*M.A. Selamat,**
A.A. Mahaidin,
S. Abdul Manaf and
T. Ria Jaafar

Advanced Materials Research Centre (AMREC),
SIRIM Berhad
Lot 34, Jalan Hi-Tech 2/3, Kulim Hi-Tech Park
09000 Kulim, Kedah, Malaysia
Tel: 04-4017263

(masri@sirim.my)

SINTERING BEHAVIOUR, MICROSTRUCTURE AND MECHANICAL PROPERTIES OF SUB-MICRON HARDMETALS POWDER PROCESSED IN NITROGEN-BASED ATMOSPHERE

RINGKASAN: *Mata alat dari karbida tungsten terekat sering digunakan dalam kerja memesin, memotong, menebuk lubang dan kegunaan lain. Sifat-sifat tungsten aloi ini adalah sensitif kepada proses dan penurunan disebabkan oleh baki keliangan. Turutan kerja-kerja penyudahan melalui proses Kajilogam Serbuk termasuklah mengadun, memadat dan menyinter di dalam pelbagai atmosfera terhadap sampel pemadatan hijau. Serbuk WC pada saiz sub-mikron (<1.0 µm) dan 10.0 µm telah disinter bersama logam pengikat 6 wt.% Co untuk menghasilkan komponen yang bebas dari liang. Serbuk yang terpadat disinter pada suhu antara 1200-1500 °C di dalam atmosfera pensinteran berasaskan nitrogen. Sehingga kini, banyak kajian telah dibuat menyatakan persinteran terbaik untuk karbida tungsten adalah melalui mekanisme fasa pensinteran cecair di dalam atmosfera vakum pada 1500 °C dan atmosfera hidrogen tulen pada 1485 °C. Walaubagaimana pun, daripada kajian ini, dapati untuk mencapai sifat-sifat mekanikal yang lebih baik, serbuk bersaiz halus adalah diperlukan dan boleh juga disinter pada atmosfera berasaskan-nitrogen. Oleh itu, tumpuan kajian ini adalah untuk membangun dan menghasilkan komponen tahan haus yang mempunyai sifat-sifat yang lebih baik atau setanding dengan yang komersial.*

ABSTRACT: Cemented tungsten carbide (WC) insert is widely used for a variety of applications such as machining, cutting, drilling and others. The properties of this tungsten heavy alloy are sensitive to processing and degraded by residual porosity. The sequences of high-end Powder Metallurgy (PM) process include mixing and compacting, followed by multi-atmosphere sintering of green compact. The sub-micron (<1.0 µm) and less than 10.0 µm of WC powders are sintered with a metal binder (6 wt.% Co) to provide pore-free part. The powder compacts were sintered at temperatures ranging from 1200-1550 °C in nitrogen-based sintering atmosphere. To date, many works in the literature mentioned that the best sintering technique of tungsten carbide was carried out via liquid phase sintering mechanism in vacuum and pure hydrogen atmosphere at 1500 and 1485 °C, respectively. However, from this study it was found that in order to attain

better mechanical properties, a fine grain size of powder is necessary and could also be sintered in nitrogen-based atmosphere. Therefore, the attention of the current work is to develop and produce wear resistant component with better properties or comparable to the commercial ones.

Keywords: Powder Metallurgy, tungsten carbide, liquid phase sintering, nitrogen-based atmosphere.

INTRODUCTION

Tungsten carbide – cobalt (WC-Co) cemented carbides, also commonly referred as hardmetals, is well known class of composite materials. It has long been realised its practical importance and often being used in wear resistant applications. They exhibit an exceptional combination of strength, hardness, toughness and wear resistance as a result of extremely different properties of their two interpenetrating constitutive phases: hard, brittle carbides and a relatively soft, ductile metallic binder. In our work, WC is the hard phase providing hardness and wear resistant while Co is the matrix phase, often referred to as the binder phase, providing strength and toughness.

