Review on Sintering Process of WC-Co Cemented Carbide in Metal Injection Molding Technology

M Prathabrao[1, a*], Sri Yulis M Amin[1, b] and M H I Ibrahim[1, c]

[1]Faculty of Mechanical and Manufacturing, University Tun Hussein Onn Malaysia, 86400 Parit Raja, Batu Pahat, Johor, Malaysia

Email: prathabrao16@yahoo.com[a*] , yulis@uthm.edu.my[b], mdhalim@uthm.edu.my[c]

Abstract. The objective of this paper is to give an overview on sintering process of WC-Co cemented carbides in metal injection molding technology. Metal injection molding is an advanced and promising technology in producing cemented nanostructured carbides. Cemented tungsten carbide (WC-Co) hard metal is known for its high hardness and wear resistance in various applications. Moreover, areas include fine grained materials, alternative binders, and alternative sintering techniques has been discussed in this paper.

Keywords: Metal Injection Molding (MIM), WC-Co, Nano grain size cemented carbide, Microwave sintering

1. Introduction

WC-Co cemented carbides, also referred to as hard metal, exhibit excellent combination of high strength and wear resistance in making the hard metal as preferred material for wear parts and cutting tools in machining since decades ago. In the production of small and complex part in bulk quantity, Metal injection Molding (MIM) has proven to be a promising technology that can produces cemented nanostructured carbides via MIM, with the application of finer grain size of particles below 1 μm, tailored with grain growth inhibitors. Considering the elevated temperature working application, grades cubic carbides such as vanadium carbide, VC, chromium carbide, Cr_3C_2, tantalum carbide, TaC, titanium carbide, TiC and Niobium Carbide, NbC are proposed by authors in journals. The main challenge in sintering stage, whereby to retain small average grain size in the sintered product is difficult because of very high sintering activity of nanopowders. The microstructure of sintered part plays important role in determining mechanical properties such as transverse rupture strength (TRS), hardness and fracture toughness of the cemented carbide. Moreover, the study on the mechanism of different sintering method, liquid phase sintering (LPS), hot isostatic pressing sintering (sinter HIP) and microwave sintering (MW) has been studied in this paper.

2. Metal Injection Molding (MIM)

Metal Injection Molding (MIM) is a newly developed technology to form metals and alloys into desired shape. MIM is a combination of conventional plastic injection molding and powder metallurgy. This process consist of four main steps which is mixing, injection molding, debinding and sintering as shown in Figure 1. During the mixing process, the metal powder is mixed with a binder at a selected volume ratio to form a homogenous feedstock. Binder is the key component in MIM that supplies the metal powders flow ability and formability necessary for molding [1-2]. The attained feedstock from mixing step is molded to produce a "green" compact and the binders hold particles together. During debinding stage, "green" compact is processed by partially removing the binder component to produce "brown" compact. Finally, sintering process is performed to give required mechanical properties for the sintered product also known as sintered body. Thus, the development and improvement of binders results in faster debinding procedures, cost reduction and less environmental defects [2].
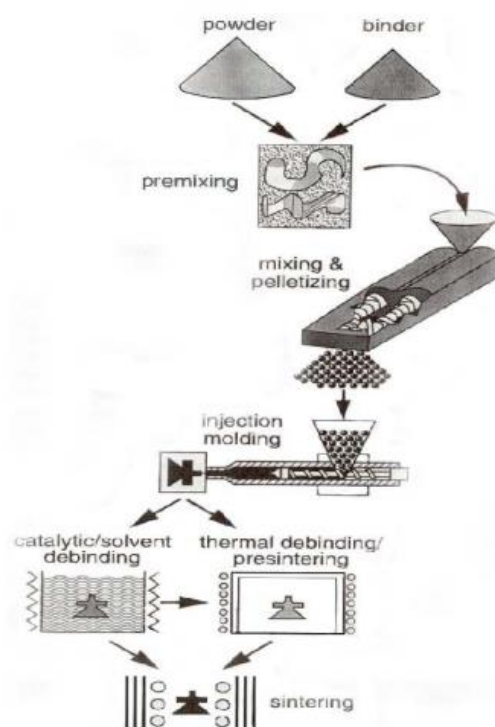

Figure 1: Schematic diagram of metal injection molding, showing the conceptual flow from powder to final structure [2]

Binders in MIM should have good flow characteristics, good debinding characteristics and favorable interactions with the metal powder used. Previous works by Prakash [3] have shown that cemented carbides with certain Fe-Ni-Co binder compositions can be of interest to the hard metal industry, in particular for applications where improved fatigue strength and toughness are required [4]. One main drawback in Fe-Ni-Co binder cemented carbides is also the more difficult control of the carbon balance, in order to achieve defect free microstructures; as well as the tendency of Fe-alloys to form martensite and react with the Fe-based workpieces during machining operations. Nickel is an interesting alternative binder, not only because of its good wettability to WC but also for a much better performance of WC-Ni cemented carbides in oxidation and corrosion conditions than that of WC-Co

cemented carbides. However the mechanical properties (hardness and strength) of WC-Ni cemented carbides are relatively inferior to those of WC-Co. The major drawback of Ni-based cemented carbides is their reduced mechanical strength [5].

