COMPOSITION AND STRUCTURE OF BIMODAL WC-Co MATERIALS RELATED TO MECHANICAL PROPERTIES AND ABRASIVE WEAR

Der-Liang Yung 1(*) Maksim Antonov 1, Irina Hussainova 1, Renno Veinthal 1, Sture Hogmark 2

1Department of Mechanical Engineering, Tallinn University of Technology, Tallinn, Estonia
2Department of Engineering Sciences, Uppsala University, Uppsala, Finland
(*)Email: der-liang.yung@ttu.ee

ABSTRACT

This study performs the comprehensive analysis with regards to the amount of ultrafine WC grains needed for the appropriate reinforcement of the metallic binder in WC-8Co cemented carbides. The ratio of coarse versus ultrafine WC grains in the bimodal system is examined. The goal is to investigate the balance of grain distribution to achieve overall improvement of the material’s mechanical and wear properties.

Keywords: cemented carbides, hardmetals, grain size manipulation, WC-Co

INTRODUCTION

Cemented carbides are an extensively studied class of materials used in applications requiring a combination of high hardness and toughness, while undergoing wear stresses in aggressive environments (Spriggs, 1995). The basic tungsten carbide cobalt (WC-Co) hardmetals have been widely deployed as tool bits for the purposes of the mining, tunnelling, machining, or drilling industries. However, the hardmetals possess a finite lifespan as the tools undergo regular wear and tear during usage. The degree of industrial relevance for hardmetals in this case is reflected by their deployment in the tunnel boring machine (TBM) technology as drag bits (Jakobsen, 2013). When a drag bit breaks down, the replacement operation is both time consuming and potentially dangerous operation (Langmaack, 2009). Any endeavour to increase the lifespan of the drag bit against a wide multitude of wear or mechanical failure during operation leads to the decrease in TBM downtime and industrial cost.

On the microscopic level, the WC-Co system offers a versatile material produced from powder metallurgical methods. Its mechanical and wear properties can be controlled by manipulating the carbide grain’s size, distribution, binder content, and even production pathway (Mannesson, 2011; Hussainova, 2014; Antonov, 2012). In terms of mechanical properties, the WC-Co system tends to balance its toughness and hardness by the amount of metallic binder. However, sacrificing too much hardness for better toughness tends to lower wear resistance against abrasive conditions. Various attempts to overcome this limitation have forced researchers to focus on using double cemented (DC) carbides, which contains granules of WC/Co cemented carbide in a matrix of cobalt. The composite exhibits a superior combination of fracture toughness and high-stress wear resistance compared to conventional cemented carbides (Deng, 2001). The early 2000s saw a method using submicron and ultrafine WC grains in refractory tool development as an ideal approach, especially when combined with improved pressing behaviour, proper doping, and optimized processing (Gille, 2001). But contemporary research has indicated that a major wear mechanism of near-nano grade WC is related to micro-cracking and micro-chipping leading to detachment of the WC-
Co agglomerates. Conversely, a major wear mechanism of coarse grade WC-Co tools is related to wear of the binder interlayers among the large WC grains (Konyashin, 2014). Recent developments have seen a novel ultra-coarse WC-Co grade with Co-based binder reinforced with nano-particles termed MASTER GRADES (Konyashin, 2005). The composite is characterized by a combination of higher hardness and transverse rupture strength compared to conventional grades of WC-Co. A recent effort to improve the classic WC-Co composite has been related to redesigning the microstructure and the proportions of grains, particularly the interaction between the large and fine grains.

