Effect of VC and C Addition on Mechanical Properties and Microstructures of WC-Co Hardmetals Processed in Nitrogen-Based Atmosphere

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Abstract
The WC-Co, WC-Co-VC and WC-Co-C samples are fabricated using powder metallurgy technique. The mixed powder is compacted under the pressure of 625 MPa, cold-isostatic pressed at 200 MPa and sintered at temperature in the range of 1350 – 1450°C nitrogen-based atmosphere. The mechanical properties of the samples are analyzed using Vicker’s microhardness tester, universal tensile machine and scanning electron microscope. Test results reveal that WC-Co-C sample has better mechanical properties as compared to WC-Co and WC-Co-VC due to the formation of homogeneous and dense structure.

Keywords: Powder metallurgy; WC-Co; VC; C addition; hardness; transverse shear strength; microstructure

1.0 INTRODUCTION

Cemented carbide is developed by a hard phase WC skeleton embedded in a tough a binder phase which usually consisting of Co. WC-Co composed two phases; hard-brittle carbide and soft-ductile cobalt. Hard-brittle carbide phase provide the hardness of the alloys meanwhile cobalt act as metal binder. Cobalt-rich liquid contains W and C assist in densification and development of rigid skeletal structure [1]. Cemented carbide in most cases is the first choice for tools for metal cutting operations because of it is not only hard and good wear resistance, but also very high toughness. Tungsten carbide (WC) The cemented carbide can also be used for wear components as well as for the engineering industry.

WC grain growth leads to increase in microstructural engrossment [2], thus reducing the hardness and strength of the alloy. Grain growth of WC grains can be solved by adding small amount of WC grain growth inhibitor, typically <1.0 wt.% of a metallic carbide such VC, Cr₃C₂, NbC, [3-5]. The addition of WC grain growth inhibitor resulted in the dissolution or reprecipitation of W and C in the liquid binder phase, which subsequently limit WC grain growth [6]. It was reported that the strength, hardness, and wear resistance of an alloy increase as the grain size decreases [7,8]. Meanwhile, adding small amount of carbon powder enable the WC-Co alloys to avoid decarburization during sintering process [3]. The decarburization of WC results in a formation of brittle W₁₋₂C phase, hence reduce the mechanical properties of the composite.

In this work, vanadium carbide (VC) and carbon (C) were added in the development of WC-Co hardmetal using powder metallurgical process. The effect of addition of these powders on the mechanical properties and microstructure of WC-Co
hardmetal will be discussed in this paper.

2.0 MATERIALS AND METHODS

In this study, three WC–Co based materials were produced using the same WC as based raw material. The raw materials were weighed according to the compositions as shown in Table 1. Each composition was mixed using tubular mixer for three hours with heptane used as a medium for wet-mixing. Tungsten-carbide balls with 10 mm diameter were used as a grinding media. The ball to the powder weight ratio was set at 30:1. The mixed powders were then dried and granulated before compaction process.

Table 1 Sample composition

<table>
<thead>
<tr>
<th>Composition</th>
<th>Weight percentage (wt %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>WC-Co</td>
<td>94.0</td>
</tr>
<tr>
<td>WC-Co-V</td>
<td>93.4</td>
</tr>
<tr>
<td>WC-Co-C</td>
<td>93.8</td>
</tr>
</tbody>
</table>

The mixed powder was compacted at a pressure of 625 MPa to a size of 16 mm x 16 mm x 3 mm. The green samples were then cold-isostatic pressed (CIP) at 200 MPa to obtain more homogeneous and denser structure. The compacted samples were sintered for 1 hour at temperature range between 1350 - 1450 °C as shown in Figure 1. The sintering process took place in a tube furnace under nitrogen-based atmosphere with a ratio of 95%N₂ and 5%H₂. Microhardness and transverse rupture strength (TRS) of the sintered samples were acquired using Vicker’s hardness tester and universal testing machine, respectively. The samples for microhardness test were ground using silicon carbide paper in the sequence of 120, 320 and 800 grit paper in order to obtain a well-defined indentation. The density of the sintered samples was determined by Archimedes method using specific gravity meter. The length, width and thickness of the sample samples were measured before and after sintering using digital vernier caliper. The percentage of volume shrinkage were calculated using the following formula:

\[
\text{% of volume shrinkage} = \frac{V_o - V_f}{V_o}
\]

Where,

- \(V_o\) = initial volume after CIP, mm³
- \(V_f\) = final volume after sintered, mm³

The microstructures of the samples were investigated by Field Emission Scanning Electron Microscopy (FESEM) at magnification of up to x 20,000. Prior to the SEM examination, the samples were cut, ground, polished to 1µm surface finish, ultrasonic cleaned and then etched using Murakami solution.

3.0 RESULTS & DISCUSSION

3.1 Microstructural Observation

Figure 2 shows the microstructure of WC-Co sintered at 1450°C used as reference microstructure a. This is the optimum temperature for WC-Co sample where it produced the highest TRS with a slight drop of hardness. The bright and grey contrast in the WC-Co microstructure as observed by backscattered electron corresponds to the WC and Co binder phase, respectively. During densification process, the WC crystal morphology change to faced platelet shape and dispersed in cobalt matrix with irregular shape. Coalescence of WC grains was also observed during densifications process.