Basically the properties of WC depend primarily on cobalt content and grain sizes of WC. It is possible to obtain different mechanical properties of the material through variations in composition. Finer grained alloys have been found to preserve their hardness at high temperature better than coarser grained alloys. However, finer grades are extremely sensitive to processing conditions and are even more prone to carbide grain growth during sintering (Schubert *et al.*, 1995). WC-Co is processed to full density by sintering at relatively high temperatures. With higher temperatures, longer times, or small particles, the bond grows more rapidly and densification becomes evident (Schubert *et al.*, 1995; Fang *et al.*, 2005; Morton *et al.*, 2005). Further reduction in the sintering temperature can be achieved by chemical additives or with the addition of appropriate grain growth inhibitors, and this is a common practice in industrial sintering processes.

The effect of sintering behaviour and grain size of WC-Co is addressed in the present work. In combination with powder parameters, the sintering cycle plays a major role in creating the final microstructure due to solid state and liquid phase sintering effect (Morton *et al.*, 2005; Eso *et al.*, 2005). The mechanisms through which the solid state densification occurs are however typical in liquid phase sintering processes, with rearrangement and solution-reprecipitation (Petersson and Angren, 2005). As reported by Lee and Kang (2006), finer size of cobalt powders is known to be effective in the reduction of residual porosity and cobalt pooling. As a result, by reducing the particle size of the minor phase in multi-component

systems, the homogeneity of localised composition is drastically improved due to a decrease in the distance between neighbouring particles of the minor phase. It has been reported that the sintering temperature for nano-sized powder can be lower than that of a large size powders due to lower melting point of the binder contributed by a large surface area (Eso *et al*., 2005).

MATERIALS AND METHOD

The tungsten carbide (<1.0 μm and 10.0 μm), and cobalt powders (<1.26 μm) supplied by Buffalo Tungsten Inc., New York were used to produce the alloys. Powders were weighed to give the compositions of 94 wt.%WC – 6 wt.%Co. Usually, cobalt content in WC-Co composition is less than 15 %, depending on the application. However, reducing Co content helps to reduce tool wear rate. Paraffin wax powder and heptane were added to the powder mixtures before wet mixing in turbula mixer for 3 hrs with 8 mm steel balls to produce homogenous mixture. After wet mixing, the powders were dried and granulated before pressing into required shape. It is noted that in order to minimise any possibility of oxidation or contamination before sintering, the powders were kept in heptane. The organic binder was removed by slow heating in oven. The ball to powder weight ratio was kept at 3:1. The samples used for this study were 15 mm x 15 mm x 3 mm thickness. The sub-micron WC-Co powders were compacted using uniaxial pressure at 590 MPa. Green density was in the range of 70-75 % relative to the theoretical density.

The powder compacts were sintered at temperatures ranging from 1200 to 1550 ^{o}C for 1 hr. Sintering was performed in nitrogen-based (95 %N_2+5 %H_2) atmosphere. To minimise the pores and gases generated during the sintering process, holding steps are introduced (450-1320-1450 ^{o}C), Figure 1(b), rather than direct heating without any steps, Figure 1(a). The heating rate was 5 ^{o}C/min up to 450 ^{o}C and 10 ^{o}C/min for the remainder of the sintering cycle. Slow cooling to room temperature was allowed to occur after the completion of the isothermal hold.

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. An INSTRON 3369 Testing Machine (Series IX Merlin) was used to measure TRS. Samples were mounted, ground and polished using successively various grade of grinding paper followed by finer diamond polishing compounds ranging from 3 to 1 μm. The samples were etched for 5 min with Murakami solution before being examined using Scanning Electron Microscopy (SEM).

