	Coarse: 2.5-6.0	4-25	Mining tools
	Extra coarse: > 0.6	4-25	Chipless metal forming
	0.5-2.0	4-20	Chemical engineering; components for corrosive environments; non-magnetic structural parts
WC-(Ti,Ta,Nb)C-Co	0.5-2.0	4-15	Indexable inserts for steel cutting
Cermets (Ti,Ta,Nb,W,Mo)(C,N)/ (Co,Ni)	0.5-2.0	4-15	Indexable inserts for steel cutting

Table 2: The effect of the individual components on performance of hardmetals

Element	The effect of the individual components
Co, (Ni), (Fe)	Toughness, corrosion properties
WC	Hardness, good wettability by Co
TiC, Ti(C,N)	Compared with WC higher hardness, lower thermal conductivity and lower solubility in ferrous alloys, main component in cermets
(Ta, Nb)C	Improved high-temperature properties and thermal shock resistance
VC, Cr ₃ C ₂	Grain growth inhibitor in WC-Co hardmetals
Mo ₂ C	Improved wettability of Ti(C,N) in cermets

Sintering is mainly carried out in vacuum furnaces using graphite-heating elements. Sintering is a very important step in which a large number of processes take place as shows in Table 3. The purpose of this study is focused on the sintering process of fine particle WC-Co powders under nitrogen-based atmosphere using liquid-phase sintering (LPS) mechanism.

