

# EFFECT OF SINTERING ATMOSPHERE ON THE MECHANICAL PROPERTIES OF SINTERED TUNGSTEN CARBIDE

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**Abstract.** One of the crucial stages in fabrication of WC-Co composite is sintering process. Inappropriate sintering state, especially sintering temperature will lead to an abnormal grain growth and thus reduce the mechanical properties of the sintered parts. Sintering atmosphere also plays a big role in oxidation, carburizing, decarburizing and nitriding on the surface of sintered parts. Prevention of any unwanted process during sintering is demanded to maintain the performance of WC-CO composites without any by-products. In this work, the effect of different sintering atmosphere and sintering temperatures was studied on the mechanical properties of WC-Co composites. 95% nitrogen (N<sub>2</sub>) mixed with 5% hydrogen (H<sub>2</sub>) gases was used as sintering atmosphere in a tube furnace whereas vacuum atmosphere was carried out in vacuum furnace. The sintering process was conducted at 1300°C and 1400°C, respectively. Higher relative density, hardness and transverse rupture strength (TRS) were observed on the sintered parts. Sintering under N<sub>2</sub>-H<sub>2</sub> atmosphere exhibited better mechanical properties. Low mechanical properties observed in vacuum atmosphere was probably due to over-sintering which led to grain growth activities and formation of  $\eta$ -phase.

## 1 Introduction

Tungsten carbide-cobalt (WC-Co) is a well-known of hard and relatively composite materials which are expected to exhibit excellent hardness, wear resistance, thermal stability and corrosion resistance [1]. WC is bonded together with Co to form cemented carbides which have been widely used as cutting tools and wear resistant parts [2]. The cooperation of hard WC phase and the soft Co binder phase has contributed to unique good combination of high hardness and transverse rupture strength (TRS) [3].

WC-Co composite is typically fabricated using powder metallurgy route where WC and Co powders were mixed, compacted and sintered. During sintering, densification of the powders takes place where WC grains with higher solubility would dissolve in the Co-rich liquid. Many sintering methods are available such as liquid stage sintering, vacuum sintering, hot isostatic pressing, microwave sintering, spark plasma sintering and many more. One of the crucial aspects during sintering is high possibility of grain growth. The inappropriate sintering state will lead to abnormal grain growth and consequently reduce the mechanical properties of WC-Co composites.

The final properties of sintered WC-Co is determined by various processing parameters such as powder size, powder composition, compaction densities and furnace parameters including sintering temperature,

sintering time and cooling rate. However, there is lack of attention on effect of sintering atmosphere. Shvab et al. [4] stated that furnace atmosphere is one of the important factors during sintering of stainless steel. During sintering process, the reaction between the furnace atmosphere and sintered parts took place. They are strongly associated with the chemical composition of the atmosphere.

In the liquid phase sintering, the sintering atmosphere consumed with nitrogen, hydrogen, argon or helium gas. The main goals were to prevent oxidation on the surface of sintered parts. Besides, on certain metal, it can avoid carburizing, decarburizing and nitriding. Another favorable sintering atmosphere is vacuum sintering. In the vacuum sintering, the chamber in which the compact parts are heated and cooled is connected to vacuum pump by means of which the chamber is usually pumped down to the desired pressure level prior to and during heating. These will equip sintering atmosphere with vacuum environment. The vacuum condition is nearly free of oxygen, nitrogen, and hydrogen. Hence, it is expected to produce better sintered parts. However, vacuum sintering is costly and only can be employed on a small scale in very special cases where it is essential for research work.

Many works related to sintering environment have been reported. Gao et al. [5] showed that synthesis of LiFePO<sub>4</sub> under vacuum condition exhibited higher charge-discharge capacity as compared to traditional Ar/N<sub>2</sub> atmosphere at constant pressure. Similarly, Zhang

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et al. [6] concluded that the effect of carbon coating on  $\text{LiFePO}_4/\text{C}$  prepared by vacuum thermal decomposition delivered better cycle and rate performances than  $\text{LiFePO}_4/\text{C}$  by conventional sintering. Recently, Yao et al. [7] have also worked on  $\text{LiFePO}_4/\text{C}$  (LPC/C) composites. They found that LPC/C composite being produced under vacuum sintering environment resulted in the formation of porous structure. The structure had excellent cycle performance as compared to argon sintering environment. Besides, the vacuum sintering reduced the optimum sintering temperature by nearly  $100^\circ\text{C}$ . In another report, Kurlov et al. [8] stated that sintering of WC-Co composite in vacuum atmosphere is accompanied by the loss of a small amount of carbon. The composite composition was slight shifted to the brittle ternary phase ( $\eta$ -phase) of  $\text{Co}_6\text{W}_6\text{C}$  and  $\text{Co}_3\text{W}_3\text{C}$  phase transformation.