Ni-Co-Cr, Ni-Si and Fe-Ni binders were also investigated. Aristizabal et al. [6] reported that despite the lower hardness of cemented carbides with Ni-Co-Cr binders, they presented the same wear performances as Co based cemented carbides in wear applications. They argue that this effects is related to the higher oxidation resistance of Ni-Co-Cr compared to Co binders and the formation of continuous oxide tribofilms which reduced friction coefficients for grade with higher binder content. Correa et al. [7] investigated the effects of adding Si to Ni binders in cemented carbides for wear parts. They concluded that there is a solution strengthening of the nickel binder by silicon, which improved significantly the mechanical properties of the Ni-Si based cemented carbides, giving flexural strength and fracture toughness higher than those observed in similar WC-Co.

Good rheological properties of binder and feedstock are one of the keys to get green parts with uniform density and no defect, besides obtaining a successful debinding and sintering process and high quality products [8]. Even though the binder acts as a temporary vehicle to support metal powder especially during mixing and injection molding, but its role is very important. Its behavior especially flow properties during molding, is the most important criterion in developing the new binder system to make sure no defect occurs during molding. It was reported that palm stearin (PS) had a good attribute as a binder system together with polyethylene (PE) [9-11]. The melting point of the PS binder was originally 61°C, whereas that of PE was 127 °C. The mixing and molding temperatures should be set above the melting point of the highest melting component of the binder to ensure that all the binders will melt and that the mold will be homogenously filled with the feedstock. Mold temperature should be kept below the melting point of the minor binder to prevent the molded part from sticking into the mold cavity. The temperature should not be raised too quickly to prevent defects, such as bubbles and cracks [12]. Besides that, a wax based multi-component binder system that contained paraffin wax (PW) as a major component to improve its rheological properties and wettability, a low-density polyethylene (LDPE) as a backbone polymer to increase the strength of green parts [13-16].

3. Nanostructured WC-Co

Nanostructured cemented carbides are the most researched powder metallurgy materials but their potential applications have not yet been defined. Nanostructured cemented carbides are characterized by a unique combination of very fine grained homogenous microstructure and good mechanical properties. Mechanical properties are directly dependent on the developed microstructure in the sintered parts, which is governed by several factors which is Tungsten Carbide (WC), crystallite size, and mean free path of the binding phase and the contiguity of WC grains [14-16]. Improvement of hardness and toughness of cemented carbides can be achieved with a decrease in WC grain size to nanoscale. Thus, considerable efforts have been made over the past years to research nanostructured cemented carbides to draw certain conclusions about hardness and toughness behavior. Nanostructured cemented carbides are produced from near nano- and nano sized WC starting powders. Biggest weakness of sintering near nano- and nano scaled powders is the retaining of a small average grain size in the sintered product [17-19].

4. Metal Injection Molding of WC-Co

Cemented tungsten carbides (WC-Co) consists of tungsten carbides grains embedded in a metal binder phase. WC-Co have been widely used as machining, cutting, mining and drilling tools, as well as wear parts and chip-less forming tools, due to their extremely high hardness, excellent wear resistance and good toughness [20]. In addition, the application of the metal binder phase provides an economical and viable method to produce cemented tungsten carbide components – liquid phase sintering.

However, it was known for long time that cemented tungsten carbides with high cobalt contents had high toughness and low hardness and those with low cobalt content had high hardness and low toughness [21, 25-26]. Therefore, the fracture toughness is improved at the expense of hardness, and vice versa. It has been shown that the ultrafine grained WC-Co materials with the submicron or Nano-WC grain size have enhanced mechanical properties such as hardness, strength and wear resistance, compared to the traditional coarse grained WC-Co materials.

Although the ultrafine cemented carbides (0.1 – 0.6 μm average size) has the higher hardness and wear resistance, the fracture toughness of ultrafine hard metals is inferior to that of coarse grained cemented carbides, which can impact the application on shock environment [27-29]. With the design of WC grain size and distribution in ultrafine hard metals can improve the fracture toughness of ultrafine hard metals obviously, and achieve the combination of proper hardness and fracture toughness in ultrafine WC-(micron WC-Co) systems [30-32]. In principle, many factors will affect the microstructures and mechanical properties of WC-Co materials during the fabrication process, including the shape and granularity of the raw WC particles, composition of the WC-Co powders, selection and content of the grain growth inhibitors, milling conditions and sintering conditions [33-36]. Chen et al. [37] studied that the effect of the matching of coarse and fine powders on the mechanical properties and microstructures of WC-10Co cemented carbides, take to obtain different granularity levels of WC powders through the air classification method, mixed with the Co powder in appropriate proportion, and achieve the double grain sized WC cemented carbides, the alloy obtained a good performance in the drilling experiments.

Li et al. [37] studied that the influence of WC particle size on WC-Co cemented carbides fracture toughness, analyses the mechanism of particle size effect on fracture toughness of cemented carbides. However, the microstructure and fracture mechanism of the ultrafine WC-(micron WC-Co) hard metals have not been investigated systematically. Palm stearin suitability is based on the rheological behavior of the feedstock after being mixed with PS-PE binder system at the powder loading of 59, 61 and 63% vol. Based on the rheological properties, it was concluded that all the MIM feedstocks shows a pseudo plastic behavior and suitable for MIM, except some feedstocks from the high powder loading 63% at high temperature, that shows dilatants behavior [11]. The thermal and physical analyses of feedstock discussed that the critical powder loading spotted for the WC-Co powder is 65%. Thus, the rheological properties of the optimal feedstock with powder loading of 61% show good pseudo plastic behavior, which is suitable for injected molding [12].