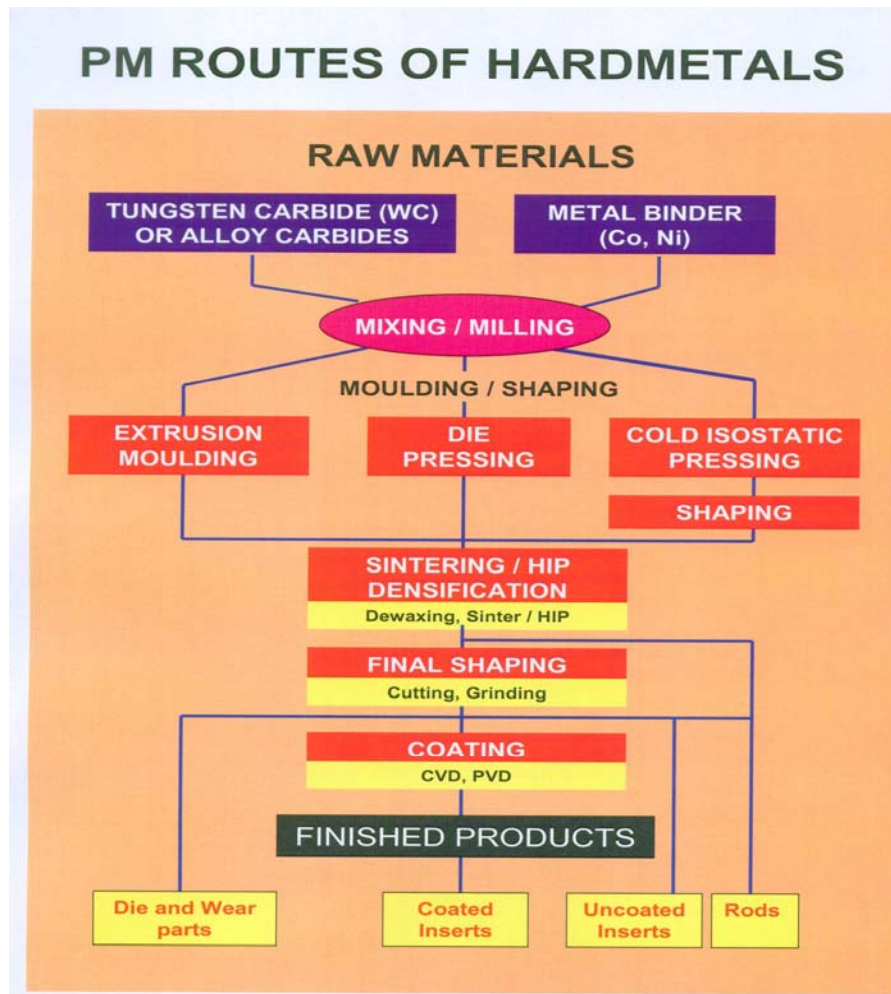


Figure 1: Manufacturing process of hardmetals through PM routes

Table 3: A number of processes during sintering of hardmetals

Process involved	Temperature involved
Melting of pressing lubricant (wax)	~60°C
Desorption of moisture	Room temperature – 150°C
Evaporation of pressing lubricant	150 – 400°C
Reduction of Co oxides and cracking of decomposition products of lubricant	300 – 500°C
Reduction of W oxides	700 – 900°C
Reduction of mixed carbides oxides	> 1000°C
Rapid shrinkage; depends on grain size of WC particles (roughly 80% of shrinkage takes place before melting of binder)	> 1100°C
Melting of binder phase	1320 – 1400°C
Grain growth and solution reprecipitation processes at sintering temperature	1400 – 1500°C

EXPERIMENTAL

Elemental powders of tungsten carbide (WC) and cobalt (Co) were used for this study. Powders were weighted to give the composition of 94wt.%WC-6wt.%Co. 60mL heptane and paraffin wax powder were added into mixture powders with 10 mm tungsten carbide balls in order to minimize any possibility of oxidation before sintering. The mixtures were blended in a tubular mixer at 85rpm for 3 hours. The ball to weight powder ratio was kept at 3:1. After wet mixing, the powders were dried at temperature slightly above the boiling point of the solvent and granulated before pressing into the shape.

Green compacts were prepared by uniaxial compaction at a pressure of 590 MPa. Specimen dimensions were 15x15x5 mm with green densities of about 70-75% of theoretical density. In addition, to obtain denser green compacts, cold isostatic pressing (CIP) was used with a compacting pressure of 300 MPa. The green compacts were sintered for 1 hour at temperature cycle in the range of 1200-1550°C under nitrogen-based atmosphere (95%N₂+5%H₂). The heating rate was 5°C/min up to 450°C and 10°C/min for the remaining of the sintering cycle before furnace cooling to room temperature.

Measurements of the hardness and transverse rupture strength (TRS) were obtained according to ASTM B294-92(2006) and ASTM B 406-96 (2005), respectively. The densities of the sintered samples were determined by Archimedes method using specific gravity meter. The hardness tests were determined using Rockwell Hardness Tester (HRA) with 60kgf load. Fracture strengths were determined using INSTRON 4505 Universal Tensile machine in transverse rupture strength (TRS), using miniature rectangular specimens with span (L) =10mm. The specimens were metallographic examined using Scanning Electron Microscopy (SEM). Samples for the metallographic examination were prepared using standard techniques and etched in Murakami's reagent which is the mixture of 10g KOH or NaOH, 10g K₃Fe(CN)₆ and 100mL distilled water.

RESULTS AND DISCUSSION

The mechanical properties of WC-Co could vary depending on sintering schedule. A uniform and high density is required after the sintering of submicron WC-6Co powders. Thus to minimize the pores and gases generated during the process, a holding steps are introduced (450-1320-1450°C) as shown in Figure 2(a). The holding at 450°C is suitable for removing all oxides [6]. Further holding step expected to promote the melting and homogenous distribution of cobalt, thus improve sintering. The effect of heating schedule presented in Table 3. The heating schedules with holding steps (450-1320-1450°C) are more effective than direct heating (450-1450°C) without any steps, Table 4. The results on sintered density of WC-6Co are given in Figure 3. It was found that the sintered density of <1.0µm WC-6Co increase rapidly above 1300°C and reached saturated value (14.8 g/cm³) at the sintering temperature 1450°C.