Shvab et al. [4] have investigated the effect of sintering atmosphere on microstructure of high Cr-alloyed sintered stainless steel. They observed that sintering in the nitrogen gas atmosphere produced coarse grain microstructures as compared to nitrogen-hydrogen atmosphere. On the other hand, Bao and Yi [9] reported that decarburizing on the sample surface occurred under both nitrogen atmosphere and mixed gases of nitrogen and hydrogen atmosphere. However, no effect on the sample surface was noticeable in argon atmosphere. Rui et al. [10] have studied the effect of sintering atmospheres on properties of stainless steel porous hollow fiber membranes. They observed that the air sintering environment and the  $\text{CO}_2$  sintering environment could lead to metal oxidation while inert atmospheres ( $\text{He}$  and  $\text{N}_2$ ) caused carbon remaining in SS hollow fibers. It is also observed that  $\text{H}_2$  atmosphere was effective in removing organic additives without metal oxidation. In other work, Tian et al. [11] investigated the effect of sintering atmosphere on corrosion resistance of nickel-ferrite oxide based inert anode. It is reported that the corrosion rate of the anode prepared in the atmosphere containing the oxygen content is lower than the anode prepared in the vacuum environment.

The above reviews emphasized the important and significant effect of sintering atmosphere on the final properties of sintered parts. Hence, this study highlighted the effect of different sintering atmosphere on the mechanical properties of WC-Co composite. Two different sintering atmospheres which were 95% nitrogen ( $\text{N}_2$ ) - 5% hydrogen ( $\text{H}_2$ ) atmosphere and vacuum atmosphere were used at different sintering temperatures of  $1300^\circ\text{C}$  and  $1400^\circ\text{C}$ . The relative density, hardness and TRS of the sintered parts were also investigated.

## 2 Experimental Works

Starting materials containing 94wt% WC, 6wt% Co and heptanes were mixed in a tabular shaker mixer using wet mixing process. The duration of the mixing was three hours at a constant speed of 56 rpm. The average particle sizes of WC and Co powder were  $0.8\ \mu\text{m}$  and  $3.51\ \mu\text{m}$ , respectively. Upon completion, the mixed powders were subjected to drying in oven at a temperature slightly

above the boiling point of heptanes for 2 hours to remove the heptanes from the mixture.

The dried mixture powders were sieved to obtain fine and uniform particle size before compacted into final shape at dimension of  $16\text{mm} \times 16\ \text{mm} \times 3\ \text{mm}$ . The powder was compacted using Automatic Hydraulic Press Machine at a pressure of 20 tons.

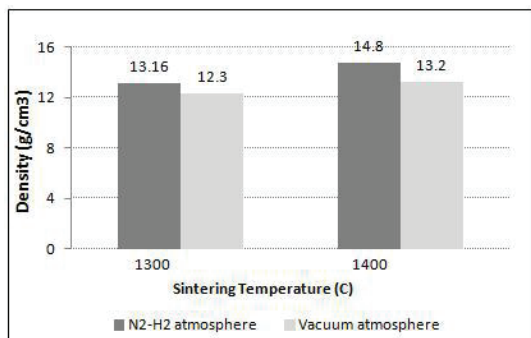
The green samples were then subjected to cold isostatic pressure (CIP) to obtain denser and uniform samples. Finally, the samples were proceeded to sintering process. Sintering was conducted at two different atmospheres; 95% nitrogen ( $\text{N}_2$ ) - 5% hydrogen ( $\text{H}_2$ ) atmosphere in tube furnace and vacuum atmosphere in a vacuum furnace at the sintering temperature of  $1300^\circ\text{C}$  and  $1400^\circ\text{C}$ , respectively.

The dimension of sintered samples was  $12.5\ \text{mm} \times 12.5\ \text{mm} \times 4.2\ \text{mm}$ . The relative density of sintered samples was measured using an electronic densimeter. The hardness of the samples was measured by Vickers Hardness tester at a load of 500 g using a diamond pyramid indentation. The transverse rupture strength (TRS) of the sintered samples was obtained using the ultimate testing machine.