Two methods of enhancing cemented carbide WC-Co wear and mechanical properties are examined concurrently: a) using ultrafine WC grains to improve the wear resistance by reinforcing the metallic binder (Yang, 2012); b) using micron WC grains to increase the toughness and resistance to crack propagation (Liu, 2014). These two concepts are well documented; however, little research has been documented about combining the two principles to make bimodal composites. The goal of this study is to create a composite material with a gradient of grain sizes, ideally a bimodal structure where coarse WC grains are surrounded by fine WC grains cemented together by a metal binder. This microstructure should in theory result in simultaneous hardening and toughening effects on the classic WC-8Co composite. The finer WC provides the hardening effect, while the coarser WC grains allow for crack bridging (Yang, 2012). A series of WC-8Co samples were synthesised in order to test the ratio of fine to coarse grain mixture and the effects on mechanical properties and abrasive wear resistance. The effect of VC and/or Cr$_3$C$_2$ grain growth inhibitors (Upadhyaya, 2001) is also studied in this research. Scanning electron microscopy (SEM) images and grain size distribution graphs are shown along with mechanical properties.

**MATERIALS AND METHODS**

**Raw Materials**

Commercial powders WC$_{100nm}$ (H.C. Starck, 99 % WC DN-4.0), WC$_{0.9µm}$ (Wolfam, 99 % WC MO9), and WC$_{10µm}$ (H.C. Starck, 99 % WC HC-1000) made up the base of our refractory carbides. Other additive carbides were sourced as followed: VC$_{0.9µm}$ (H.C. Starck, 99 % VC-8002), and Cr$_3$C$_2$ (1.8-2.0µm) (PPM Ltd, 99 % CrC-7002). Binder material was Co$_{0.3µm}$ (PK-1Y, 9721-79, 99.25 %).

**Samples Produced**

To make bimodal samples, there must be a ratio (proportionally) between large to ultrafine grains. The process was divided into two-steps. The first step involves creating a binder material embedded with ultrafine WC grains. The next step involves adding sufficient coarse WC grains so as the concentration of cobalt in material is always weighted at 8 wt. %. Of course, the ratio of WC$_{10µm}$ to WC$_{100nm}$ depended on the initial ratio of WC to Co in the binder phase. Creating the binder phase impregnated with WC$_{100nm}$ required a range between 32 – 56 wt % of metallic cobalt. In fact, the difference between the samples BM1, BM2, and BM3 is the difference of WC$_{100nm}$ to Co binder content in each. The ratios were selected to be divisible to obtain the necessary 8 wt % Co in the final product.

All samples were subjected to ball milling using WC-Co balls at a ratio of 6:1 wt with ethanol for 24 h before being dried and sieved. BM1, BM2, BM3 are the series detailing the effect of the ratio of WC$_{100nm}$-Co in the binder material. These ratios of differing amounts of WC$_{100nm}$ would ultimately yield different ratios between WC$_{10µm}$ and WC$_{100nm}$ grains. The samples were sintered under sinter-HIP conditions at either 1425 °C or 1450 °C (heating rate 10 °C
min\(^{-1}\) with 15 min vacuum dwell and 15 min Ar (30 MPa). The B4 sample is the same as BM2, but the WC\(_{10\mu m}\) grains are replaced with WC\(_{0.9\mu m}\). BX5 follows the sample steps of the BM2 synthesis, but with VC/Cr\(_3\)C\(_2\) dopants added. Table 1 shows all the various samples synthesised and tested. Furthermore, samples CL1 and CL2 represent reference samples.

Table 1 - Materials and composition

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Composition</th>
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<tbody>
<tr>
<td>BM1</td>
<td>WC(<em>{10\mu m})-WC(</em>{100nm})-8Co (ratio 8:1)*</td>
</tr>
<tr>
<td>BM2</td>
<td>WC(<em>{10\mu m})-WC(</em>{100nm})-8Co (ratio 8:1)*</td>
</tr>
<tr>
<td>BM3</td>
<td>WC(<em>{10\mu m})-WC(</em>{100nm})-8Co (ratio 8:1)*</td>
</tr>
<tr>
<td>B4</td>
<td>WC(<em>{0.9\mu m})-WC(</em>{100nm})-8Co (ratio 8:1)</td>
</tr>
<tr>
<td>BX5</td>
<td>WC(<em>{10\mu m})-WC(</em>{100nm})-8Co-VC-Cr(_3)C(_2) (ratio 8:1)</td>
</tr>
<tr>
<td>CL1</td>
<td>WC(_{0.9\mu m})-8Co</td>
</tr>
<tr>
<td>CL2</td>
<td>WC(_{10\mu m})-8Co</td>
</tr>
</tbody>
</table>

