The Effect of Adding Carbon and Vanadium Carbide on Microstructure and Mechanical Properties of Ultra-Fine WC-Co Composite

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ABSTRACT

Tungsten carbide cobalt (WC-Co) composite is commonly fabricated using powder metallurgy route such as mixing, compaction and sintering process. During the sintering process, densification of the powders takes place where WC grains having higher solubility would dissolve in the Co-rich liquid. One of the crucial aspects during sintering process is grain growth. The inappropriate sintering state will lead to an abnormal grain growth, which consequently will deteriorate the mechanical properties of WC-Co composites. Thus, a suitable grain growth inhibitor is recommended to be added in WC-Co composites to minimize the problem. In the present work, the effect of adding carbon (C) and vanadium carbide (VC) on the mechanical properties of ultra-fine WC-Co composite is investigated. The amount of Co and C is fixed at 6wt% and 0.2wt%, respectively, while the amount of VC is varied in the range of 0 to 1wt%. It is observed that, an addition of C and VC in the WC-Co composite is able to control the abnormal of grain's growth. The relative density decreases with the increasing of wt% of VC. Similar trend is observed for hardness and

ISSN 1823- 5514, eISSN 2550-164X
Received for review: 2017-04-08
Accepted for publication: 2017-06-05
Published: 2018-02-15

transverse rupture strength (TRS). An increasing of the wt% of VC will cause excessive VC particles sited in the WC/Co grains boundary, thus hinder the liquid Co wettability to fill in the porosity between WC particles. The present of porosity will consequently permit grains growth activities. The finest grains size is achieved at the formulation 2 with 0.2wt% C and 0.4 wt% VC. The maximum hardness and TRS is attained at a similar formulation. The hardness of WC-Co composite with 0.2wt% of C and 0.4wt% of VC was approximately 40% much higher than commercial cutting insert.

Keywords: *Ultrafine WC-Co composite, Carbon, Vanadium Carbide, mechanical properties*

Introduction

Tungsten carbide-cobalt (WC-Co) composite is well known as a composite material which is expected to exhibit excellent hardness, wear resistance, thermal stability and corrosion resistance [1, 2]. The WC is bonded together with Co to form cemented carbides which have been widely used as cutting tools and wear resistance parts [3, 4]. The cooperation of hard WC phase and the soft Co binder phase has contributed to unique combination of high hardness and transverse rupture strength (TRS) [5].

Typically, the properties of WC-Co composite depend primarily on Co content and grain size of the WC. The Co content is usually prepared in the range of 3 – 30wt% and the grain size of the WC is widespread from micron to nanometer [2, 6]. The Co is commonly incorporated in WC composite as a result of its good wetting behavior and excellent solubility among WC particles. The fracture toughness of WC composite increases greatly with an increasing of Co content [7]. On the other hand, it is known that by developing nanometer grain size, the properties likes hardness, strength, fatigue and wear resistance are also improved [8].

The WC-Co composite is typically fabricated using powder metallurgy route where WC and Co powders are mixed, compacted and sintered. During the sintering process, the densification of the powders takes place where the WC grains having higher solubility would dissolve in the Co-rich liquid. One of the crucial aspects during sintering is high possibility of grain growth. The problem becomes worse during sintering of ultrafine or nanocystalline WC. The inappropriate sintering state will lead to an abnormal of grain growth, which is consequently will reduce the mechanical properties of WC-Co composites.

To solve the problem, an addition of suitable grain growth inhibitor is proposed. The most common grain growths inhibitors have been used previously in the WC–Co composite are VC, Cr_3C_2, BbC, Mo_2C, TaC, TiC

and ZrC. Among those, VC and Cr_3C_2 have been claimed as the most effective grain growth inhibitor due to their high solubility and mobility in Co phase [2, 9]

Numbers of scientific papers reported about the abnormal grain growth especially on nano-sized WC-Co composites [10-15]. The grain size of sintered WC became larger at higher sintering temperature, slower and longer holding time. The grain growth reduced the hardness and fracture toughness of the sintered samples [7]. As remarked by Poetschke et al. [11], the grain growth in a liquid phase sintering was derived from the diffusion of atoms to form larger grains. Atoms dissolved within the liquid phase and re-precipitated at existing solids. The larger grain later grew at the expense of smaller grains which are dissolved in the liquid phase. This behavior was known as Ostwald ripening.