## 3 Results and Discussion

### 3.1. Relative Density

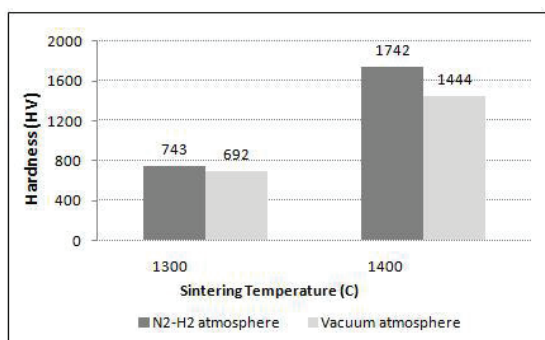
Figure 1 shows the comparison of relative density sintered at  $1300^\circ\text{C}$  and  $1400^\circ\text{C}$  in different atmosphere. It is noted that the relative density of the sintered parts at the sintering temperature of  $1400^\circ\text{C}$  is higher as compared to sintering temperature of  $1300^\circ\text{C}$ . During sintering process, elimination of the pore region occurs which lead to the improvement of parts density. As the temperature was increased to  $1400^\circ\text{C}$ , higher thermal energy was produced and gave better driving forces for the binder to completely fill out the pore region, thus increasing the relative density. It is also perceived that the relative density of the parts sintered in  $\text{N}_2\text{-H}_2$  atmosphere was slightly higher as compared to parts sintered in vacuum atmosphere. The relative density of sintered parts sintered in  $\text{N}_2\text{-H}_2$  atmosphere at the sintering temperature of  $1300^\circ\text{C}$  is  $13.6\ \text{g/cm}^3$ . While the relative density of sintered part sintered in vacuum atmosphere at similar sintering temperature is  $12.3\ \text{g/cm}^3$ . Respectively, the relative density of sintered parts sintered in  $\text{N}_2\text{-H}_2$  atmosphere at  $1400^\circ\text{C}$  is  $14.8\ \text{g/cm}^3$ . While the relative density of sintered part sintered in vacuum atmosphere at similar sintering temperature is  $13.2\ \text{g/cm}^3$ . These could be associated with the window sintering band [7] sintering at vacuum atmosphere reduced the optimum sintering temperature as compared to inert gas atmosphere. Although the parts were sintered at similar sintering temperatures, the parts which were sintered at vacuum atmosphere could exceed the window sintering range and became over-sintered band. Consequently, it led to grains coarsening phenomena.



**Figure 1.** Relative density comparison at the sintering temperature of 1300°C and 1400°C

### 3.2 Hardness

Figure 2 shows the comparison of the hardness of sintered sample at different sintering temperatures and atmosphere. Generally, the hardness of the sintered samples increases with the increasing of sintering temperature. As the sintering temperature increases from 1300°C to 1400°C, the hardness was reported increases drastically from 743 HV to 1742 HV. The drastic increase on the hardness at sintering temperature of 1400 °C for both sintering atmospheres is probably resulted from full densification on the sintered parts. High temperature generates higher thermal energy which provides a better driving force for the binder phase, thus increases the relative density. The hardness trend was consistent with the relative density. The hardness results are seen to be correlated with the relative density. Low relative density on the sintered parts sintered at vacuum atmosphere was consequently contributed to low hardness.



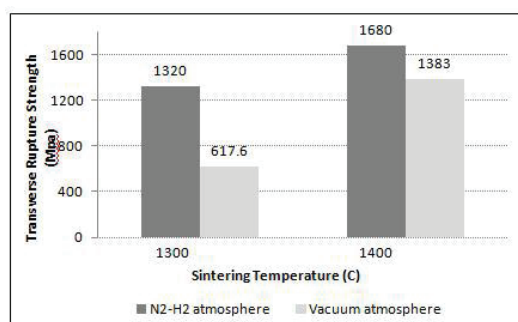
**Figure 2.** Hardness comparison at the sintering temperature of 1300°C and 1400°C

### 3.3 Transverse Rupture Strength (TRS)

The variation of TRS as a function of sintering temperature at different atmosphere is shown in Figure 3. The parts sintered at 1300°C in N<sub>2</sub>-H<sub>2</sub> atmosphere shows a TRS value of approximately 1320 MPa. The TRS was increased to 1680 MPa as the sintering temperature was raised to 1400°C. As for vacuum sintering atmosphere, the TRS was observed at 617.6 MPa at sintering temperature of 1300°C and increased to 1383 MPa at the sintering temperature of 1400°C. It is believed that the gradually increasing of the sintering temperature helps in

promoting sintering process and eliminating pore thus improves the TRS value. The full densification at 1400°C is entirely reducing the strain points along the rupture mechanism and increasing TRS value.

