Transition of W₂C to WC during carburization of tungsten metal powder

Georg Mühlbauer⁎, Gabriele Kremsera, Andreas Bocka, Jonathan Weidowb, Wolf-Dieter Schubertc

aWolfram Bergbau und Hütten AG, 8543 St. Martin i.S., Austria
bChalmers University of Technology, 41296 Göteborg, Sweden
cTechnische Universität Wien, 1040 Wien, Austria

ARTICLE INFO

Keywords:
WC
W₂C
Carburization
Phase boundary
EBSD

ABSTRACT

The properties of cemented carbides are heavily influenced by the tungsten carbide (WC) powders used in its production. Overall particle size of the WC is most influential, however, in the medium- and coarse-grained tungsten carbide particle range the internal crystallographic structure of the polycrystalline WC is important as well. To investigate the crystal formation of WC and its resulting structure, selected crystal growth experiments were performed. The transition of ditungsten carbide (W₂C) into tungsten carbide (WC) during carburization of tungsten powder was studied.

The experimental strategy was to obtain W₂C along with WC within the growing carbide particles. Electron microscopy methods were utilized to study the growth mechanism during conversion of W₂C into WC, and to detect the existence of preferred crystallographic orientations during the transition process.

1. Introduction

Industrial production of tungsten carbide powder is typically achieved by mixing tungsten metal powder with stoichiometric amounts of carbon black and subsequent heat treatment in hydrogen atmosphere at temperatures of 1050 °C to 2100 °C [1]. It is well known that the carburization follows a two-stage reaction with the intermediate product ditungsten carbide W₂C:

W → W₂C → WC

Diffusion investigations of the carburization reaction by McCarty et al. revealed a fast initial formation of W₂C followed by a much slower reaction of W₂C into WC [2].

A more detailed process was described by Zhengji [3]: First, carbon in direct contact with the tungsten surface reacts to WC, forming a rim consisting of fine grained WC. Subsequently, starting from the WC rim, the tungsten metal converts to W₂C. As long as metallic W is present in the core of the particle, conversion to W₂C is continuing without significant growth of the outer WC rim. After all metallic W is converted to W₂C the WC rim grows inwards until the carburization reaction to WC is finished.

The carburization atmosphere significantly influences the process and the carbon distribution in the final product. If the reaction takes place in vacuum, inhomogeneities and an incomplete reaction can be observed in the final product. However, reaction in presence of hydrogen or hydrogen containing gas-mixtures leads to well homogenized powders [1]. This is due to the hydrogen atmosphere’s reaction with carbon to form volatile hydrocarbons. These hydrocarbons induce a chemical vapor transport of carbon to the WC surface and thus render a homogeneous carbon distribution in the powder [4]. Fig. 1 illustrates a schematic of the carburization process including the chemical vapor transport by hydrocarbons.

During sintering of cemented carbides WC/WC grain boundaries within the WC particles are wetted and penetrated by the liquid cobalt binder (see Fig. 2) depending on their interface energy. High angle grain boundaries comprise a higher interface energy and therefore are penetrated more easily than coincidence grain boundaries [6] [7] [8]. Consequently, the inner crystallographic structure of used tungsten carbide particles has a strong impact on the properties of the resulting cemented carbides, especially when using polycrystalline medium- or coarse-grained tungsten carbide powder.

In recent years, the influence of Σ2 WC/WC coincidence grain boundaries on the properties of cemented carbides was investigated [6] [9] [10]. These low energy grain boundaries are not wetted during sintering and were observed in WC powder particles as well as tungsten carbide grains in cemented carbides. It was demonstrated that these boundaries are formed during the powder production stage [6] [9]. As of now, the origin of these Σ2 grain boundaries in WC is not entirely understood.

For that matter, the objective of the present work is to gain a better
understanding how WC particle properties and internal structure are influenced by the production conditions. The conversion of W₂C to WC is believed to be the crucial step in defining the inner crystallographic structure of WC particles. Therefore, investigations were focused on the transition of W₂C to WC and formation of WC/WC grain boundaries within the particle.

Experiments with varying atmosphere, carbon balance, and temperature were performed. Suitable electron microscopy methods were applied to investigate the processes occurring during the conversion of W₂C to WC.

2. Experimental

2.1. Sample preparation

Three sets of experiments were performed to investigate the conversion of W₂C to WC. Table 1 summarizes the experimental conditions for the resulting six samples.

The first class (samples A and B) were produced by placing tungsten metal powder on a graphite plate. The plate was placed in a graphite crucible and tempered in a laboratory tube furnace at a temperature of 1500 °C. The atmosphere in the furnace was chosen to be either vacuum or flowing hydrogen. Fig. 3 depicts a schematic of the experimental setup. The cross section of the powder bed after heat treatment was prepared by infiltration in epoxy resin.

The second set of samples (samples C and D) were produced by blending tungsten metal powder with different amounts of carbon black in a plastic ball mill. The mixture was filled into a graphite crucible and carburized in a laboratory tube furnace in flowing hydrogen. After heat treatment, the product was gently deagglomerated in a mortar. For further investigations, copper embeddings of the powders were made.

