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

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ABSTRACT

Cemented tungsten carbide is widely used for a variety of machining, cutting, drilling and other applications. 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, compacting and followed by multi-atmosphere sintering of green compact were analysed. The sub-micron (<1.0µm) and less than 10.0µm of WC powders are sintered with a metal binder 6%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 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 we found that in order to attain better mechanical properties, a fine grain size of powder is necessary and could be sintered in nitrogen-based atmosphere, too. Therefore, the attention of this work is to develop and produce wear resistant component with better properties or comparable to the commercial ones.

General Terms

Cemented carbide.

Keywords

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

1. INTRODUCTION

WC-Co cemented carbides, also commonly referred as hardmetals, and is well known as a class of composite materials. It has long been realised that it served a tremendous practical importance and often 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, tungsten carbide (WC) is the hard phase providing hardness and wear resistant while cobalt (Co) is the matrix phase, in hardmetal tungsten carbides 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 consolidation [1]. 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 [1-3]. Further reduction in the sintering temperature can be achieved by chemical additives, and this is a common practice in industrial sintering processes.

The effect of sintering behaviour and grain size of WC-Co will be addressed in the present work. In combination with powder parameters, the sintering cycle plays a large role in creating the final microstructure due to solid state and liquid phase sintering effect [3,4]. The mechanisms through which the solid state densification occurs are however typical liquid phase sintering processes with rearrangement and solution-reprecipitation [5]. As reported by Lee et al. [6], fine size of cobalt powders are known to be effective in the reduction of residual porosity and cobalt pooling. As a result, 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 the sintering temperature for nano-sized powder can be lower than that a large size powders due to lower the melting point of the binder contributed by a large surface area [4].

2. MATERIALS AND METHODS

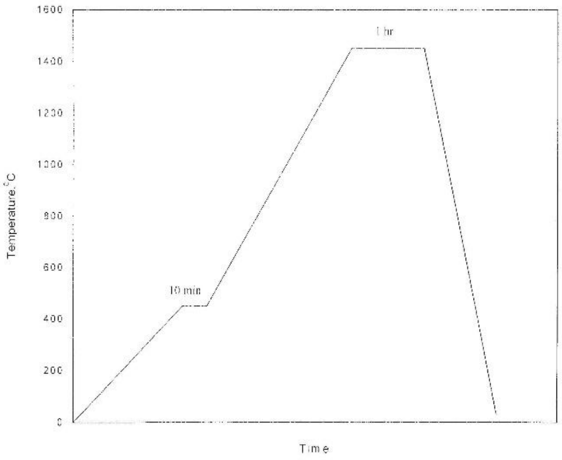
Elemental powders of tungsten carbide (<1.0µm and 10µm), and cobalt (<1.26µm) supplied by Buffalo Tungsten Inc., New York were used to produce the alloys. Powders were weighed to give the compositions of 94%WC-6%Co. Paraffin wax powder and heptane were added to the powder mixtures before wet mixing in turbula mixer for 3h with 8mm steel balls. 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 weight powder ratio was kept at 3:1. The samples used for this study are 15mm x 15mm x 3mm thickness. The sub-micron WC-Co powders were compacted by the application of a uniaxial pressure at 590MPa. Green density was in the average of 70-75% relative to the theoretical density.

The powder compacts were sintered at temperatures ranging from 1200 to 1550°C for 1h. Sintering was performed in nitrogen-based (95%N2+5%H2) atmosphere. The heating rate was 5ºC/min up to 450ºC and 10ºC/min for the remainder of the sintering cycle. Slow cooling to room temperature was allowed to occur after the completion of the isothermal hold.

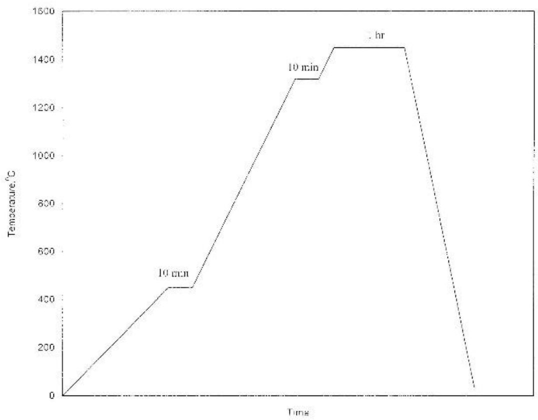
Measurements of the hardness and transverse rupture stress (TRS) were obtained according to ASTM B294-92 (2006) and ASTM B 406-96 (2005), respectively. The densities of the sintered samples were determined by Archimedes method using Specific Gravity Meter. An INSTRON 3369 Testing Machine (Series IX Merlin) was used to measure TRS. Samples were mounted, ground and polished using successively finer diamond polishing compounds ranging from 3 to 1µm. Mounts were etched for 5 min with Murakami solution before being examined using Scanning Electron Microscopy (SEM).