5. Grain Growth Inhibitor (GGI)

One of the biggest problems of sintering near nano- and nano scaled powders is the retaining of a small average grain size in the sintered product [24]. Many attempts to achieve nanostructured cemented carbides failed because of very high sintering activity of WC Nano powders. For that reason the addition of grain growth inhibitors, GGI, is required. Small amounts of GGI's are added to starting powders [38]. The most common ones are vanadium carbide, VC, chromium carbide, Cr_3C_2, tantalum carbide, TaC, titanium carbide, TiC and niobium carbide, NbC. Their primary effect is to retain the particle size of starting powders in the sintered product, meanwhile, not only influencing the mechanical properties; increasing the value of hardness at room temperature, but also affecting the toughness, hardness and creep resistance at elevated temperatures [39].

6. Sintering Process

Since the first WC-Co hard metals have been invented and produced more than 70 years ago, activity in research and development laboratories has been directed to the improvement of the characteristics of these alloys and to optimize them for the ever increasing utilization possibilities. Particularly in the field of machining – a main utilization field of hard metals – during the further development of the materials to be processed, new hard metal alloys were continuously developed, which were

characterized by an increase in not only the wear resistance of the cutting bodies, but also their strength [40]. The need for hard metals with improved properties, particularly increased hardness and strength coupled to increased ductility and toughness, has focused attention on the development of grades with finer and finer – grained powders and cemented carbides.

Nowadays, submicron and ultrafine grades of WC – Co, with a WC grain size of 0.4 – 1.0 µm, still dominate the market for cemented carbides. Essentially, they are desired to be sintered from WC – Co superfine powder with a WC grain size up to 0.3 µm or nanocomposite powder with a grain size below to 0.1 µm (100nm) [41-42]. Sintering of cemented carbides is conducted most commonly in vacuum [43-45]. But one of the crucial aspects in fine-grained hard metal sintering is the strong tendency of the very fine WC grains to coarsen, due to their high interface energies as well as differences in individual grain sizes, constituting the driving force for the growth process.

Many researchers developed novel approaches to control rapid growth, such as adding grain growth inhibitors (VC, Cr_3C_2, TaC or their combinations), conducting the sintering at lower temperature with the aid of plasma pressure compaction (P^2C) [46], spark plasma system (SPS) [47] plasma activated sintering (PAS) [48], pulse current process [43], microwave process [43] and hot isostatic pressing (Sinter + HIP or sinter hip / SIP) [43]. Packed particles heated near their melting temperature bond together by sintering. As diffusion accelerates at higher temperatures, sintering is manifested by bonding between contacting particles. Sintering occurs over a range of temperatures, but is accelerated as the particles approach their melting range. For solid – state sintering, it is appropriate to think of sintering with respect to the melting temperature. Snow sinters to form ice at temperatures near – 15 ℃, while hard metals requires temperatures in excess of 1000 ℃ [49].

6.1. Liquid Phase Sintering (LPS)

Liquid phase sintering (LPS) is applied to alloys and composites that melt over a range of temperatures. In the typical situation, the solid grains are soluble in liquid. This solubility causes the liquid to wet the solid, providing a capillary force that pulls the grains together. At the same time, the high temperature softens the solid, further assisting densification. High – diffusion rates are associated with liquids, giving fast sintering or lower sintering temperatures. Important technical advances in LPS came in the 1930s with the development of several materials; cemented carbides (WC–Co), porous bronze (Cu–Sn), tungsten heavy alloys (W-Ni-Cu), copper steels (Fe-Cu-C), and cermet's (TiC-Fe) [49].

6.1.1. The mechanism of LPS

A conceptual view of the events taking place, as sketched in Figure 2 for the case of two mixing powders. The solid grains undergo solid-state sintering during heating. Depending on the solid-liquid solubility relations, different microstructure evolution pathways are possible. The newly formed liquid penetrates between the solid grains, dissolves the sinter bonds, and induces grain rearrangement. Further, because of solid solubility in the liquid, the liquid improves transport rates responsible for grain coarsening and densification. The surface energy associated with pores leads to their annihilation, while there is progressive microstructure coarsening and bonding to increase rigidity. The LPS are ideal for densifying hard materials that cannot be fabricated using other manufacturing approaches. The WC-Co system is a prime example, where the eutectic at 1310 ℃ enables the bonding of micro meter size WC grains into a dense component, such as drill or cutting insert. However, the common form of LPS is persistent LPS, where at the sintering temperature the solid is soluble in the liquid. On cooling, the liquid solidifies to produce a composite microstructure with tailored properties [50-53].
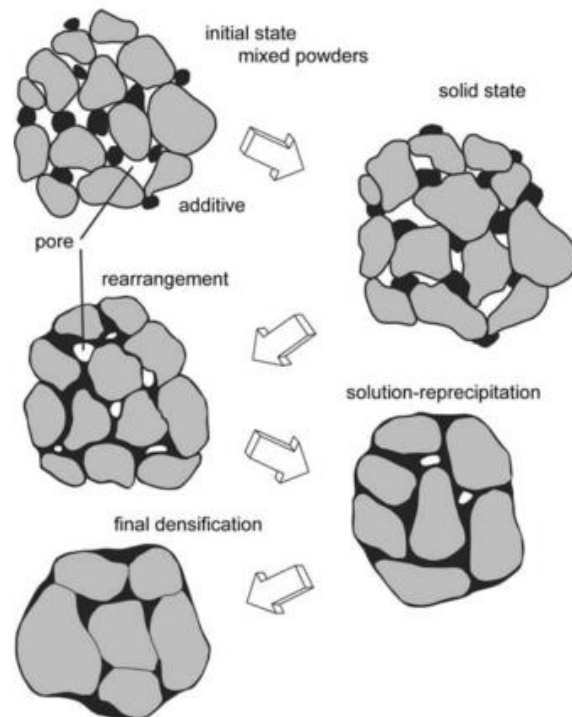
Figure 2: A schematic of the microstructure changes during LPS, starting with mixed powders and pores between the particles. During heating the particles sinter, but when a melt forms and spreads the solid grains rearrange. Subsequent densification is accompanied by coarsening. For many products there is pore annihilation as diffusion in the liquid accelerates grain shape changes that facilitates pore removal [49].