For the third class (samples E and F) tungsten metal powders were mixed in a steel ball mill with 3.16% carbon black (theoretical balance for stoichiometric W₂C). The mixture was filled into a graphite crucible.

![Fig. 1. Schematic process of carburization of W metal to WC – based on [4].](image1)

![Fig. 2. Disintegration of WC particles by cobalt, samples sintered 1 min at 1300 °C, 1330 °C and 1350 °C [5].](image2)

<table>
<thead>
<tr>
<th>Sample</th>
<th>W - FSSS a.s.</th>
<th>C-balance</th>
<th>Atmosphere</th>
<th>Tₐ</th>
<th>tₜ</th>
<th>Furnace</th>
<th>Deagglomeration</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>4.25 μm</td>
<td>0%</td>
<td>H₂</td>
<td>1500 °C</td>
<td>3.5 h</td>
<td>lab</td>
<td>No</td>
</tr>
<tr>
<td>B</td>
<td>4.25 μm</td>
<td>0%</td>
<td>vacuum</td>
<td>1500 °C</td>
<td>2.5 h</td>
<td>lab</td>
<td>No</td>
</tr>
<tr>
<td>C</td>
<td>4.25 μm</td>
<td>3.16%</td>
<td>H₂</td>
<td>1500 °C</td>
<td>1.5 h</td>
<td>lab</td>
<td>Mortar</td>
</tr>
<tr>
<td>D</td>
<td>4.25 μm</td>
<td>4.67%</td>
<td>H₂</td>
<td>1500 °C</td>
<td>1.5 h</td>
<td>lab</td>
<td>Mortar</td>
</tr>
<tr>
<td>E</td>
<td>10.2 μm</td>
<td>3.16%</td>
<td>H₂</td>
<td>2000 °C</td>
<td>1.5 h</td>
<td>ind</td>
<td>No</td>
</tr>
<tr>
<td>F</td>
<td>4.25 μm</td>
<td>3.16%</td>
<td>H₂</td>
<td>1500 °C</td>
<td>1.5 h</td>
<td>ind</td>
<td>No</td>
</tr>
</tbody>
</table>

C-balance: addition of carbon black to tungsten metal powder.
Tₐ: carburization temperature.
tₜ: time at carburization temperature.
lab: laboratory Al₂O₃ tube furnace.
ind: industrial graphite pusher type furnace.
and carburized in an industrial graphite pusher type furnace at 1500 °C and 2000 °C, respectively. After carburization the slightly sintered powder was not deagglomerated but carefully broken into pieces. A copper-embedding was produced by infiltrating a resulting piece with molten copper.

2.2. Metallographic preparation

Electron microscopy investigations require careful metallographic preparation. In particular scanning electron microscopy (SEM) investigation employing the channeling effect and electron backscatter diffraction (EBSD) necessitate a very high surface quality. To obtain such quality, copper empeddings were mounted in bakelite and polished with diamond suspension down to either 1 μm or 0.25 μm. Final polishing was performed with a Struers OP-S suspension. For some investigations NH₃ and H₂O₂ was added to the OP-S, acting as a chemical etchant. Embeddings in epoxy resin were prepared in a similar way.

Final polishing for EBSD investigation of sample D was performed using ion beam techniques (Gatan 691 precision polishing system (PIPS)) [11].

2.3. Analysis

Two techniques were primarily used to investigate the produced samples, SEM imaging and EBSD analysis. Channeling effect gives contrast variation in backscatter electron images depending on crystal orientation (“how dense the orientation is”) and therefore visualize the inner structure of particles. EBSD results in more detailed information of the structure by defining crystallographic phase and crystal orientation of grains. It enables visualizing relative orientations of crystallites and thus to define the nature of grain boundaries present within the particles (large angle, coincidence).

EBSD analysis was performed either in a Leo Ultra 55 FEG SEM with EBSD system manufactured by HKL using software Channel 5 on sample D and sample E, F in a Zeiss Ultra 55 with EBSD system manufactured by EDAX with Thorlabs Scientific Camera using software EDAX TSL OIM Analysis V7.3.

The crystal structure of W₂C can be described as a slightly distorted hexagonal close packing of tungsten atoms. The carbon atoms occupy half of the octahedral interstices. Occupancy can be ordered, with the type and degree of ordering depending on temperature [12] [13]. In this study, to improve indexing on the used equipment and with the investigated samples, two different modifications were used for EBSD analysis: for sample D space group P6₃/mmc (No. 194; statistical occupation of the interstices), for samples E and F space group P3̅1m1 (No. 164; ε-Fe₂N-type).

3. Results

3.1. Influence of the preparation technique on the visualization of WC and W₂C

Final polishing with OP-S suspension was performed either with or without addition of chemicals (NH₃, H₂O₂). Although ammonia and hydrogen peroxide help to improve the surface quality during finishing, a completely different response can be observed for WC, W₂C and W. OP-S suspensions with addition of NH₃/H₂O₂ act as an etching solution for both W₂C and W. Therefore, to preserve the W₂C substructure final polishing must be done with pure OP-S solution. In this case extended polishing times are necessary.

