Optimized production route of WC powder pre-alloyed with Ta for fine grained cemented carbides

J. Weidow a,⁎, E. Halwax b, W.-D. Schubert b

a Chalmers University of Technology, 41296 Göteborg, Sweden
b Vienna University of Technology, 1060 Vienna, Austria

Abstract

Powders of hexagonal (W,Ta)C were produced following a two-step carburization process with (W,Ta)2C powder as an intermediate product. XRD measurements indicate that higher temperatures during the first carburization step increase the fraction of Ta in the (W,Ta)2C structure where lower temperatures during the second carburization step seems to increase the fraction of Ta in the (W,Ta)C structure. Lower temperatures during the carburization steps increase the fraction of Σ2 WC/WC grain boundaries and cause the formation of what is interpreted as Σ4 boundaries. The (W,Ta)C powders can be successfully used to produce fine grained WC-Co based cemented carbides. The pre-alloying with Ta appears to have a softening effect on the material.

© 2016 Elsevier Ltd. All rights reserved.

Keywords:
EBSD
Electron backscatter diffraction
Doping
SEM
Scanning electron microscopy

1. Introduction

Cubic carbides such as TiC, NbC and TaC are frequently added to the powder mixture in the production of cemented carbides in order to improve the as-sintered material properties. Sintering of WC, Co and TaC powder mixtures causes Ta to partially substitute for W in the structure for reprecipitated parts of WC grains [1]. As an example, for a WC-TaC-Co material with 16.20 mass% Ta and 5.51 mass% Co sintered at 1430 °C, the Ta solubility in WC was found to be 0.959 ± 0.009 at.% [2]. Further increasing the amount of Ta in the WC structure is advantageous as it would provide an additional degree of freedom in the cemented carbide production process which possibly would result in improved material properties.

One method to achieve a WC-Co based cemented carbide with increased Ta content in the WC structure would be to manipulate the WC powder so that it contains Ta from the very beginning, i.e. a (W,Ta)C powder. As metal diffusion is not expected to occur at normal sintering temperatures (1400–1450 °C), undissolved parts of WC grains should maintain the high concentration of Ta [3]. The phase diagrams for the W-Ta-C system show that the solubility of Ta in WC is about 12 at% at 1500 °C, and about 15% at 1750 °C, while the solubility of Ta in W is known to be much smaller [4]. It has been shown that by performing a two-step carburization of a W + Ta powder mixture, with (W,Ta)2C as an intermediate product, it is possible to produce a (W,Ta)C powder with a Ta/(Ta + W) ratio of 0.086 [5]. This means that the concentration of Ta in the (W,Ta)C powder is over four times higher than what has been measured for Ta in WC grains of an as-sintered cemented carbide produced from pure WC powder. This two-step procedure follows the guidelines published in patent application [6].

It is the aim of this study to investigate how the powder production parameters can be optimized in order to increase the amount of Ta being dissolved in the WC structure. It is also the aim to investigate what effects the Ta pre-alloying has on the microstructure and material properties of fine-grained cemented carbides.

2. Experimental

Two powder series were produced. In the first powder series, 0.84 μm FSSS (as-supplied) W powder was carburized together with Ta2O5 at 1450 °C resulting in a (W,Ta)2C powder (X1). This powder was carburized a second time at various temperatures leading to the formation of (W,Ta)C powders P1–P3. As a reference to these powders, a mixture of the same W powder and Ta2O5 powder was directly carburized in a one-step process to give (W,Ta)C (P4). The second series was similar to the first. Here a 0.83 μm FSSS (as-supplied) W powder was used and the first carburization step was instead performed at 1630 °C. This resulted in (W,Ta)2C powder X2 and (W,Ta)C powders P5–P7. The amount of Ta2O5 added was based on the aim to have a WC powder with Ta corresponding to 3.0 wt% TaC.