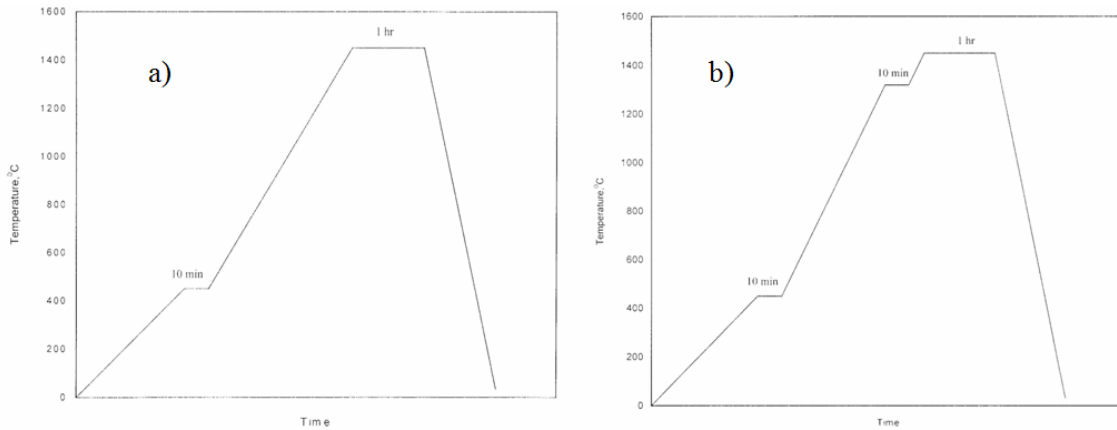


Figure 2: Heating schedule for WC-6Co powders compacted at 590MPa; (a) 450-1450°C and (b) 450-1320-1450°C, 1hr holding time

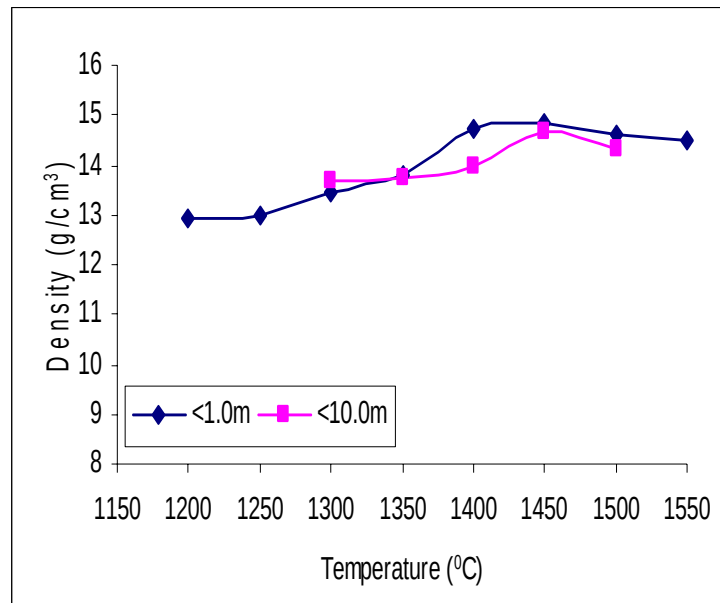


Figure 3: The experimental result on the relationship between density of sintered WC-6Co and sintering temperature.

In general, the WC grains tend to show an elongated rectangular shape as shown in Figure 4. At temperature 1300°C, Co particle with the increases of sintering temperature becomes to be wetting and WC grains are dispersed in the cobalt matrix. Large WC grains are randomly dispersed in fine grain matrix, Figure 4(c). The shape of sintered WC-6Co started changed at 1500°C by considerable coarsening structure. The microstructure considered as oversintered condition. It was observed that present work has shown that it is possible to successfully sintered WC-6Co in nitrogen-based atmosphere. It was found that sintering in nitrogen-based atmosphere not only decreases the optimum sintering temperature to 1450°C compared with 1500°C in vacuum [5] but

it is a good practice to sinter WC-6Co at this condition which is more cheaper, safety and environmentally friendly.