After LPS, the microstructure consists of the solid grain with a solidified liquid network, and possibly residual pores are retained for lubrication, frangibility, or filtration attributes. Thus, liquid phase sintered microstructures exist in several variants with differences in the amount, size, shape and distribution of the phases. Accordingly, substantial performance differences result, especially in properties such as hardness, strength, and elastic modulus. This is especially true for the WC – Co cemented carbides. The study of LPS focuses on linking composition, processing, and properties, with recent attention to improved dimensional precision. The glue between these factors is in the microstructure. A homogenous green structure greatly improves the LPS response. Most effective is placement of the liquid phase on the interface between the solid grains [54-55].

6.2. Microwave Sintering (MS)

Microwave sintering (MS), as a novel technology, has been employed in powder metallurgy for the last few years [56]. It has several advantages, including volumetric heating, non-thermal effect, selective heating over the conventional method [57]. These typical characteristics are beneficial to prepare materials such as accelerated heating rate, shortened processing cycle, high energy efficiency, and being environmentally friendly [58-59]. The microstructures can be improved greatly in terms of fine grain size, uniform cobalt distribution for WC-Co alloys, which can enhance the mechanical properties [60]. It is reported that the microwave sintered sample shows almost no grain growth and the cobalt phase dissolved nearly no tungsten and the sample always showed enhanced mechanical

properties and better resistance towards both erosion and corrosion [61]. It is well known that carbon content plays an important role in the morphologies and microstructures.

In conventional sintering processing, the vacuum was employed to avoid the atmosphere effect on carbon content in WC – Co alloy. Nevertheless, vacuum condition is difficult to achieve in microwave furnace because of arc discharge at higher temperature ($\geq$ 1400 ℃) [62]. Therefore, the atmosphere such as Nitrogen, N_2, Argon, Ar and Hydrogen, H_2 are widely employed in microwave sintering [63]. It can be seen that the sintering atmosphere has an important effect on the microstructures. The carbon content in cemented carbide plays an important role to the morphologies and microstructures. Moreover, the carbon activity in the microwave furnace chamber is expected to be extremely sensitive because of many factors such as moisture level, purity of the protective atmosphere, oxygen content in raw materials, etc [64].

6.3. Comparison of Microwave Sintering (MS) and Conventional Sintering

Microwave sintering of cemented carbides like WC – Co also has been investigated since 1991 after pioneering work of Cheng [65-67] and thereafter by Porada [68-70]. Breval [67] et al. investigated on the microwave sintering of 0.1 – 1μm sized WC particles with cobalt as binder and compared the results with conventional sintering of the same powders. They reported that the microwave sintered sample hardly exhibits any growth and the cobalt phase does not reveal any dissolution of tungsten whereas in the conventionally sintered one. Porada and here group showed that the microwave reaction sintering of W, C, and Co powders yielded sintered WC-6Co compacts with fine and uniform microstructure (with an average grain size of 0.6μm) which exhibited a 10% increase in hardness values in comparison to tools made by conventional route [68-70].

As is well known, microwave sintering greatly reduces the time as well as the energy expended when compared to conventional sintering due to the inherent different in the heating mechanism of the two methods and the possibility of achieving very fast heating rates in the former. A typical comparison of the sintering schedules as depicted in Figure 3 shows that there is considerable reduction in the sintering time when microwaves are employed for heating the sample; 165 min for microwave sintering as compared to 330 min for conventional sintering. Figure 4 shows the photographs of the compacts before and after microwave sintering.