The powders were analyzed with X-ray diffraction (XRD) using a PANalytical X'Pert PRO powder diffractometer (CuKα radiation, X'Celerator detector, Ni Kβ filter). Before analysis, the powders
Table 1

(W,Ta)2C powder details, silicon used as an internal standard.

<table>
<thead>
<tr>
<th>Powder</th>
<th>Carburization temperature (°C)</th>
<th>Lattice parameter a (nm)</th>
<th>Lattice parameter c (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>W,C</td>
<td>–</td>
<td>0.51910</td>
<td>0.47379</td>
</tr>
<tr>
<td>X1</td>
<td>1450</td>
<td>0.51931</td>
<td>0.47295</td>
</tr>
<tr>
<td>X2</td>
<td>1630</td>
<td>0.51989</td>
<td>0.47357</td>
</tr>
</tbody>
</table>

Table 2

(W,Ta)C powder details.

| Powder | Originating (W,Ta)C powder | Carburization temperature (°C) | Particle size (μm) | Total C content (wt%) | Cubic (Ta,W)C (wt%) | Lattice parameter a (nm) | Lattice parameter c (nm) | Calculated Ta content in (W,Ta)C (at%)
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>WC</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>P1</td>
<td>X1</td>
<td>1450</td>
<td>0.90</td>
<td>6.21</td>
<td>1.65</td>
<td>0.29063</td>
<td>0.28375</td>
<td>2.1 ± 0.7</td>
</tr>
<tr>
<td>P2</td>
<td>X1</td>
<td>1630</td>
<td>1.04</td>
<td>6.24</td>
<td>1.74</td>
<td>0.29070</td>
<td>0.28388</td>
<td>1.7 ± 0.7</td>
</tr>
<tr>
<td>P3</td>
<td>X1</td>
<td>1950</td>
<td>1.42</td>
<td>6.20</td>
<td>1.75</td>
<td>0.29080</td>
<td>0.28383</td>
<td>1.6 ± 0.7</td>
</tr>
<tr>
<td>P4</td>
<td>–</td>
<td>1950</td>
<td>1.12</td>
<td>6.11</td>
<td>2.67</td>
<td>0.29076</td>
<td>0.28384</td>
<td>2.2 ± 0.7</td>
</tr>
<tr>
<td>P5</td>
<td>X2</td>
<td>1450</td>
<td>1.24</td>
<td>6.15</td>
<td>0.80</td>
<td>0.29084</td>
<td>0.28394</td>
<td>4.1 ± 0.7</td>
</tr>
<tr>
<td>P6</td>
<td>X2</td>
<td>1630</td>
<td>1.32</td>
<td>6.18</td>
<td>0.91</td>
<td>0.29087</td>
<td>0.28388</td>
<td>3.4 ± 0.7</td>
</tr>
<tr>
<td>P7</td>
<td>X2</td>
<td>1950</td>
<td>2.27</td>
<td>6.22</td>
<td>1.46</td>
<td>0.29087</td>
<td>0.28388</td>
<td>3.8 ± 0.7</td>
</tr>
</tbody>
</table>
materials C1–C5 and C9–C10, somewhat higher for materials C6 and C7 and somewhat lower for material C8. It was also noted that the coercivity increased and the hardness decreased for materials C1 to C3, for C5 to C7 and for C8 to C10.

SEM micrographs of cemented carbides C1–C7 are shown in Fig. 3. The WC grain size appears to increase from C1 to C3 and from C5 to C7.

Data from EBSD analysis of as-sintered materials C1–C5 and C8–C10 are shown in Table 5. In general, the WC grain size increases and the fraction of \( \Sigma 2 \) WC/WC grain decreases for materials C1 and C2 to C3 and from C5 and C8 to C9 and C10.