Table 4: Mechanical properties of <1.0 μ m WC-6Co powders compact + CIPped and sintered at different conditions

Heating schedule, °C	Hardness, HRA	Sintered density, g/cm ³
450 – 1450	85.3	14.53
450 – 1320 – 1450	86.5	14.82

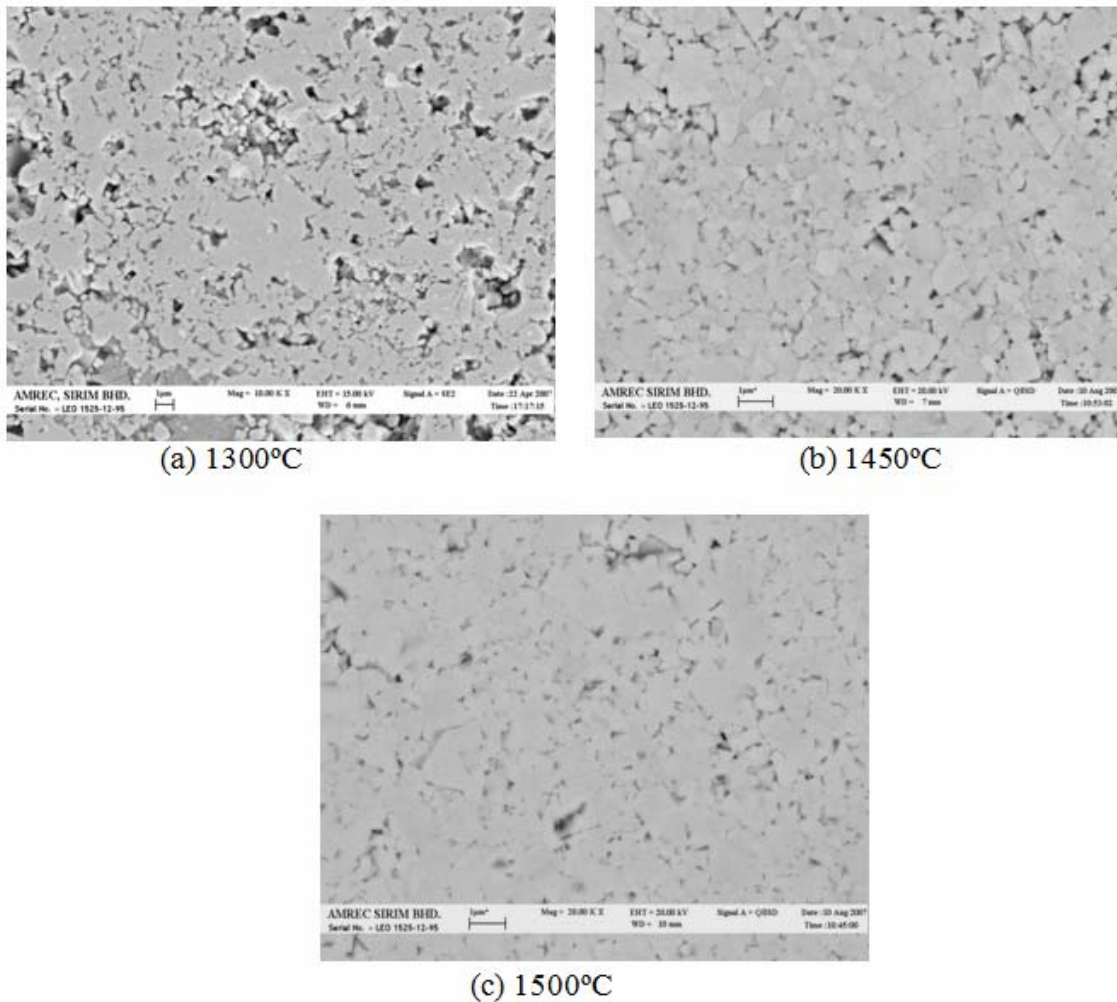


Figure 4: SEM micrographs of sintered samples showing the change in WC grain size and morphology at given sintering temperatures.