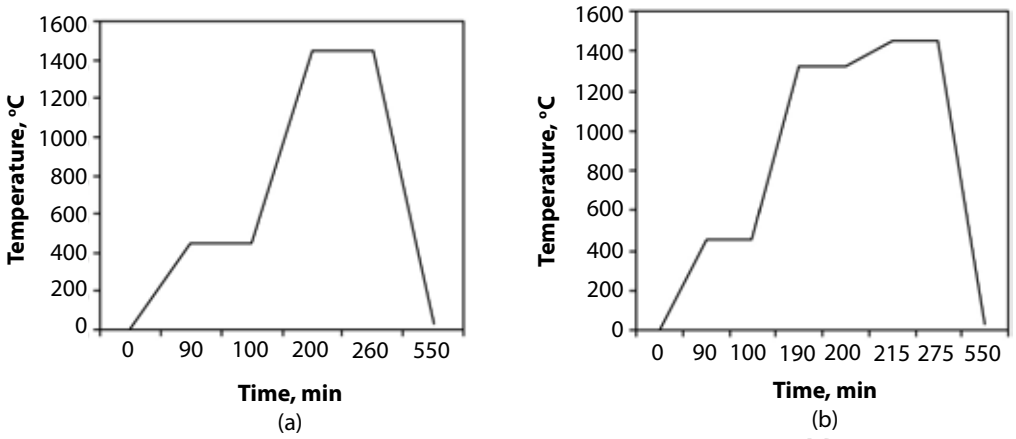


Figure 1. *Sintering schedule for WC-6Co powders compacted at 590 MPa; (a) 450-1450 °C and (b) 450-1320-1450 °C, 1 hr holding time.*

RESULTS AND DISCUSSION

The main purpose of this work was to investigate the differences of sintering behaviour of WC powder, which contains 6 wt.% cobalt, in nitrogen-based sintering atmospheres and traditional sintering technique. The investigation of the powders was based in terms of high density and good microstructures (grain growth and uniform carbides distribution) with acceptable mechanical properties including higher hardness and strength. The physical and mechanical properties of WC-Co could vary depending on sintering schedule.

Utilising holding step during sintering is expected to promote the melting and homogenous distribution of cobalt, thus improve sintering properties. The effect of heating schedule is presented in Table 1. The heating schedules with holding steps (450-1320-1450 °C) are more effective than direct heating (450-1450 °C) without any steps. The first step in Figure 1(b) was intended to eliminate residual gases and the second step was to promote the melting and homogenous distribution of cobalt (Lee and Kang, 2006). In practice, slow heating is used because of binder removal constraints and thermal inertia (resistance to temperature change) of furnaces. During slow heating, significant shrinkage was observed prior to liquid formation (Eso *et al.*, 2005; Petersson and Agren, 2005).

Table 1. Mechanical properties of <1.0 μm WC-6Co powders compacted at 590 MPa and sintered with and without holding steps.

Heating schedule, °C	Hardness, HR_A	Sintered density, g/cm³
450 - 1450	85.3	14.53
450 - 1320 -1450	86.5	14.82

The sintered densities of WC-6Co powders were determined over the range 1200-1550 °C, as shown in Figure 2. The liquid phase sintering (LPS) mechanism occurred during sintering process which is composed of four stages (Eso *et al.*, 2005; German *et al.*, 1988). Initially, during heating, solid state densification occurred as a result of chemical potential gradients. When the first cobalt liquid forms (at ~1300 °C), additional densification occurred since the volume of liquid increase rapidly. This Co liquid is not in equilibrium with WC. Consequently, it spreads rapidly, penetrating along interparticle contacts where it lubricates the sliding of WC particles in consecutive manner. This allows pore filling by both solid (WC) and liquid (Co) flow, and is termed as rearrangement. Subsequently, solution-reprecipitation occurred (Eso *et al.*, 2005; Petersson and Agren, 2005; German *et al.*, 1988).