Initially, the microwave sintering in case of microcrystalline powder was carried out at two different temperatures, 1450 and 1550 ℃, to find out at what temperature, a higher density could be achieved. It was found that at only a temperature set point of 1550 ℃, a considerably higher density was obtained, though the sample densified well at 1450 ℃ when sintering was carried out conventionally. In case of nanocrystalline powder, different temperatures from 1100 ℃ up to 1550 ℃ were employed to verify if a well sintered sample could be obtained at a much lower temperature than samples sintered conventionally. However, as seen from Figure 5, microwave sintering of nanocrystalline powders also did not yield samples of higher density unless the temperature set point was 1550 ℃, and this was true whether the sample was a compact made from microcrystalline powders or nanocrystalline powders. This is due to the expectation to observe a microwave effect, due to which sintering could be expected to take place at a lower temperature and which could be more pronounced especially in case of nanocrystalline powders [71].
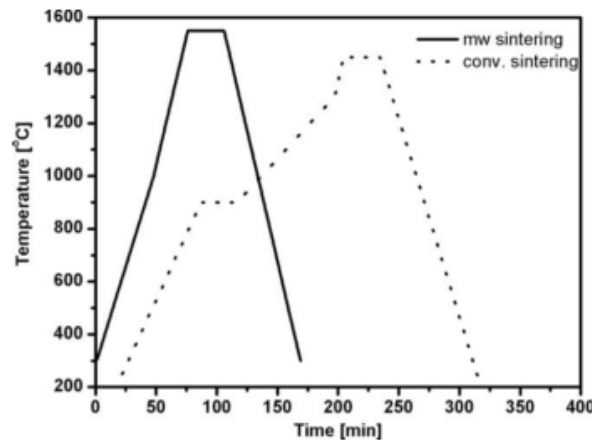
Figure 3: Comparison of sintering schedules employed for conventional and microwave processing [71]

Figure 4: Photographs of the WC–12Co compacts derived from microcrystalline powders after microwave sintering in a 90N2–10H2 atmosphere, before (left hand side) and after (right hand side) sintering [71].

In all the microwave sintered samples, the periphery was seen to be less sintered when compared to the center of the sample. This aspect in the first instance was observed as a porosity difference between the periphery and center. Microwave processing is well-known to cause a volumetric heating where the heating takes place uniformly within the sample since the process is an energy conversion (microwave to heat energy) unlike a conventional heating, where heating takes place by energy transfer from the heating elements to the sample [72].
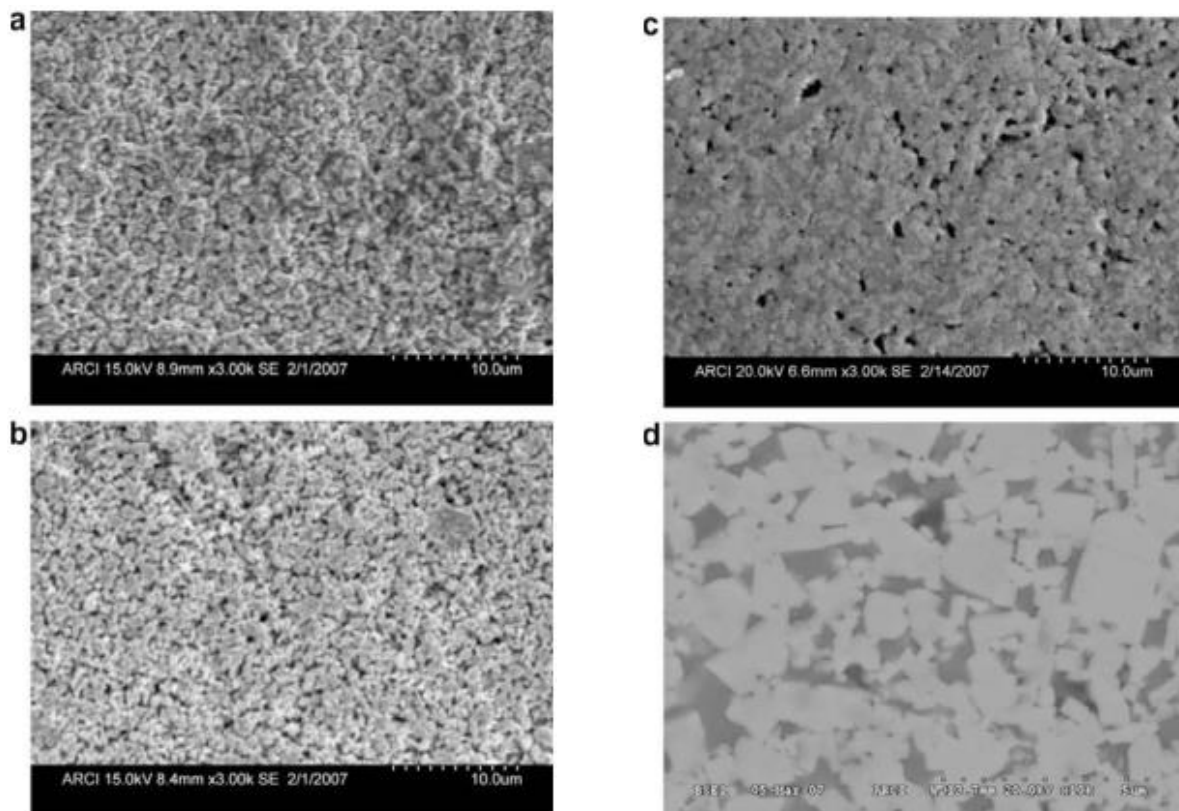
Figure 5: SEM image of microwave sintered nanocrystalline powder processed at different temperature set points; (a) 1250 ℃. (b) 1350 ℃ (c) 1450 ℃ and (d) 1550 ℃ [72]

7. Conclusion

Based on this study it can be concluded that, metal injection molding (MIM) is newly developed technology to form metals and alloys into desired shape. Since this MIM technology is growing rapidly in Malaysia, hence it will give a good prospect for Malaysian Industries to get involved in this technology and share the benefits. Besides that, this technology helps through characterization of metal powders and binder components. The addition of grain growth inhibitor (GGI) to the starting powder also been reviewed and the role of GGI is to increase the value of hardness, fracture toughness and creep resistance at certain temperature. The use of microwave for sintering of green compacts during powder metallurgy process is emerging as a novel and innovative technology with many advantages over conventional sintering. The comparison of microwave sintering over conventional sintering has been discussed.