3. RESULTS AND DISCUSSION

The main purpose of this work was to investigate of the differences in sintering behaviour of WC powder, which contain 6wt% cobalt, in nitrogen-based sintering atmospheres. 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. A uniform and high density is required after the sintering of sub-micron WC-6Co powders. Thus to minimise the pores and gases generated during the process, a holding steps are introduced (450-1320-1450ºC) as shown in Figure 1(b). The holding at 450ºC is suitable for removing all oxides [6].



(a)



(b)

Fig. 1. Heating schedule for WC-6Co powders compacted at 590MPa;
(a) 450-1450°C and (b) 450-1320-1450°C, 1h holding time

Table 1. Mechanical properties of <1.0µm WC-6Co powders compacted at 590MPa and sintered at different conditions.

Heating Schedule, °C	Hardness, HR_A	Sintered Density, g/cm^3
450 – 1450	85.3	14.53
450 – 1320 – 1450	86.5	14.82

Further holding step expected to promote the melting and homogenous distribution of cobalt, thus improve sintering. The effect of heating schedule presented in Table 1. The heating schedules with holding steps (450-1320-1450ºC) are more effective than direct heating (450-1450ºC) without any steps. The first step in Figure

1(b) was intended to eliminate residual gases and the second step to promote the melting and homogenous distribution of cobalt. In practice, heating is slow because of the constraints of binder removal and thermal inertia of furnaces. During slow heating, significant shrinkage is observed prior to liquid formation [4,5].

The sintering curves of WC-6Co powders were determined over the range 1200-1550°C, Figure 2. The liquid phase sintering (LPS) mechanism was applied during sintering process with composed of four stages [4,7]. Initially, during heating, solid state densification occurs as driven by chemical potential gradients. When the first cobalt liquid forms (at ~1300ºC), additional densification occurs since the volume of liquid increase rapidly. This liquid of Co is not in equilibrium with the WC. Consequently, it spreads rapidly, penetrating along interparticle contacts where it lubricates the sliding of WC particles past one another. This allows, pore filling by both solid (WC) and liquid (Co) flow, termed rearrangement. Subsequently, solution-reprecipitation occurs [4,5,7].

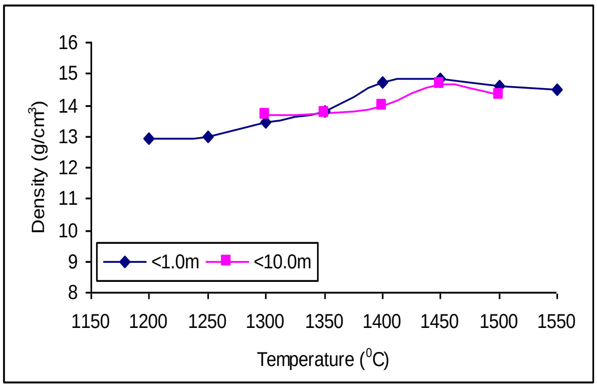
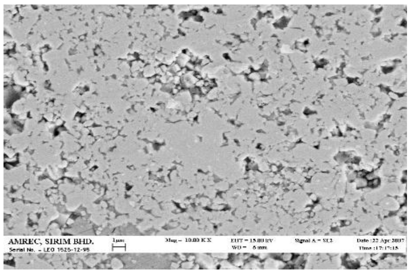


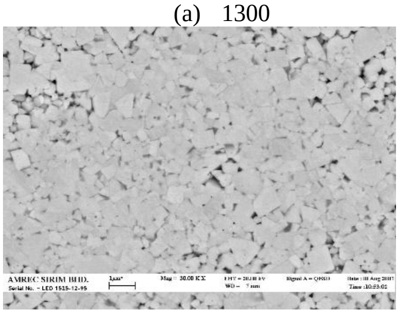
Fig. 2. The experimental result on the relationship between density of sintered WC-6Co and sintering temperature.

In this work, it was found that the sintered density of <1.0μm WC-6Co increase rapidly above 1300ºC, and reached saturated value (14.8g/cm3) at the sintering temperature 1450ºC. A similar result was obtained for <10.0μm sample. The only difference being that the sintered density of the micron-size sample is lower than the sub-micron samples. As such this is agreement with Fang etc. [2] and Sailer etc. [8], who also attributed that, the ultrafine-grained hardmetals exhibit high density values.