* based on increasing Co binder content

Testing

The test samples were grinded and then polished down to 1\(\mu m\) using diamond paste before undergoing tests including Vickers hardness, fracture toughness by Palmqvist via indentation under 147 N load (Sergejev, 2006), density by Archimedes, and transverse rupture strength. Abrasive wear testing was done based on ASTM-132 (ASTM-132, 2001) pressing a sharp corner of the block sample against SiC paper. The parameters were 12 RPM, using P180 SiC paper, with a 0.5 N load for a distance of 135.7 m for 1 h. The mean free paths of Co in our samples were determined using SEM images and the Intercept Method (Abrams, 1971). Grain size distribution takes into consideration the bimodal uniqueness and a dual graph is plotted with relative frequency and the volume fraction of the grains based on SEM images (Horiba, 2014).

RESULTS AND DISCUSSIONS

*Effect between coarse to ultrafine WC ratios*

The morphology of the ultrafine WC powder T2 after high energy milling with Co is shown in Fig. 1. The SEM clearly shows the ultrafine grains of WC embedded into the larger Co particles. When mixed with the coarser WC\(_{10\mu m}\) grains, the samples BM1, BM2, and BM3 would have varying different proportions between coarse to ultrafine WC grains. With increasing micron-sized WC, the density decreases; this is also reflected in research done by Liu et al. 2014. However, contrary to their research, we detected a steady increase in composite hardness with increasing WC\(_{10\mu m}\) amount and a non-linear correlation with toughness properties. The results show an obvious correlation between the addition of micron-sized WC grains and enhanced mechanical properties of ultrafine WC-Co cemented carbides (Liu, 2014), although in this study, the reverse method is taken. The same principle of using micron WC particles imbues the composite to resist crack propagation and improve the toughness. BM2 seems to stand out from the other samples with the highest toughness properties: \(K_{IC}\), 12.41 MPa\(\cdot\)m\(^{1/2}\); TRS, 3012 MPa.
The same BM1-BM3 samples were also sinterHIPed at 1425 °C to determine whether a slightly lower temperature would produce better samples. The results are shown in Table 3.

At first, it would appear that sample BM2-1425 °C gets an increase in TRS value due to the lower sintering temperature, however, at the cost of lower fracture toughness and densification. All other samples sintered at 1425 °C displayed poorer mechanical properties. Upon further examination of the SEM images, BM2-1425 °C is littered with WC η-phases and a non-homogeneous dispersion of WC grains leading to widening mean free path (MFP), see Fig. 2D. The slightly lowered sintering temperature does produce WC micron grains that are rounder and less jagged than those sintered at 1450 °C, see Figs. 2A-C. The rounded WC grains are distinctive characteristics of the commercial MASTER GRADES series introduced by Konyashin et al, 2005. Although the smallest WC grains used in this study were ~100 nm, the sintering of ultrafine WC leads to grain growth during sintering, especially at the early stages. The initial rapid grain growth is at least partially attributed to the process of coalescence of grains via elimination of common grain boundaries (Wang, 2008). The grain growth of the ultrafine WC grains follows the classic change during the heating process from equi-axis to a faceted platelet shape between 800 °C to 1200 °C (Fang, 2005). Continuous grain growth during liquid-phase sintering may be considered as an Ostwald ripening process.
Smaller WC particles dissolve due to their higher dissolution potential and re-precipitate after diffusion through the binder at coarser WC grains (Gille, 2002). The coarsening of the ultrafine grains is attributed to the lower mechanical properties of these bimodal samples. Nevertheless, samples such as BM2 still exhibit the classic bimodal characteristic with dual grain sizes, where the smaller grains are surrounding the larger WC grains as seen in the cross-section SEM, see Fig. 3. The coarse WC grains appear to suffer from a shearing stress causing intragranular cracks during bending, while the smaller grains appear to have undergone intergranular fracturing.