### 4. Discussion

The presence of both WC and W in powder X1 shows the difficulty in the production of a homogenous powder mixture. The absence of TaC is supposed to mean that all of the Ta should substitute for W in any of the phases being formed, i.e. \((\text{W,Ta})_2\text{C}, (\text{W,Ta})\text{C}\) and \((\text{W,Ta})\). The larger lattice parameters for the W2C phases strongly indicate that Ta has in fact substituted for W in this phase. From a comparison with literature values, the lattice parameters indicate that the change in lattice parameters corresponds to homogeneous \((\text{W,Ta})_2\text{C}\) mixed crystals with 5 (X1)
and 8–11 (X2) mole% TaC, respectively. The margin is due to the uncertainty in the lattice parameter determination and the uncertainty in the measurements in the literature [8]. The difference between the two powders can be attributed to a higher temperature in the carburization process enabling a larger fraction of Ta to replace W in the W2C structure.

The relatively small change in lattice parameters compared to the uncertainty of the measurement makes XRD rather inappropriate to quantify the composition of the (W,Ta)C phase. The only significant difference is that the Ta content in the (W,Ta)C phase is greater for powders P5–P7 than powders P1–P4. Instead, the concentration of cubic (Ta,W)C phase is considered to be a better method as for a known total amount of Ta it shows how much Ta must be present in the hexagonal (W,Ta)C phase. It must be remembered that we do not know the exact composition of the cubic (Ta,W)C phase for the different carburization temperatures. For a comparison, the solubility of W in TaC is approximately 18 at.% at 1700 °C [8]. Being aware of these difficulties, the fraction of cubic (Ta,W)C significantly increases from P5 to P7, we also believe that the Ta content in the hexagonal (W,Ta)C grains decreases from P5 to P7. This is in agreement with our previous study showing that a lower temperature in the second step of a two-step carburization process is beneficial for the Ta content in the (W,Ta)C structure [5]. Finally, the content of cubic (Ta,W)C for powder P4 is much greater than for the other powders. This together with the small lattice parameters suggests that the Ta content of (W,Ta)C in P4 is low, which means that a one-step carburization process gives less Ta dissolved in WC than a two-step process. We thus conclude that the two-step method we have used to produce a WC powder pre-alloyed with Ta is in fact working.

The EBSD analyses of the powders showed the big importance of the temperature in the second carburization step when it comes to the grain size. They also showed that the larger this temperature is, the smaller is the aspect ratio, which means the more round the grains are. It is well known that Σ2 WC/WC grain boundaries are formed already in the WC production process [9]. The relatively low temperature in the carburization process means that the enthalpy dominates the expression for

![Fig. 2. WC/WC grain boundary distribution in powder P1 together with a distribution for a material with random grain boundaries (R).](image-url)
the Gibbs free energy and it is therefore easy to understand that there is a high probability for the formation of the special low energy $\Sigma_2$ grain boundaries. That the fraction of $\Sigma_2$ WC/WC grains decreased from P1 to P3 and from P5 to P7 is in agreement with our previous study for strongly pre-alloyed powers [5]. A higher temperature causes the enthalpy to be less dominating. The presence of a peak in the WC/WC grain boundary misorientation profile at 60° is believed to correspond to a $\Sigma_4$ grain boundary. Lay and Loubradou conclude that a 60° rotation around the [T2T0] axis results when two WC grains with different $\Sigma_2$ relationships to a third grain are in contact with each other [10]. With the same argument as for the $\Sigma_2$ grain boundary, the $\Sigma_4$ grain boundary appears to a larger extent at lower carburization temperatures. The peak at low angles corresponds to low angle grain boundaries.