There has been a large number of research claimed that the most successful way of controlling the grain growth in the WC-Co composite is grain growth inhibitor [2, 3, 7]. Ren et al. [3] added ZrC nano-powder in binderless WC powder which was sintered using spark plama sintering. They reported that the coarsening of WC grain growth was suppressed with an addition of 1wt% of ZrC nano-powder, thus resulted in more homogenous microstructure, higher hardness and fracture toughness.

Wu et al. [2] investigated the effect of adding Cr_3C_2 powder in WC-Co alloys. The results showed that an increase of the Cr_3C_2 content was capable in refining the WC grains. In other work, Poetschke et al. [10] studied the influence of VC and Cr_3C_2 grain growth inhibitors in the sintering of binderless WC. The results showed that both carbides reduced grain growth, but Cr_3C_2 transformed into finer microstructure as compared to VC. Similar finding was reported by Boony et al. [15]. The addition of 0.8wt% of Cr_3C_2/VC in WC-Co composite has increased the hardness and reduced grain size of WC which has significantly accelerated the wear performance.

Xiao et al. [16] investigated the effect of VC and NbC inhibitors in the ultrafine WC-10wt%Co composite. They concluded that VC and NbC inhibitors can refine the WC grains and consequently increase the hardness and fracture toughness. The smallest grains are achieved at 470 μm at 1wt% of VC when sintered at 1350ºC. In addition, Kumar and Singh [13] also explored the effect of the VC inhibitor in ultrafine WC-20wt%Co composite. The outcomes revealed the optimized properties were achieved at the composition of WC-20%Co-7.5%VC. The average grain size was 102 nm and the hardness and fracture toughness were 1870.6 kgf/mm^2 and 14.4 MN/mm$^{3/2}$, respectively. They have concluded that the VC exhibits a strong ability in suppressing the grain growth continuation of WC. However, as compared with Cr_3C_2, the VC deteriorated the homogeneity in the microstructure and exaggerated the distribution range of the WC grain sizes.

The best combination to obtain high hardness and toughness is achieved at the formulation of WC-10wt%Co - 0.6wt%Cr_3C_2 - 0.06wt%La_2O_3.

Mahmoodan et al. [17] were also interested in investigating the grain growth inhibitors. They added 0.6% TaC and 0.7% VC in the WC-10%Co composite. The grain size of the sintered samples was observed at the average of 0.38µm. It is also reported that the hardness of the sintered samples were increased up to 24% more than the inhibitor-free samples. Likewise, the fracture toughness was 35% higher than the inhibitor-free samples.

In the present work, efforts are focused on the influence of C and VC addition in the WC-Co composite. As we know, the carbon content plays an important role in the morphology and microstructure of sintered samples. Decarburizing of WC, which would form a W_2C phase is observed at the initial of WC phase, especially when ultrafine and nano-size of WC is used. By adding extra C, the formation of W_2C phase could be suppressed. In this study, the amount of Co and C are fixed at 6wt% and 0.2wt%, respectively while the amount of VC is varied in the range of 0 to 1wt%. The microstructure, density, hardness and fracture toughness of the ultra-fine WC-Co composite are investigated.

Experimental

Samples preparation

The starting materials consist of WC powders, Co powders, C powders and VC powders. The average sizes of WC, Co, C and VC powders are 0.2 µm, 1.26 µm, 150 µm and 5 µm, respectively. Samples was prepared using five different formulations are listed in Table 1. The amount of Co and C are fixed at 6wt% and 0.2wt%, respectively.

The mixing was conducted in a wet mixing condition using heptane as a wetting agent. The mixing process was done in a tabular shaker mixer for three hours at a speed of 56 rpm. Upon completion, the mixture was placed in the drying oven at a temperature slightly above the boiling point of heptanes for 2 hours to remove the heptane from the mixture. The dried mixture powders were sieved to obtain fine and uniform particle size range. The mixtures were prepared at 9 gm and inserted in the die cavity having size of 15 mm X 15 mm. The mixture was then compacted using Automatic Hydraulic Press Machine at a pressure of 18 tons.