Fig. 1 - SEM (BSE) micrographs of sinterHIPed microstructure: A) BM1, B) BM2, C) BM3, D) BM2-1425 °C
Fig. 3 - BM2 sample cross section after transverse rupture strength bending. The arrows point at the intragranular fractures.

The grain size and volume distribution are shown in Fig. 4 for the three samples. As can be

Fig. 2 - Grain size and volume fraction distribution graphs: A) BM1, B) BM2, C) BM3
seen in Fig. 4B, BM2 with a ratio of 8:1 between coarse and ultrafine WC grains, shows a fairly even distribution between two particle size ranges: 1-2 µm and 4-5 µm. The ultrafine grain particles undergo as much as tenfold grain growth during sinterHIP as outlined in the changes to ultrafine grain morphology explained by Wang, 2008 and Fang, 2005. Another study also concluded that adding significantly coarser WC grains (0.9µm + 10% 63µm) causes faster grain growth since the coarse grains can consume the smaller grains (Mannesson, 2001). As for an apparent absence of the coarser WC10µm grains, this can be attributed to the ball milling, which was meant to mix the WC10µm. It is well known that the main mechanism of ball milling is a fracturing of the WC particles as well as mixing the Co binder around the WC particles (Mandel, 2014). To counteract this phenomenon, the container used during our milling process was meant to lessen impact energy between the refractory milling balls and the walls of the container. Furthermore, the milling time was reduced to 4 h, which is more attuned a mixing process therefore limiting the refinement of the coarse WC grain. Much of the volume fraction in our samples is skewed towards the 4-5 µm grains. BM2 has a structure of two distinctly separated WC particles sizes, and this could be attributed as to why the mechanical properties of BM2 are better than BM1 and BM3. 

Changing grain size proportions

Previously published research on bimodal WC-Co production examined WC_{ultrafine} to WC_{micron} grain sizes mixtures. Yang et al, 2012 studied a WC_{100nm} to WC_{1µm} ratio of ~7.6:1 wt, while Liu et al, 2014 studied a WC_{200nm} to WC_{1µm} ratio of ~8:1 wt. In the latter case, a series of alloys were created with varying proportions of coarse grain ratios; one of their alloys (~8:1 ultrafine to micron WC) showed an intercept point where hardness and fracture toughness properties were highest. Both these studies echo the same principles of the research done in this study, where the ratio of 8:1 could be an ideal ratio when mixing ultrafine to micron or vice versa. In our study, to further test the effect of using WC_{10µm} or WC_{0.9µm} in combination with WC_{100nm}-Co particles, two additional test samples were produced. Sample B4, WC_{0.9µm}-WC_{100nm}-8Co was included to determine whether narrowing the gap between the two WC grain sizes would make any difference in structural properties. The second sample BX5 is similar to sample BM2, but doped with VC/Cr3C2, WC_{10µm}-WC_{100nm}-8Co, as outlined in Table 1. Samples CL1 and CL2 are classic WC-8Co with either 1µm or 10µm WC grains respectively.