8. Acknowledgement

References

[1]   Abolhasani H, Muhamad N. A new starch-based binder for metal injection molding. Journal of Materials Processing Technology. 2010 Apr 1; 210(6):961-8.

[2]   German RM, Bose A. Injection Molding of Metals and Ceramics Metal Powder Industries Federation. Princeton, NJ. 1997.

[3]   Prakash L. A review of the properties of tungsten carbide hardmetals with alternative binder systems. In13 th International Plansee Seminar'93. 1993 May (Vol. 2, pp. 80-109).

[4]   Gille G, Bredthauer J, Gries B, Mende B, Heinrich W. Advanced and new grades of WC and binder powder–their properties and application. International Journal of Refractory Metals and Hard Materials. 2000 Mar 1;18(2):87-102.

[5]   Norgren S, García J, Blomqvist A, Yin L. Trends in the P/M hard metal industry. International Journal of Refractory Metals and Hard Materials. 2015 Jan 31;48:31-45.

[6]   Aristizabal M, Ardila LC, Veiga F, Arizmendi M, Fernandez J, Sánchez JM. Comparison of the friction and wear behaviour of WC–Ni–Co–Cr and WC–Co hardmetals in contact with steel at high temperatures. Wear. 2012 Mar 20;280:15-21.

[7]   Correa EO, Santos JN, Klein AN. Microstructure and mechanical properties of WC Ni–Si based cemented carbides developed by powder metallurgy. International Journal of Refractory Metals and Hard Materials. 2010 Sep 30;28(5):572-5.

[8]   Rhee BO, Jung YC, Lee JH. The rheological characterization of PIM feedstocks at low shear rates. Powder Injection Molding Technologies. 1998;23:79-91.

[9]   Subuki I. Injection moulding of 316l stainless steel powder using palm stearin based binder system (Doctoral dissertation, Ph. D. Thesis. Universiti Teknologi Mara, Malaysia).

[10]   S.Y. M.Amin., N. Muhamad, & K.R.Jamaludin, 5th Powder Metallurgy Symposium and Exhibition, Kuala Lumpur (2011).

[11]   Amin SY, Muhamad N, Jamaludin KR, Fayyaza A, Yunn HS. Ball milling of WC-Co powder as injection molding feedstock. InApplied Mechanics and Materials 2012 (Vol. 110, pp. 1425-1430). Trans Tech Publications.

[12]   Amin SY, Muhamad N, Jamaludin KR, Fayyaz A, Yunn HS. Characterization of the feedstock properties of metal injection-molded WC-Co with palm stearin binder system. Sains Malaysiana. 2014 Jan 1;43(1):123-8.

[13]   Fayyaz A, Muhamad N, Sulong AB, Yunn HS, Amin SY, Rajabi J. Micro-powder injection molding of cemented tungsten carbide: feedstock preparation and properties. Ceramics International. 2015 Apr 30;41(3):3605-12.

[14]   Liu ZY, Loh NH, Tor SB, Khor KA, Murakoshi Y, Maeda R. Binder system for micropowder injection molding. Materials Letters. 2001 Mar 31;48(1):31-8.

[15]   Loebbecke B, Knitter R, Haußelt J. Rheological properties of alumina feedstocks for the low-pressure injection moulding process. Journal of the European Ceramic Society. 2009 Jun 30;29(9):1595-602.

[16]   Loh NH, Tor SB, Tay BY, Murakoshi Y, Maeda R. Fabrication of micro gear by micro powder injection molding. Microsystem Technologies. 2008 Jan 1;14(1):43-50.

[17]   Fabijanić TA, Alar Ž, Ćorić D. Influence of consolidation process and sintering temperature on microstructure and mechanical properties of near nano-and nano-structured WC-Co cemented carbides. International Journal of Refractory Metals and Hard Materials. 2016 Jan 31;54:82-9.

[18]   Fabijanić TA, Alar Ž, Pötschke J. Potentials of nanostructured WC–Co hardmetal as reference material for Vickers hardness. International Journal of Refractory Metals and Hard Materials. 2015 May 31;50:126-32.

[19]   Al-Aqeeli N, Saheb N, Laoui T, Mohammad K. The synthesis of nanostructured wc-based hardmetals using mechanical alloying and their direct consolidation. Journal of Nanomaterials. 2014 Jan 1;2014:18.

[20]   Jia K, Fischer TE, Gallois B. Microstructure, hardness and toughness of nanostructured and

conventional WC-Co composites. Nanostructured Materials. 1998 Jul 31;10(5):875-91.

[21] Fang ZZ, Wang X, Ryu T, Hwang KS, Sohn HY. Synthesis, sintering, and mechanical properties of nanocrystalline cemented tungsten carbide–a review. International Journal of Refractory Metals and Hard Materials. 2009 Mar 31;27(2):288-99.

[22] Richter V, Poetschke J, Holke R, Michaelis A. Nanoscaled Hardmetals–Fiction or Reality. InProceedings of the 18th International Plansee Seminar 2013 Jun (pp. 1257-1273).