Table 1. Samples formulation

Metal powder	WC (wt%)	Co (wt%)	C (wt%)	VC (wt%)
Average size (µm)	0.2	1.6	150	3.5
Formulation 1	93.8	6.0	0.2	0.2
Formulation 2	93.6	6.0	0.2	0.4
Formulation 3	93.4	6.0	0.2	0.6
Formulation 4	93.2	6.0	0.2	0.8
Formulation 5	93.0	6.0	0.2	1.0

The green samples were then subjected to cold isostatic pressure (CIP) to obtain denser and uniform samples. The compaction pressure was set at 30000 psi which is equivalent to 207 MPa. Finally, the samples were sent to the sintering process. Sintering was conducted in 95% nitrogen (N_2) - 5% hydrogen (H_2) atmosphere in a tube furnace at the sintering temperature of 1400ºC.

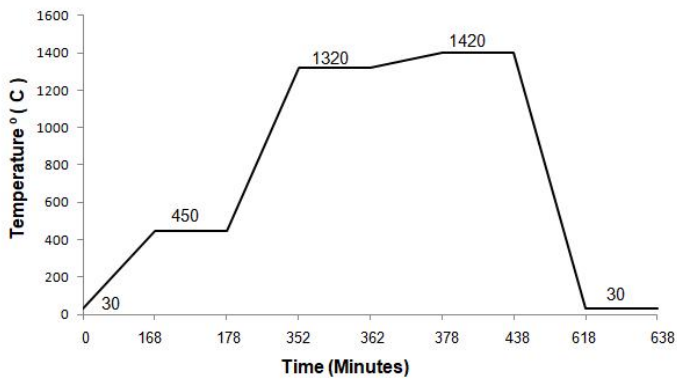

Figure 1: Heating profile of sintering process

The sintering process involved 4 stages which were pre-heating, heating, 2nd stage heating and cooling. At the pre-heating stage, the green samples were slowly heated from room temperature to 450ºC at a heating rate of 5ºC/min. The samples were held at 450ºC for 10 minutes before continuing heating to 1320ºC. At this stage, the heating rate was 10ºC/min and holding time was 10 minutes. At the third stage, the samples were continuously heated to 1400ºC at the heating rate of 10ºC/min. At this temperature, the holding time was one hour. Finally, the samples were cooled until 30ºC at a cooling rate of 7.6ºC/min. The sintering heating profile is represented in Figure 1.

Microstructure characterization

The microstructure of the sintered samples was analyzed using a metallographic cross section. The grain structures were examined by scanning electron microscope (SEM).

Mechanical characterization

The mechanical properties such as density, hardness and TRS were studied as a function of VC addition. The relative density was measured using Archimedes methods. The hardness measurement was done using Vickers Hardness tester at a load of 500g. The diamond pyramid indentation was carried out randomly on the surface of sintered samples for at least five located points. The average values were reported. Finally, the transverse rupture strength (TRS) was obtained using the Universal Testing Machine.

Results and Discussion

Microstructure

Figure 2 shows the microstructure of the sintered samples at various formulations. As overall, the WC grains have a typical prismatic and trigonal shape. A slight change in the microstructure morphology is observed when the wt% of VC increases. The brighter areas are WC particles, while the dark areas are the matrix containing of Co-VC-C. It is noticeable that formulation 4 exhibited abnormal microstructure. The abnormal morphology on the samples of formulation 4 could probably due decarburization behavior which leads to formation of W_2C. The W_2C exhibits epitaxial growth on WC grains and forms nearly complete shell around the WC particles [18].

From Figure 2, it can be observed that the average grain sizes for all formulations are less or equivalent to 200 nm. The sizes are appoximately similar as initial powder sizes which are in the range of ultrafine scale. The finding has proven that, an addition of C and VC are able to hinder the grain growth activities. During the liquid phase sintering process, Co dissolves among the WC particles. With the presence of VC inhibitors, the particles were soluble in the binder and segregated at the WC/Co grain boundary. The present of VC inhibitors has altered the WC/Co grain boundary by forming mixed crystals or new phases, reducing the interface energy and therefore the driving force for grain growth [19]. These will slow down the diffusion process and inhibits the grain growth [2]

However, the grain sizes for formulation 5 which containing 1wt% of VC were observed slightly bigger as compared to other formulation. As amount of VC added to the composition, more VC atoms are distributes along the grain boundary. Too much of VC in the Co binder could affects the

wetting ability of the Co binder to penetrate between the WC particles. These will allow the grain to growth [2].