The mechanical properties and wear rate of the five samples are displayed in Table 4. The control CL1 and CL2 both exhibit the characteristics of their respective grain sizes with decreasing density and reduced hardness, but an increase in strength when going from micron to coarse WC grains. Even when comparing BM2 and B4, the difference between using micron or coarse WC grains is reflected in the density, hardness, and toughness properties, but their wear rates are similar. Since B4 has a narrower grain distribution, see Fig. 5A, it has lower mechanical properties and wear resistance, even with the higher hardness. It has also been shown in field testing of tool bits for the mining industry, the mechanical properties of hardness is not always a determining factor in abrasive wear resistance (Konyashin, 2010). As shown in Table 4, BM2 containing a mixture of coarse and ultrafine WC grains performs better under abrasive wear conditions than conventional products of the same binder composition. In correlation with some contemporary research on the topic of bimodal WC-Co systems, our results show that fracture toughness and strength of the WC/Co composite besides hardness is decisive for the abrasive resistance. This is especially evident from the test results of sample BX5, comparing data shown in Table 4 and the grain distribution in Fig. 5B.
Table 4 - Mechanical and wear properties of reference and selected samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Relative density [%]</th>
<th>Hardness [HV30]</th>
<th>$K_{IC}$ [MPa*m$^{1/2}$]</th>
<th>TRS [MPa]</th>
<th>Wear rate [mm$^3$/N<em>m</em>10$^{-7}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>CL1</td>
<td>98.1</td>
<td>1715 ± 22</td>
<td>10.09 ± 2.5</td>
<td>1355 ± 51</td>
<td>2.60 ± 0.02</td>
</tr>
<tr>
<td>CL2</td>
<td>97.0</td>
<td>1350 ± 7</td>
<td>12.21 ± 1.5</td>
<td>2584 ± 98</td>
<td>2.43 ± 0.02</td>
</tr>
<tr>
<td>BM2</td>
<td>98.4</td>
<td>1282 ± 16</td>
<td>12.41 ± 1.8</td>
<td>3012 ± 8</td>
<td>2.19 ± 0.03</td>
</tr>
<tr>
<td>B4</td>
<td>99.0</td>
<td>1653 ± 15</td>
<td>9.04 ± 2.4</td>
<td>2256 ± 51</td>
<td>2.22 ± 0.01</td>
</tr>
<tr>
<td>BX5</td>
<td>98.9</td>
<td>1287 ± 13</td>
<td>12.03 ± 1.4</td>
<td>3468 ± 192</td>
<td>2.00 ± 0.03</td>
</tr>
</tbody>
</table>

In the sample BX5, the addition of grain growth inhibitors is supposed to suppress the coalescence of coarse and ultrafine grains leading to excessive WC grain growth in the binder phase. The grain growth inhibitors were incorporated during the synthesis of the binder material. Examining the grain size distribution in Fig. 5B, and comparing it to Fig. 4C, there is evidently a shift towards smaller grain size for the ultrafine WC grains. The grain growth inhibitors suppress the coarsening of the ultrafine WC grains. This is also demonstrated by Fig. 6. The mechanical properties when grain growth of the ultrafine WC grain is suppressed should be emphasized: both the TRS value and wear resistance of the composite are greatly enhanced. BX5 displays 10 to 20 % higher wear resistant as compared to other samples in Table 4, even though its hardness is lowered compared to CL1 or CL2, and comparable to BM2. These results certainly motivate continued research of bimodal composites. The major advantage with bimodal composites is the fact that it does not change the basic chemical or elemental composition of the material, but merely redesign how they are synthesised. In this case, tungsten carbide and cobalt chemically remains the same, but the grain composition and distribution are changed to offer new properties. The addition of grain growth inhibitors such as VC and Cr$_3$C$_2$ is also nothing new. The pathway taken to the end product offers a potential engineered product that can be taken seriously by industry given their fondness to deal with familiar materials and minimise the need for drastically new approaches to manufacturing.
CONCLUSION

In this study, it has been shown that the toughness of the classic WC-8Co can be enhanced by introducing a suitable distribution of different size grains in the system. Experiments reveal that bimodal materials can outperform the unimodal samples in terms of strength and abrasive wear resistance. The sample BM2 demonstrates that ratio of 8:1 wt. of coarse to ultrafine grains seems to be the ideal proportion for systems with bimodal grain size distributions. Our research shows that using coarse WC particle offers the possibility to produce a WC-8Co with mechanical properties of $K_{IC} \approx 12.4 \text{ MPa}\cdot\text{m}^{1/2}$, and TRS $\approx 3010 \text{ MPa}$ for sample BM2. Adding grain growth inhibitors in BM2 to form BX5 yielded at least a 10% better abrasive wear resistance and bending strength as compared to BM2.

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