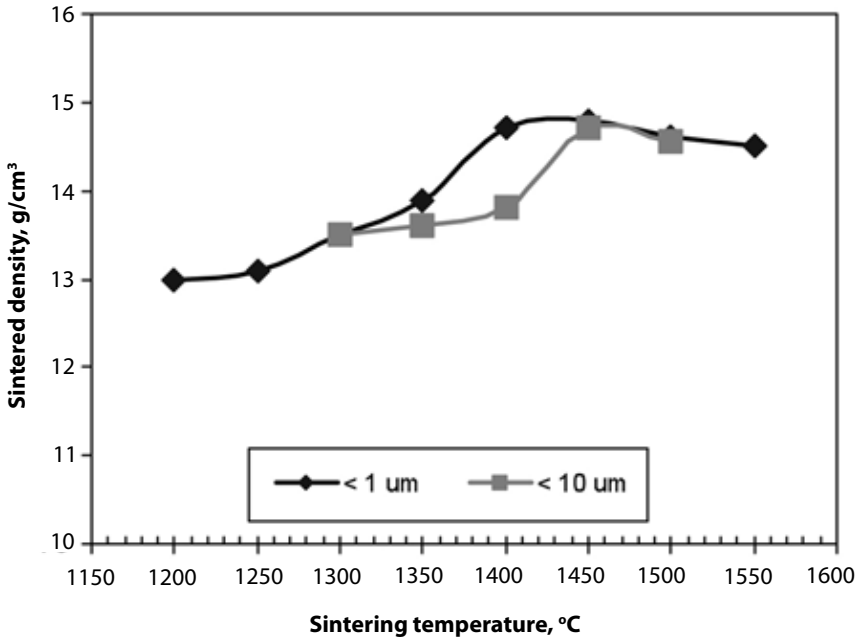


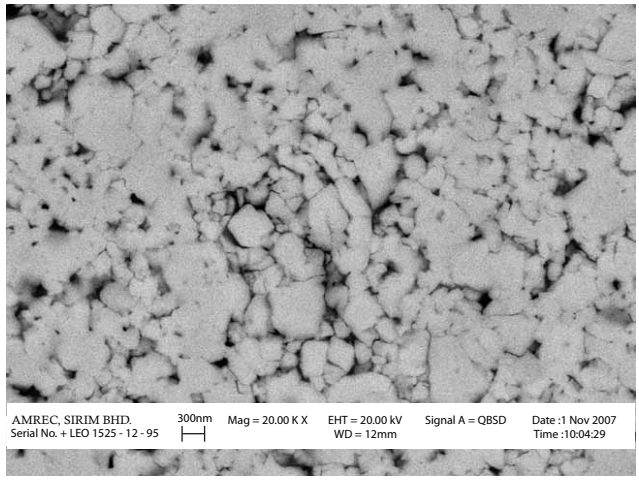
Figure 2. *The experimental result on the relationship between density of sintered WC-6Co and sintering temperature.*

In this work, it was found that the sintered density of sub-micron WC-6Co (<1.0 μm) increased rapidly above 1300 ºC, and reached saturated value (14.8 g/cm^3) at the sintering temperature of 1450 ºC. A similar result was obtained for <10.0 μm powder sample. The only difference being that the sintered density of the micron-size sample is lower than the sub-micron samples at that temperature range. This phenomenon is in agreement with Fang *et al*. (2005) and Sailer *et al.* (2001), who also attributed that, the ultrafine-grained hardmetals exhibit high density values.