Figure 3 and Figure 4 show the effect of the sintering temperature on the microstructure changes on sintered samples. It was observed that the WC grain size is smaller in size with addition of VC in the WC-Co based material as compared with the addition C. This phenomenon shows that the VC particle is good as grain growth inhibitor as observed elsewhere due to
precipitation of VC in WC grain boundaries [9, 10]. However, the addiction of VC resulting, increased in pore density due to coalescence of pores during sintering process (Figure 3a). As the sintering tempertaure increased to 1400 °C and above, the SEM microstructure revealed the reduction in pore density due to coalescence WC grains as well as migration of cobalt [Figure 3b and 3c]. As for the addition of C, as the sintering temperature increased to 1400 °C and above, the grain size of WC become larger due to the grain growth that occurs during liquid phase sintering by coalescence or coarsening. Smaller WC grains with higher solubility dissolve in the liquid and reprecipitate to form larger grains [1] as shown in Figure 4b and 4c. Figure 4c shows over-sintered microstructure which results increase in pore density.

### 3.2 Density

Density of the sample with addition of 0.6%VC is relatively low compare to sample WC-Co and sample with the addition of 0.2wt%C except at the sintering temperature of 1350°C (Figure 5). As the sintering tempertaure increased, it was observed that the density of the sample with the addition of the 0.6% VC are the lowest due to increase in pores in the microstructure (Figure 3). However, sample with the addition of 0.2wt%C is comparable to WC-Co and slightly higher at 1450°C. From the graph, it can be seen that all the samples achieved the highest density at sintering temperture of 1450°C. It was observed that the percentage of volume shrinkage increased with increasing sintering temperature (Figure 6) which may caused increased in density by assuming that not much changes in the weight of the sample after sintering.

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**Figure 3** Microstructure changes of sintered WC-Co-VC with increasing temperature; (a) 1350°C, (b) 1400°C, (c) 1450°C
3.3 Percentage Of Volume Shrinkage

Figure 6 shows that percentage of volume shrinkage increased as sintering temperature increases due to increase in pore density (Figure 3 and 4). It can be seen from Figure 6 that the sample with addition of 0.2% C has the highest percentage of shrinkage. The percentage of shrinkage volume of sample with addition of 0.6 %C produced the lowest result due to less grain growth which subsequently resulting less pore density.

### Table 2: Hardness and TRS test results

<table>
<thead>
<tr>
<th>Samples</th>
<th>Sintering Temperature (°C)</th>
<th>Hardness (HV)</th>
<th>TRS (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>WC-Co</td>
<td>1350</td>
<td>1630</td>
<td>772</td>
</tr>
<tr>
<td></td>
<td>1400</td>
<td>1710</td>
<td>1340</td>
</tr>
<tr>
<td></td>
<td>1450</td>
<td>1680</td>
<td>1673</td>
</tr>
<tr>
<td>WC-Co-VC</td>
<td>1350</td>
<td>845</td>
<td>237</td>
</tr>
<tr>
<td></td>
<td>1400</td>
<td>1356</td>
<td>269</td>
</tr>
<tr>
<td></td>
<td>1450</td>
<td>1465</td>
<td>337</td>
</tr>
<tr>
<td>WC-Co-C</td>
<td>1350</td>
<td>1419</td>
<td>850</td>
</tr>
<tr>
<td></td>
<td>1400</td>
<td>1793</td>
<td>1357</td>
</tr>
<tr>
<td></td>
<td>1450</td>
<td>1703</td>
<td>1265</td>
</tr>
</tbody>
</table>

3.4 Mechanical Properties

Addition of VC and C in the WC-Co based hardmetal resulted in the changes of mechanical properties as shown in Table 2, Figure 7 and Figure 8. Test results shows that the all samples have higher hardness at the sintering temperature of 1400°C. From microstructural observation, it could be seen at this temperature the sample has less pore density, thus resulted in higher hardness (Figure 3 and Figure 4). It was observed that the hardness of sample with addition of 0.2% C is higher than the sample with addition of 0.6%VC. This phenomenon was taught due to the formation of more homogeneous structure with the addition of C (Figure 4). On the other hand, the structure becomes porous with the addition of VC. The hardness slightly reduced as the sintering temperature is increased to 1450°C due to over-sintered phenomenon for WC-Co and WC-Co-C sample. Microstructure of WC-Co-VC sample shows coalescence WC grain (Figure 3c) with increasing sintering temperature which resulted in continuous increase of hardness and TRS.
The addition of the VC in the composition resulted in the abrupt drop of TRS due to formation porous structure. On the other hand, TRS of sample added with C shows the highest reading due to homogenous structure even though irregular particle shapes and sizes. Based on the test results, it could be concluded that the addition of C produced the highest mechanical properties at sintering temperature of 1400°C results among the three samples. The improvement of the mechanical properties of this sample is taught to be due to the formation more homogenous structure with addition of the C in the sample. Based on mechanical properties, WC-Co-C sample was selected as the best sample because it produced hardness at sintering temperature of 1400°C (Figure 8) with acceptable transverse rupture strength.

4.0 CONCLUSIONS

In this work, WC6Co cemented carbides without and with 0.6 wt.% VC or 0.2 wt.% C addition have been successfully produced by powder metallurgy route and sintered under nitrogen-based atmosphere. Based on mechanical properties and microstructural observation, the following phenomena could be concluded;

a) VC work well as grain growth inhibitor
b) Rapid drop of TRS on the addition of VC resulting from formation of porous structure
c) WC-Co-C sample shows better mechanical properties compared to WC-Co-VC due to formation of homogenous structure.
d) Optimum sintering temperature is selected 1400°C for sample with the addition of 0.2 % carbon which produced higher hardness and TRS.

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