It is also clearly seen that the TRS values obtained in a N<sub>2</sub>-H<sub>2</sub> sintering atmosphere exhibited higher values as compared to vacuum sintering atmosphere. This could be probably due to grains coarsening phenomena in parts which were sintered in vacuum atmosphere. As claim by Yao et al. [7] sintering under vacuum atmosphere required lower sintering. Thus, the grain growth occurred at the sintering temperature of 1400°C in vacuum atmosphere, was possibly due to over-sintered. In addition, the low TRS value could be also due to the formation of η-phase that made the WC-Co composite extremely brittle.



**Figure 3.** TRS comparison at sintering temperature of 1300°C and 1400°C

## 4 Conclusion

In this work, WC-Co composite was prepared by the powder metallurgy method and sintered at different sintering atmosphere; N<sub>2</sub>-H<sub>2</sub> atmosphere and vacuum atmosphere at two different sintering temperatures; 1300°C and 1400°C. The results revealed that the relative density, hardness and TRS were increased as the sintering temperature was higher. High temperature promotes the densification process and effectively eliminates the pore. Simultaneously, higher relative density, hardness and TRS were observed on parts sintered in the N<sub>2</sub>-H<sub>2</sub> atmosphere. Low mechanical properties exhibited on the parts sintered in vacuum atmosphere probably was due to over-sintering. Over-sintering led to grain growth activities and formation of η-phase which produced the brittle WC-Co composite. Further studies should be conducted to reveal a clear explanation on the relation between hardness properties and relative density, over sintering stage and mechanism of η-phase formation.

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## References

1. Q. Yang, J. Yang, H. Yang, J. Ruan, The effects of fine WC contents and temperature on the microstructure and mechanical properties of inhomogeneous WC-(fine WC-Co) cemented carbides, *Ceramics International*, **Vol 42**, pp 18100–18107(2016)
2. X. Ren, Z. Peng, C. Wang, H. Miao, Influence of nano-sized La<sub>2</sub>O<sub>3</sub> addition on the sintering behavior and mechanical properties of WC–La<sub>2</sub>O<sub>3</sub> composites *Ceramics International*, **Vol 41**, pp 14811–14818 (2015)
3. C. B. Wei, X.Y. Song, J. Fu, X.M. Liu, Y. Gao, H.B. Wang, S.X. Zhao, Microstructure and properties of ultrafine cemented carbides – Differences in spark plasma sintering and sinter-HIP. *Material Science and Engineering*. **Vol A 552**, pp 427 – 433 (2012)
4. R. Shvab, E. Dudrova, O. Bergman, S. Bengtsson, Effect of sintering atmosphere on the microstructure of high Cr-Alloyed sintered stainless steel. *Powder Metallurgy Progress*, **Vol 13**, No 3 – 4, pp 103 – 108 (2013)
5. L. J. Gao, Y.L. Zhang, Preparation of LiFePO<sub>4</sub> positive electrode material by vacuum calcination and its electrochemical performance in Lithium-ion batteries, *J. Nanchang Univ. (Nat. Sci.)*, **Vol 32**, pp 239–242 (2008)
6. L. L. Zhang, G. Peng, X.L. Yang, P.C. Zhang, High performance LiFePO<sub>4</sub>/C cathode for lithium ion battery prepared under vacuum conditions. *Vacuum*, **Vol 84**, pp 1319–1322 (2010)
7. Y. Yao, P. Qu, X. Gan, X. Huang, Q. Zhao, F. Liang, Preparation of porous-structured LiFePO<sub>4</sub>/C composite by vacuum sintering for lithium-ion battery. *Ceramics International*, **Vol 42**, pp 18303–18311 (2016)
8. A. S. Kurllov, A.I. Gusev, A.A. Rempel, Vacuum sintering of WC-8 wt.% Co hardmetals from WC powders with different dispersity. *International Journal of Refractory Metals and Hard Materials*, **Vol 29**, pp 221 – 231 (2011)
9. R. J. Bao, J. Yi, Effect of sintering atmosphere on microwave prepared WC–8wt.%Co cemented carbide. *Int. Journal of Refractory Metals and Hard Materials*, **Vol 41**, pp 315–321 (2013)
10. W. Rui, C. Zhang, C. Cai, X. Gu, Effects of sintering atmospheres on properties of stainless steel porous hollow fiber membranes. *Journal of Membrane Science*, **Vol 489**, pp 90–97 (2015)
11. Z. L. Tian, W. C. Guo, Y. Q. Lai, K. Zhang, J. Li, Effect of sintering atmosphere on corrosion resistance of cermet inert anode for aluminum electrolysis. *Trans. Nonferrous Met. Soc. China*, **Vol 26**, pp 2925–2929 (2016)