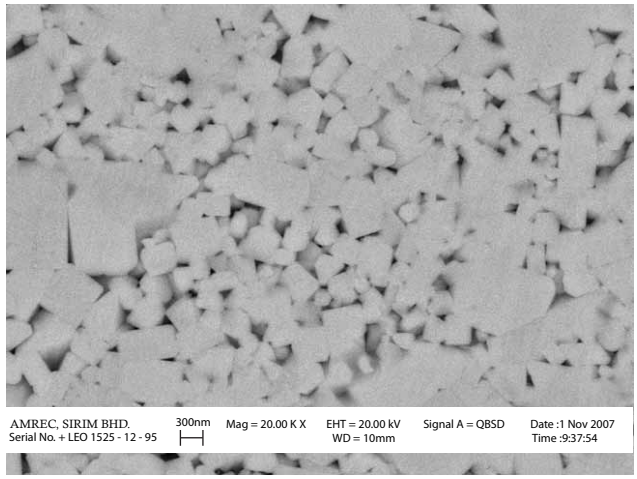
When a compact of sub-micron WC-6Co powder was sintered through heating schedules with holding steps, the small size of WC grains was maintained as shown in Figure 3(b). The small WC grains in the alloy are associated with the heating time sufficient to reduce the defects, such as the rough surface and strains (Morton *et al.*, 2005), which are caused by the strong impact during mixing. The ledges or strains on the rough surface of WC particles promote a rapid grain growth. In general, the WC grains tend to show a 'rectangular shape' at sintering temperature of 1450 ºC as shown in Figure 3(b). At sintering temperature above 1300 ºC, Co particle starts to wet and with increasing sintering temperature, WC grains are dispersed in the cobalt matrix. Large WC grains are randomly dispersed in fine grain matrix. While sintering at temperature much below 1300 ºC, excessive amounts of residual porosity was produced, as shown in Figure 3(a). As the sintering temperature increased, corresponding WC grain growth was observed. When the sintering reached 1500 ºC, coarsening structure of WC appeared, giving oversintered microstructures correlated with the distortion of the samples, as shown in Figure 3(c). This distortion was associated with the formation of excess liquid phase. As reported by Eso *et al.* (2005), Petersson and Agren (2005) and German *et al.* (1988), it is estimated that 35 % vol. liquid is needed to obtain full density by rearrangement processes.

It was observed in the present work that it is possible to successfully sinter WC-6Co powder in nitrogen-based (95 %N_2+5 %H_2) atmosphere. It was demonstrated that sintering atmosphere clearly led to the reduction in sintering temperature to 1450 ºC compared to the same alloys sintered in vacuum (1500 ºC) and pure hydrogen atmosphere (1485 ºC) (Fang *et al.*, 2005; Morton *et al*., 2005). Therefore, the use of gas mixtures (nitrogen + hydrogen) in sintering atmospheres are important since the hydrogen provides oxide reduction, while nitrogen, is neutral with respect to oxide reduction, and is used to minimise explosive dangers.

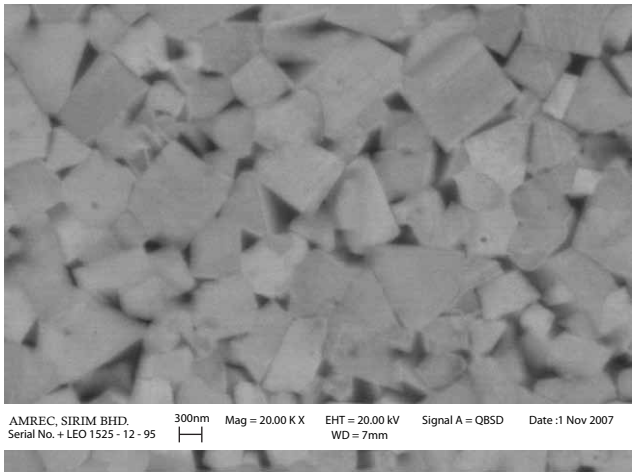
Hence, the atmosphere selection for sintering is also important, because it could determine the thermodynamic reactions between sintering powder and process atmosphere for the reduction of surface oxides during sintering. It is also a good practice to sinter WC-6Co powder at this condition which is cheaper and safer. Since the sintering temperature is reduced in nitrogen based atmosphere than in vacuum and pure hydrogen, the sintering time is shortened and energy consumption can be reduced. Thus, it is more environmentally friendly.