The mechanical properties of WC-6Co sintered samples increase gradually in the higher temperature range as shown in Table 5. The increment of hardness and strength are due to formation of liquid phase, which leads the sintered density to increase especially at

temperature 1400°C. The results in Table 5 indicate that it was influenced by the process of compaction. Samples speculated that, a friction was developed between the powders and the die wall causes the formation of non-uniform microstructure and mechanical properties in the sintered WC-6Co. This is similar to what have been reported in the Gwan-Hyoung work [6].

Table 5 also shows the TRS values of sintered <1.0µm sample. The TRS values for all samples increased marginally and being maximum at temperature 1450°C. The TRS value can be co-related to the sintered porosity values of samples, such that an increase in porosity lowers the TRS value.

Table 5: Physical and mechanical properties of sintered 1.0µm WC-6Co samples

Sintering temperature, °C	Sintering density, g/cm ³	Hardness, HRA	Transverse Rupture Strength, MPa
1200	12.93	83.3	172
1250	13.01	83.5	190
1300	13.43	84.6	548
1350	13.79	86.6	772
1400	14.74	87.6	1340
1450	14.82	86.5	1573
1500	14.63	81.2	1216
1550	14.49	79.2	793
<i>Commercial uncoated WC</i>	<i>14.9</i>	<i>88.7</i>	<i>1900</i>

CONCLUSION

Sub-micron powders of WC-6Co were produced by wet mixed in tubular. Sintering of WC-6Co in nitrogen-based atmosphere is acceptable to get 99% of theoretical density and produced good microstructure and mechanical properties at lower temperature than in vacuum. It was verified that the effect of powder size give a significant results on the sintering properties. The results of this study can be summarized as follows:

- 1) Heating schedules affected the microstructure and properties of sintered WC-6Co. It was confirmed that heating schedules with holding steps are more effective than a direct heating.
- 2) Compacting + CIPped process give a uniform hardness and density to sintered samples.
- 3) A good densification of sintered WC-6Co was achieved, compatible with the commercial values.
- 4) It was reached a satisfactory value of hardness, 87 HR_A, but need further study to improve the TRS values.
- 5) Sintering at 1500°C or higher temperature will coarsening the WC structure and weaken the properties of the sintered samples.

ACKNOWLEDGMENTS

The work was partly supported by SIRIM Berhad funded by the government science-fund project Ministry of Science, Technology and Innovation (MOSTI), Malaysia.

REFERENCES

- [1]. K. JA. Brookes (1998). *Hardmetals and other hard materials*, 3rd ed. (International Carbide Data, UK
- [2]. H. VD. Berg (2007). Hardmetals: trends in development and application, *Powder Metallurgy*, **50(1)**, 7-10
- [3]. Z. Baojun, Q. Xuanhui and T. Ying (2002). Powder injection molding of WC-8%Co tungsten carbide, *Int. J. of Refractory Metals & Hard Materials*, **20**, 389-394
- [4]. M.A. Selamat (2004). *Sintering behaviour, microstructure, mechanical and cutting performance of sintered high-speed steel proceed in nitrogen-based atmospheres*, Ph.D. thesis. Mechanical and Manufacturing Engineering, University of Bradford, UK.
- [5]. C.W. Morton, D.J. Wills and K. Stjernberg (2005), The temperature ranges for maximum effectiveness of grain growth inhibitors in WC-Co alloys, , *Int. J. of Refractory Metals & Hard Materials*, **May**, 287–293.
- [6]. G.H. Lee and S. Kang (2005). Sintering a nano-sized WC-Co powders produced by a gas reduction-carburization process, *J. Alloy and Compounds*, **Aug**, 281-289.