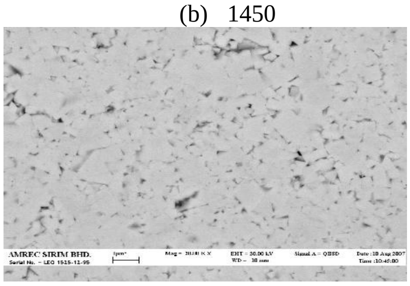
When a compact of sub-micron WC-6Co powder was sintered through heating schedules with holding steps, the small size of WC grains was maintained as shown in Figure 3. The small WC grains in the alloy are associated with the heating time sufficient to reduce the defects, such as the rough surface [3] and strains, 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 1450ºC as shown in Figure 3(b). At sintering temperature above 1300ºC, 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. While, sintering at temperature much below 1300°C would produce excessive amounts of residual porosity, Figure 3(a). As the sintering temperature was increased, corresponding WC grain growth was observed. When the sintering reached 1500°C, coarsening structure of WC appeared, giving oversintered microstructures correlated with the distortion of the samples, Figure 3(c). This distortion was associated with the formation of excess liquid phase. As reported by many workers [4-7], it is estimated that 35-volume percent liquid is needed to obtain full density by rearrangement processes.



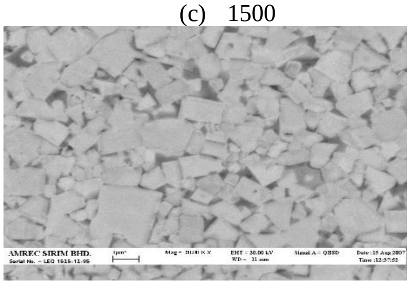
(a) 1300



(b) 1450



(c) 1500



(d) Commercial WC tool insert

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

It was observed in the present work that it is possible to successfully sintered WC-6Co powder in the nitrogen-based (95%N2+5%H2) atmosphere. It was demonstrated that atmosphere sintering clearly led to reduction in sintering temperature to 1450ºC compared to the same alloys sintered in vacuum (1500ºC) and pure hydrogen atmosphere (1485ºC) [2,3]. Therefore, the use of gas mixtures (nitrogen + hydrogen) in sintering atmospheres are important since the hydrogen provides oxide reduction, while nitrogen, neutral with respect to oxide reduction, is used to minimise explosive dangers. Hence, the atmosphere selection for sintering 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 more cheap, safety and environmentally friendly.

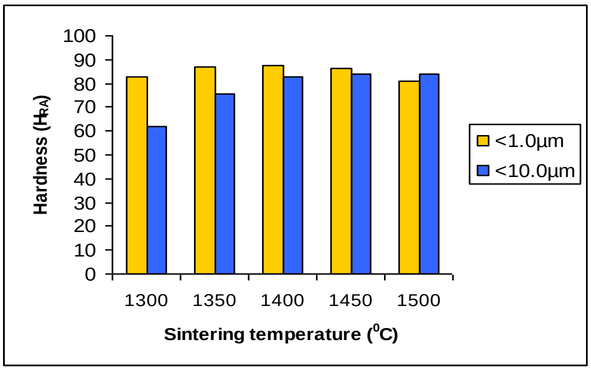


Fig. 4. The relationship between hardness particle size 1.0 µm and 10.0µm of WC at various sintering temperature.

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 are reached up to 88HR_A, which are comparable with the commercial ones. This higher hardness may be associated with the finer WC structure distribution. The increment of hardness and transverse rupture strength (TRS) are due to formation of liquid phase, which leads the sintered density to increase especially at sintering temperature 1450ºC. 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 <10.0µm sintered WC-6Co from previous work are shown in Table 3. The mechanical properties of this micron-size powder were lower against 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.

Table 2. Physical and mechanical properties of sintered 1.0µm WC-6Co samples.

Sintering temperature, °C	Sintering density, g/cm3	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
Commercial uncoated WC	*14.9*	*88.7*	*1900*

Sintering temperature, °C	Sintering density, g/cm3	Hardness, HRA	Transverse Rupture Strength, MPa
1300	13.71	61.7	158
1350	13.74	75.4	303
1400	13.96	82.5	926
1450	14.67	84.1	448
1500	14.29	84.2	951

4. CONCLUSION

From this work, sub-micron size of WC-6Co powders could be processed by wet mixing in turbula for less than 3h compared with more than 17h by wet milling process. Sintering of WC-6Co powders in nitrogen-based atmosphere is acceptable to reach ~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 gives significant results on the sintering properties. The results of this study can be summarised as follows:

i. Compacting process will give impact of hardness and density to sintered samples. In the future work, cold isostatic pressing (CIP) should be carried out in order to reduce the number of pores by providing a uniform pressure over entire specimen.
ii. 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.
iii. The good densification of sintered WC-6Co was achieved (~14.8 g/cm3), compatible with the commercial values.
iv. It was reached a satisfactory value of hardness, ~ 88HRA, but need further study to improve TRS values.
v. Sintering at 1500ºC or higher will coarsening the WC structure and weaken the properties of the sintered samples.

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