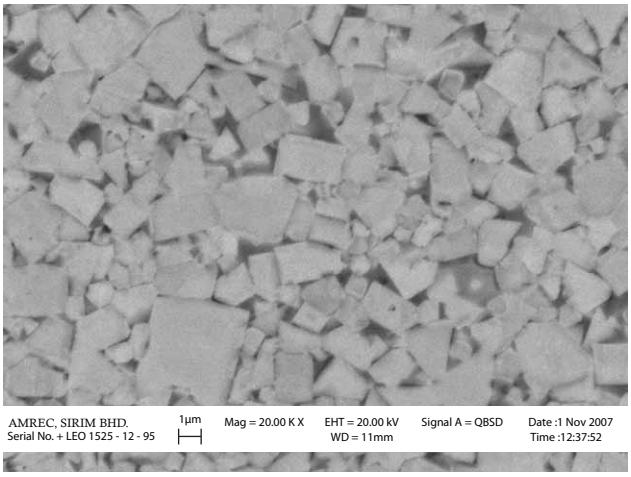
(a) 1300 °C



(b) 1450 °C



(c) 1500 °C



(d) commercial WC tool insert

Figure 3. *SEM micrographs of sintered sub-micron WC-Co samples showing the change in WC grain size and morphology at given sintering temperature (a) – (c); and (d) commercial uncoated WC cutting tool insert.*

The mechanical properties of WC-6Co sintered samples increase gradually in the higher sintering temperature range as shown in Figure 4. The maximum hardness values of sintered WC-6Co reached up to 88 HR_A, which are comparable with the commercial ones. This higher hardness may be associated with the finer WC structure distribution. The increase in hardness and Transverse Rupture Strength (TRS) are due to the formation of liquid phase, which leads the sintered density to increase especially at sintering temperature of 1450 °C. The TRS values for all samples increased marginally and being higher at this temperature as shown in Table 2. The hardness and TRS values for <10.0 µm sintered WC-6Co from previous work (Selamat *et al.*, 2010) using the same parameters and sintering atmosphere are shown in Table 3. The mechanical properties of this micron-size powder were lower than the sub-micron sintered samples. This can be co-related to the sintered porosity values of samples, such that an increase in porosity lowers the TRS value.

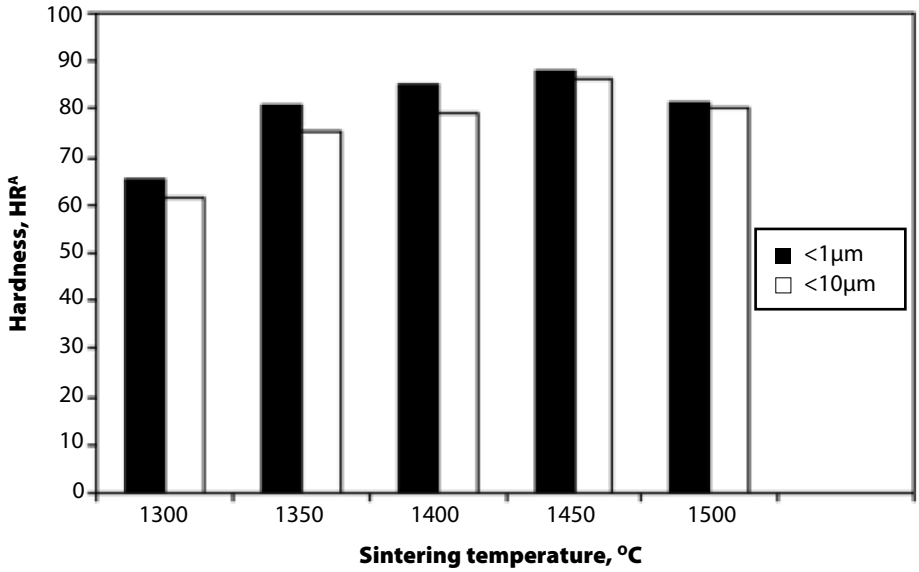


Figure 4. *The relationship between hardness particle size < 1.0 µm and 10.0 µm of WC at various sintering temperature.*

Table 2. Physical and mechanical properties of sintered sub-micron WC-6Co (< 1.0 µm) samples.