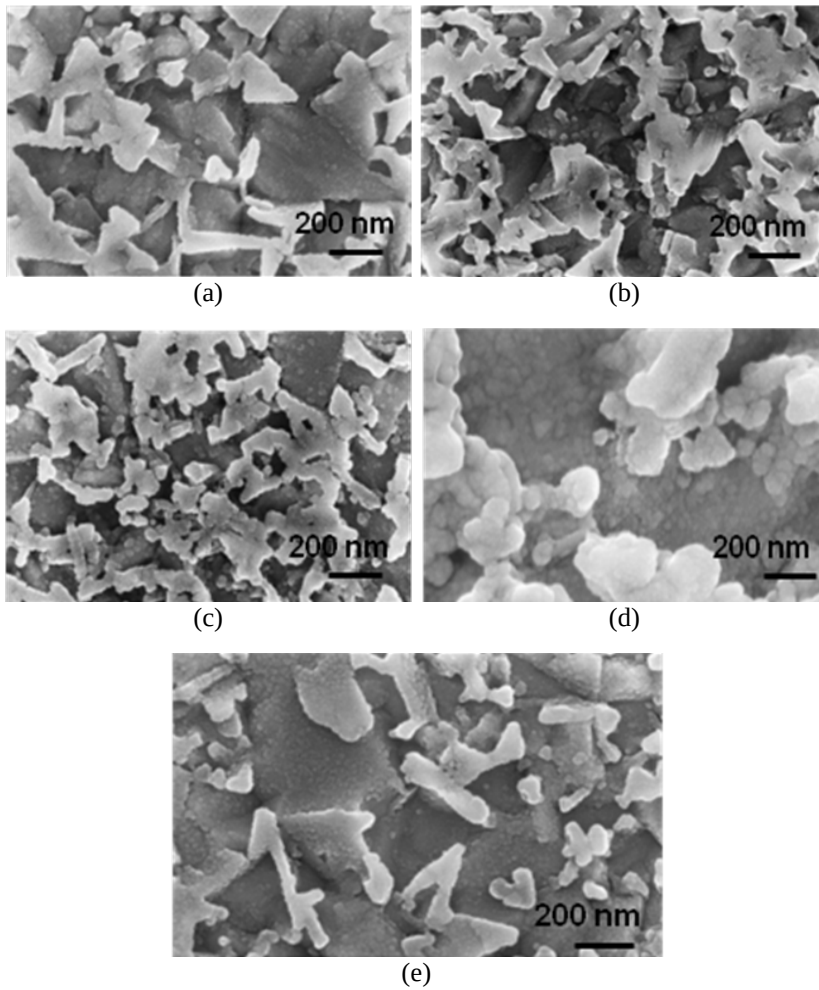

Figure 2: Microstructure of the sintered samples at 50.00kX magnification. (a) Formulation 1, (b) Formulation 2, (c) Formulation 3, (d) Formulation 4, (e) Formulation 5

Relative density

Figure 3 shows the influence of VC addition towards the relative densities of the sintered samples. It can be clearly observed that the relative density decreases when the wt% of VC increases. During sintering process, the elimination of the pore region occurs which leads to an improvement of parts density. An increasing of the wt% of VC causes excessive VC particles sited in the WC/Co grain boundary thus hinders the liquid Co wettability to fill in the porosity of the WC particles. It will consequently reduce the density. In addition, as reported by Kumar and Singh [13], the present of VC particles sited in the WC/Co grain boundary contributed to the formation of thin layer of VC encapsulation of WC particles and lead to separation of neighbor WC particles. This phenomenon will increase the porosity generation which consequently reduces the density.

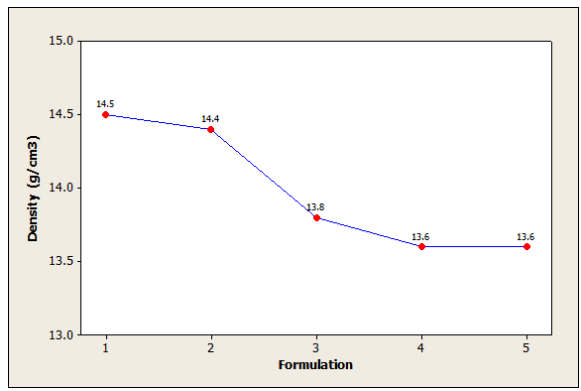

Figure 3: Relative density of the sintered samples at various formulations

Hardness

Figure 4 shows the effect of VC increment on the hardness of sintered samples. It is shown that formulation 2 containing 0.4wt% VC has the highest hardness with the value of 2725 HV. The hardness obtained is 40% higher as compared to commercial cutting insert with a hardness of 1967 HV.