Optical microscopy and SEM imaging (Fig. 3) showed that we successfully produced cemented carbides of the different powders P1–P7. As the carbon potential has a big effect not the least on the grain

Fig. 3. SEM backscatter detector micrographs of cemented carbides C1–C7.
and grain size of possible cubic carbides and potentially also the composition of binder phase, the WC grain size, the volume fraction of 13.00 GPa in the (100) direction and 22.00 GPa in the (0001) direction. It is not therefore believed that the cubic TaC phase will have any significant positive effect on the hardness for these materials. In addition, optical microscopy and EBSD shows that the TaC grain size is larger than the WC grain size. It might therefore even be that the TaC phase makes the material softer. In order to investigate any effect on the hardness of the Ta doping of the WC grains, the hardness was plotted as a function of the WC grain size (Fig. 4). The error bar of the hardness mean value is calculated with a 95% confidence interval (five indents per material). Two materials stand out, C5 and C8. Both are less hard than can be expected from their grain size. These are the materials we believe have the largest amount of Ta in the WC grains. We thus deduce from our results that doping of Ta in the WC crystals has a softening effect on the material. WC powder pre-alloyed with Ta has successfully been used to produce coarse grained WC-Co based cemented carbides with a confirmed high concentration of Ta remaining in the WC structure [12]. The Young’s moduli of the doped crystals were significantly lower than for undoped WC, as measured by nano-indentation in agreement with the lowering of the elastic constants, from ab initio calculations [12]. Our results are therefore in agreement with this study.

The fraction of Σ2 WC/WC grain boundaries in the as-sintered materials has decreased compared to what existed in the originating powders. This in agreement with the theory that these boundaries exists already in the powder and does not form during sintering [9]. It was noted that no peak existed at 60° in the misorientation profile of the WC/WC grain boundaries. This does not surprise as when the fraction Σ2 boundaries decrease due to the grain coarsening process, so do the Σ4 boundaries.

5. Conclusions

Hexagonal (W,Ta)C powders were produced with (W,Ta)2C as an intermediate product following a two-step carburization process. XRD measurements indicate that a higher temperature during the first carburization step increases the fraction of Ta in the (W,Ta)2C structure. XRD measurements indicate that a lower temperature during the second carburization step increases the fraction of Ta in the (W,Ta)C structure. The pre-alloyed powders had a high fraction of Σ2 WC/WC grain boundaries and a small fraction of what has been interpreted as Σ4 WC/WC grain boundaries. The powders carburized at lower temperatures had a larger fraction of these low energy boundaries. The (W,Ta)C powders were successfully used to produce cemented carbides. The pre-alloying with Ta appeared to have a softening effect of the material.

Acknowledgements

Thanks for advice and helpful comments are due to Hans-Olof Andrén from Chalmers University of Technology, Susanne Norgren from Sandvik Mining, Ernesto Coronel, Marie Lundbäck and José García from AB Sandvik Coromant R&D, Jan Qvick from Seco Tools AB and Gabriele Kremser and Andreas Bock from Wolfram Bergbau und Hütten AG.

References

Jonathan Weidow was born in 1980 and studied physics at Chalmers University of Technology. After a post-doc at Vienna University of Technology he now has a position as university lecturer at Chalmers. His main interest is on characterization of the microstructure of metallic materials with a special focus on cemented carbides. Jonathan has more than 20 publications in refereed journals and was awarded with the 2015 Sawamura Award from the Iron and Steel Institute of Japan.

Erich Halwax was born in 1951 and studied chemistry in the Vienna Technical University. He did his doctoral thesis with Horst Völlenkle on the crystal structure analyses of various alkali metal germanates. He has been an Assistant Professor since 1990 with main interests in powder diffraction, especially quantitative phase analysis.

Wolf-Dieter Schubert was born in 1951. He is professor at the Institute of Chemical Technologies and Analytics at Vienna University of Technology and head of a research group focused on the metallurgy of less common metals. His main expertise is on refractory metals and cemented carbides. He has more than 100 publications in refereed journals, several book contributions, co-author of the monography on TUNGSTEN: Properties, Chemistry, Technology of the Element, Alloys and Chemical Compounds (ISBN 0-306-45053-4). He is technical consultant of the International Tungsten Industry Association and has recently received the Skaupy-Award by the German Association of Powder metallurgy.