Sintering temperature, °C	Sintering density, g/cm³	Hardness, HR_A	Transverse Rupture Strength, MPa
1200	12.93	60.5	350
1250	13.01	61.2	450
1300	13.5	65.5	765
1350	13.89	81.3	954
1400	14.74	85	1340
1450	14.82	87.8	1573
1500	14.63	81.2	1216
1550	14.49	79.2	793
Commercial uncoated WC	*14.9*	*88.7*	*1700*

Table 3. Physical and mechanical properties of sintered 10.0 µm WC-6Co samples, (Selamat *et al.*, 2010).

Sintering temperature, °C	Sintering density, g/cm³	Hardness, HR_A	Transverse Rupture Strength, MPa
1300	13.52	61.7	585
1350	13.64	75.4	850
1400	13.83	82.5	1291
1450	14.67	86	1485
1500	14.55	80.2	1090

CONCLUSION

It can concluded that sub-micron size of WC-6Co powders could be processed by wet mixing in turbula for less than 3 hrs compared with more than 17 hrs by wet milling process, hence the reduced time consumption. Sintering of WC-6Co powders in nitrogen-based atmosphere makes it possible to reach ~99 % of theoretical density and produced good microstructure and mechanical properties at lower sintering temperature than in vacuum. It was verified that the effect of powder size gives significant results on the sintering properties.

Compacting process gives impact on hardness and density of sintered samples. In future, cold isostatic pressing (CIP) will be carried out in order to reduce the percentage of pores by providing a uniform pressure over the entire specimen. Heating schedules affects the microstructure and properties of sintered WC-6Co. The heating schedules with holding steps are more effective than a direct heating in achieving higher hardness.

Good densification of sintered WC-6Co closed to commercial parts is possible to achieve (~14.8 g/cm^3) by this method. Although hardness of ~ 88 HR_A is quite satisfactory, the TRS values can be further improved through further investigations. Sintering at 1500 ^oC or higher will result in coarsening of the WC grain structure and reducing the properties of the sintered samples.

ACKNOWLEDGMENT

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

REFERENCES

Eso, O., Fang, Z. and Griffo, A. (2005). Liquid Phase Sintering of Functionally Graded WC-Co Composites. *International Journal of Refractory Metals & Hard Materials*, **23**: pp 233-241.

Fang, Z., Maheshwari, P., Wang. X., Sohn. H.Y., Griffo, A. and Riley, R. (2005). An Experimental Study of the Sintering of Nanocrystalline WC-Co Powders. *International Journal of Refractory Metals & Hard Materials*, **23**: pp 249-257.

German, R.M., Farooq, S. and Kipphut, C. (1988). Kinetics of Liquid Phase Sintering. *Materials Science and Engineering*, **A 105/106**: pp 215-224

Lee, G.H. and Kang, S. (2006). Sintering a Nano-sized WC-Co Powders Produced by a Gas Reduction-carburization Process, *Journal of Alloy and Compounds*, **419**: pp 281-289.

Morton, C.W., Wills, D.J. and Stjernberg, K. (2005). The Temperature Ranges for Maximum Effectiveness of Grain Growth Inhibitors in WC-Co Alloys. *International Journal of Refractory Metallurgy & Hard Materials*, **23**: pp 287–293.

Petersson, A. and Agren, J. (2005). Sintering Shrinkage of WC-Co Materials with Different Composition. *International Journal of Refractory Metallurgy & Hard Materials*, **23**: pp 258-266.

Sailer, T.M, Herr, M., Sockel, H.G., Schulte, R., Feld, H. and Prakash. L.J. (2001). Microstructure and Mechanical Properties of Ultrafine-grained Hardmetals, *International Journal of Refractory Metallurgy & Hard Materials*, **19**: pp 555-559.

Schubert, W.D., Bock, A. and Lux, B. (1995). General Aspects and Limits of Conventional Ultrafine WC Powder Manufacture and Hard Metal Production, *International Journal of Refractory Metals & Hard Materials*, **13**: pp 281–296.

Selamat, M.A., Abdul Manaf, S., Mohamad Diah, N. and Ria Jaafar, T. (2010). Powder Metallurgy Processing of Hardmetal Powder, *Solid State Science and Technology*, **18(1)**, pp 194-201.