[23] Li T, Li Q, Fuh JY, Yu PC, Lu L. Two-material powder injection molding of functionally graded WC–Co components. International Journal of Refractory Metals and Hard Materials. 2009 Jan 31;27(1):95-100.

[24] Chang SH, Chen SL. Characterization and properties of sintered WC–Co and WC–Ni–Fe hard metal alloys. Journal of Alloys and Compounds. 2014 Feb 5;585:407-13.

[25] Liu C, Lin N, He Y, Wu C, Jiang Y. The effects of micron WC contents on the microstructure and mechanical properties of ultrafine WC–(micron WC–Co) cemented carbides. Journal of Alloys and Compounds. 2014 May 5;594:76-81.

[26] Lin N, He Y, Wu C, Zhang Q, Zou J, Zhao Z. Fabrication of tungsten carbide–vanadium carbide core–shell structure powders and their application as an inhibitor for the sintering of cemented carbides. Scripta Materialia. 2012 Nov 30;67(10):826-9.

[27] Zhao S, Song X, Wei C, Zhang L, Liu X, Zhang J. Effects of WC particle size on densification and properties of spark plasma sintered WC–Co cermet. International Journal of Refractory Metals and Hard Materials. 2009 Nov 30;27(6):1014-8.

[28] Sun L, Jia C, Cao R, Lin C. Effects of Cr 3 C 2 additions on the densification, grain growth and properties of ultrafine WC–11Co composites by spark plasma sintering. International Journal of Refractory Metals and Hard Materials. 2008 Jul 31;26(4):357-61.

[29] Kim HC, Shon IJ, Yoon JK, Doh JM. Consolidation of ultra fine WC and WC–Co hard materials by pulsed current activated sintering and its mechanical properties. International Journal of Refractory Metals and Hard Materials. 2007 Jan 31;25(1):46-52.

[30] Eroglu S, Baykara T. Effects of powder mixing technique and tungsten powder size on the properties of tungsten heavy alloys. Journal of Materials Processing Technology. 2000 Jun 15;103(2):288-92.

[31] Armstrong RW, Cazacu O. Indentation fracture mechanics toughness dependence on grain size and crack size: application to alumina and WC–Co. International Journal of Refractory Metals and Hard Materials. 2006 Mar 31;24(1):129-34.

[32] Deng X, Patterson BR, Chawla KK, Koopman MC, Fang Z, Lockwood G, Griffo A. Mechanical properties of a hybrid cemented carbide composite. International Journal of Refractory Metals and Hard Materials. 2001 Nov 30;19(4):547-52.

[33] Wang X, Fang ZZ, Sohn HY. Grain growth during the early stage of sintering of nanosized WC–Co powder. International Journal of Refractory Metals and Hard Materials. 2008 May 31;26(3):232-41.

[34] Gille G, Bredthauer J, Gries B, Mende B, Heinrich W. Advanced and new grades of WC and binder powder–their properties and application. International Journal of Refractory Metals and Hard Materials. 2000 Mar 1;18(2):87-102.

[35] Zhang FL, Wang CY, Zhu M. Nanostructured WC/Co composite powder prepared by high energy ball milling. Scripta materialia. 2003 Dec 31;49(11):1123-8.

[36] Carroll DF. Sintering and microstructural development in WC/Co-based alloys made with superfine WC powder. International Journal of Refractory Metals and Hard Materials. 1999 May 31;17(1):123-32.

[37] Liu C, Lin N, He Y, Wu C, Jiang Y. The effects of micron WC contents on the microstructure and mechanical properties of ultrafine WC–(micron WC–Co) cemented carbides. Journal of Alloys and Compounds. 2014 May 5;594:76-81.

[38] Weidow J, Norgren S, Andrén HO. Effect of V, Cr and Mn additions on the microstructure of WC–Co. International Journal of Refractory Metals and Hard Materials. 2009 Sep

30;27(5):817-22.

[39] Gille G, Szesny B, Dreyer K, Van Den Berg H, Schmidt J, Gestrich T, Leitner G. Submicron and ultrafine grained hardmetals for microdrills and metal cutting inserts. International Journal of Refractory Metals and Hard Materials. 2002 Jan 31;20(1):3-22.

[40] Rödiger K, Dreyer K, Willert-Porada M, Gerdes T, inventors; Widia GmbH, assignee. Hard metal or cermet sintered body and method for the production thereof. United States patent US 6,293,986. 2001 Sep 25.

[41] Lassner E, Schubert WD. Properties, Chemistry, Technology of the Element, Alloys, and Chemical Compounds. Vienna University of Technology, Vienna, Austria, Kluwer. 1999:124-5.

[42] Shao GQ, Duan XL, Xie JR, Yu XH, Zhang WF, Yuan RZ. Sintering of nanocrystalline WC-Co composite powder. Reviews on Advanced Materials Science. 2003 Dec;5(4):281-6.

[43] Kneringer G. 14th International Plansee Seminar'97: Late papers. Plansee AG; 1997.

[44] Cha SI, Hong SH, Ha GH, Kim BK. Microstructure and mechanical properties of nanocrystalline WC-10Co cemented carbides. Scripta Materialia. 2001 May 18;44(8):1535-9.

[45] Cha SI, Hong SH, Ha GH, Kim BK. Mechanical properties of WC–10Co cemented carbides sintered from nanocrystalline spray conversion processed powders. International Journal of Refractory Metals and Hard Materials. 2001 Nov 30;19(4):397-403.