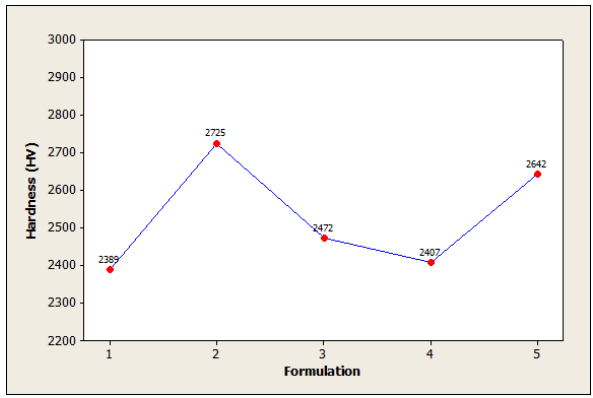

Figure 4: Hardness of the sintered samples at various formulations

According to Hall–Petch relationship [3, 16,], the hardness is determined by the grain size, and fine microstructure leads to higher hardness. The presence of VC has hindered grain growth activities which lead to more homogenous and finer WC grains. Thus, it contributes to an increasing of the hardness. However, as the amount of VC continues to increase, the hardness decreases. The lowest hardness value observed in the sample in formulation 4 is due to the present of W_2C.

Transverse Rupture Strength (TRS)

Figure 5 shows the relation of TRS with wt% of WC. Similar finding was observed where the maximum of TRS was achieved at a present of 0.4 wt% of VC as in formulation 2. The finding is in a good agreement with the grains microstructure and hardness results. Maximum TRS is gained at 0.4 wt% of VC with the value of 2041MPa. As we know, the fracture toughness is influenced by many factors with complicated mechanisms. It is believed that the low density as well as the poor microstructure characteristics such as high porosity leads to the lowest fracture toughness. High density observed in formulation of 0.4 wt% VC indicated good microstructures with less pores which consequently increased the TRS.

In addition, high TRS at formulation with 0.4 wt% of VC could be also explained by interfaces effect. Fine grain sizes will lead to the increasing of interfaces between WC grains and the Co binder. The fractions of crack path through WC and Co binder interfaces will increase and contribute to a significant amount of fracture energy. Thus, the phenomoneon improves the overall TRS [14].

Although TRS is known inversely proportional to the hardness, the addition of carbon in these formulations could probably hinder the formation of η-phase which is finally contributing to high TRS value [20].

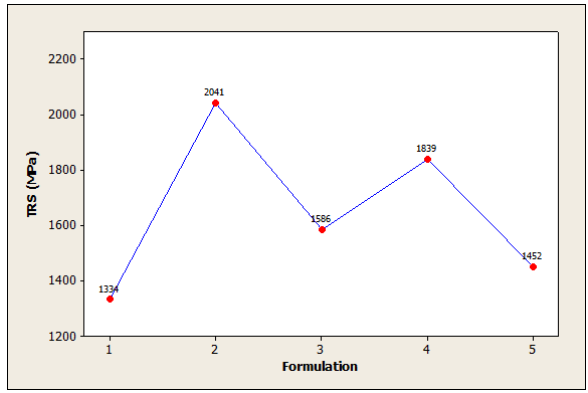

Figure 5: TRS of the sintered samples at various formulations

Conclusion

The effect of adding carbon and vanadium carbide on the mechanical properties of ultra-fine WC-Co composite has been investigated. It is noted that the addition of C and VC in WC-Co composites is able to control the abnormal grains growth. The relative density was decreased as an increasing of wt% of VC. Similar trend was observed for hardness and TRS. An increasing of the wt% of VC will cause excessive VC particles sited in the WC/Co grains boundary, thus hinder the liquid Co wettability to full in the porosity of WC particles. The present of VC significantly prevented grains growth activities.

The finest grains size was achieved at the formulation 2 with 0.2wt% C and 0.4 wt% VC. In addition, the maximum hardness and TRS was attained at a similar formulation. The hardness of WC-Co composites with 0.2wt% of C and 0.4wt% of VC is approximately 40% much higher than commercial cutting insert.

Acknowledgements

This research work was financed by the Government of Malaysia under the e-Science fund project of the Ministry of Science, Technology and Innovation

(MOSTI) (Project No: 06-01-01-SF0702). The authors are gratefully recognized all the supports, scientific contributions and collaboration from the supportive partners of Advanced Material Research Centre (AMREC).

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