[46] Sampath A, Stiglich JJ, Sudarshan TS, Singh R, Choi KS. Fast consolidation of WC–Co. Powder metallurgy. 2002 Feb 1;45(1):25-7.

[47] Yamamoto G, Omori M, Hashida T, Kimura H. A novel structure for carbon nanotube reinforced alumina composites with improved mechanical properties. Nanotechnology. 2008 Jun 24;19(31):315708.

[48] Groza JR, Dowding RJ. Nanoparticulate materials densification. Nanostructured materials. 1996 Oct 31;7(7):749-68.

[49] German RM, Suri P, Park SJ. Review: liquid phase sintering. Journal of Materials Science. 2009 Jan 1;44(1):1-39.

[50] Lenel FV. Sintering in the Presence of a Liquid Phase. AIME TRANS. 1948 Jun;15(4):1-9.

[51] Kingston WE. The physics of powder metallurgy. McGraw-Hill; 1951.

[52] Gurland J, Norton JT. Role of the binder phase in cemented tungsten carbide-cobalt alloys. Trans. AIME. 1952 Oct;194(10):1051-6.

[53] Parikh NM, Humenik M. Cermets: II, Wettability and microstructure studies in liquid-phase sintering. Journal of the American Ceramic Society. 1957 Sep 1;40(9):315-20.

[54] Riedel R. Handbook of ceramic hard materials. Wiley-VCH Verlag GmbH; 2000.

[55] Luyckx S, Love A. The dependence of the contiguity of WC on Co content and its independence from WC grain size in WC–Co alloys. International Journal of Refractory Metals and Hard Materials. 2006 Mar 31;24(1):75-9.

[56] Bykov YV, Rybakov KI, Semenov VE. High-temperature microwave processing of materials. Journal of Physics D: Applied Physics. 2001 Jul 7;34(13):R55.

[57] Demirskyi D, Ragulya A, Agrawal D. Initial stage sintering of binderless tungsten carbide powder under microwave radiation. Ceramics International. 2011 Mar 31;37(2):505-12.

[58] Demirskyi D, Borodianska H, Agrawal D, Ragulya A, Sakka Y, Vasylkiv O. Peculiarities of the neck growth process during initial stage of spark-plasma, microwave and conventional sintering of WC spheres. Journal of Alloys and Compounds. 2012 May 15;523:1-0.

[59] Guo Y, Yi J, Luo S, Zhou C, Chen L, Peng Y. Fabrication of W–Cu composites by microwave infiltration. Journal of Alloys and Compounds. 2010 Mar 4;492(1):L75-8.

[60] Bao R, Yi J, Zhang H, Peng Y. A research on WC–8Co preparation by microwave sintering. International Journal of Refractory Metals and Hard Materials. 2012 May 31;32:16-20.

[61] Breval E, Cheng JP, Agrawal DK, Gigl P, Dennis M, Roy R, Papworth AJ. Comparison between microwave and conventional sintering of WC/Co composites. Materials Science and

Engineering: A. 2005 Jan 25;391(1):285-95.

[62] Tompsett GA, Conner WC, Yngvesson KS. Microwave synthesis of nanoporous materials. ChemPhysChem. 2006 Feb 13;7(2):296-319.

[63] Zhou C, Yi J, Luo S, Peng Y, Li L, Chen G. Effect of heating rate on the microwave sintered W–Ni–Fe heavy alloys. Journal of Alloys and Compounds. 2009 Aug 12;482(1):L6-8.

[64] Bao R, Yi J. Effect of sintering atmosphere on microwave prepared WC–8wt.% Co cemented carbide. International Journal of Refractory Metals and Hard Materials. 2013 Nov 30;41:315-21.

[65] Cheng J. Study on microwave sintering technique of ceramics materials. PhD ThesisChina Wuhan University of Technology, Wuhan, China. 1991.

[66] Cheng JP, Agrawal DK, Komarneni S, Mathis M, Roy R. Microwave processing of WC-Co composites and ferroic titanates. Material Research Innovations. 1997 Jun 1;1(1):44-52.

[67] Breval E, Cheng JP, Agrawal DK, Gigl P, Dennis M, Roy R, Papworth AJ. Comparison between microwave and conventional sintering of WC/Co composites. Materials Science and Engineering: A. 2005 Jan 25;391(1):285-95.

[68] Gerdes T, Whxert-Porada M. Microwave sintering of metal-ceramic and ceramic-ceramic composites. InMRS Proceedings 1994 (Vol. 347, p. 531). Cambridge University Press.

[69] Ro K, Dreyer K, Gerdes T, Willert-Porada M. Microwave sintering of hardmetals. International Journal of Refractory Metals and Hard Materials. 1998 Dec 31;16(4):409-16.

[70] Kolaska H, Willert-Porada M, Rodiger K, Gerdes T, inventors; Widia GmbH, assignee. Composite and process for the production thereof. United States patent US 6,124,040. 2000 Sep 26.

[71] Sunil BR, Sivaprahasam D, Subasri R. Microwave sintering of nanocrystalline WC–12Co: Challenges and perspectives. International Journal of Refractory Metals and Hard Materials. 2010 Mar 31;28(2):180-6.

[72] Holcombe CE, Dykes NL. Importance of "casketing" for microwave sintering of materials. Journal of materials science letters. 1990 Apr 1;9(4):425-8.