On the other hand, etch-polishing is an easy approach to verify the existence of W₂C besides WC within a carbide particle. After such treatment W₂C is preferentially leached out of the carbide particle which can be visualized as dark spots using backscattered electron techniques. Fig. 4 demonstrates a WC/W₂C particle before and after polishing with OP-S + NH₃/H₂O₂. After polishing an empty space appears in the carbide particles indicating the presence of W₂C prior to polishing.

3.2. Influence of atmosphere/carbon transport

Two carburization experiments of tungsten metal powder on a graphite plate were performed. One in hydrogen atmosphere (sample A) and one in vacuum (sample B):

A cross-section of the powder carburized in hydrogen revealed an inner and an outer region (Fig. 5). X-ray diffraction of epoxy resin-embedded samples confirmed the occurrence of two phases: W₂C and WC. Employing SEM techniques combined with conventional metallography, the outer material was identified as fully carburized WC, the inner material was shown to consist of W₂C particles without WC rim. Particles in the transition area between both regions showed a continued growth of the WC rim. When final polishing was done with
addition of NH$_3$/H$_2$O$_2$, the growing WC rim indicated the presence of a large number of WC platelets growing into the W$_2$C core. Fig. 5 depicts schematically the two different areas of sample A (left) and a particle with platelet structure as can be observed in the transition of W$_2$C → WC.

Visual inspection of the sample carburized in vacuum (sample B) revealed a homogenous build-up of the powder bed (Fig. 6). XRD analysis identified metallic tungsten. SEM investigations, however, indicated the existence of W$_2$C and WC in close proximity to the graphite plate. Albeit carburization for 3.5 h at 1500 °C, W$_2$C was only found at the utmost distance of 20 μm from the graphite plate. And only those particles in direct contact with the graphite plate transformed into WC. No diffusion of carbon into particle areas above the graphite plate occurred. Fig. 6 depicts schematically the cross section of sample B (left) and a particle in direct contact with the graphite plate (right). During carburization, due to carbon uptake, the particle sank partly into the graphite plate. The surface of the graphite plate then indicates the separation of WC and W$_2$C in such particles. Above the dotted line no WC was found.

3.3. Platelet structure of WC

Further investigations were performed on homogenized material (samples C and D): tungsten metal powders mixed with carbon black. Sample C was produced to comprise only of a W$_2$C core with a small WC rim. In some cases, the WC rim was found to be incomplete (Fig. 7a). This might be due to demolition of the WC rim during powder deagglomeration.

Sample D was reacted to exist of a mixture of WC and W$_2$C. In this sample the occurrence of WC platelets was observed. Most of the platelet grains appear small (Fig. 7b) with the exception of a few having grown fast into the W$_2$C cores (Figs. 4 and 7c) forming large, elongated WC grains.

SEM investigations employing the channeling effect reveal no indications of differing growth rates of crystal domains. Therefore, additional EBSD investigations were performed on sample D. Primarily, EBSD was used to clearly distinguish WC from W$_2$C. Furthermore, the nature of phase boundaries between WC and W$_2$C grains was studied. The deviation angle between (0 0 1) plains in WC and (0 0 1) plains in W$_2$C (space group no. 194) was then evaluated and a frequency distribution by deviation angle was calculated (Fig. 8). It was noticed that a deviation angle of < 3° occurs more often than statistically expected. Considering the fraction of phase boundary lengths, the fraction with a deviation angle of 0–3° is about 15% (0–3° was used to define the so called special phase boundary in EBSD measurements). Additionally, the occurrence of Σ 2 WC/WC coincidence grain boundaries was examined. About 32% of the overall WC/WC grain boundary length represents such coincidence grain boundaries. Fig. 9 depicts EBSD results of sample D. The upper half displays the phases WC (red) and W$_2$C (green) as different colors. Additionally, occurrence of Σ 2 WC/WC coincidence grain boundaries is highlighted in white. The lower half shows common W$_2$C/WC phase boundaries in cyan and the special phase boundaries with deviation angles of 0–3° in red.

For further EBSD investigations a third set of samples was produced.
to study if platelet structures also appear at carburization temperatures of 2000 °C and if the behavior is similar to carburization at 1500 °C. Samples E and F were produced with addition of 3.16% carbon to yield W2C. Due to the preparation in graphite crucibles and hydrogen atmosphere, the outer zones of the powder bulk were already fully carburized. For the investigation, the transition area W2C → WC was isolated.

The inner structure of the sample carburized at 2000 °C (sample E) was similar to samples carburized at 1500 °C but grain sizes are obviously bigger. This applies to both the W2C and the growing WC. Untypical for such high carburization temperatures is the appearance of small WC grains close to the particle surface. While platelet structures appear to be coarser when compared to samples carburized at 1500 °C a similar orientation between the tungsten atom sub lattice in WC and the adjacent W2C was observed. Fig. 10 demonstrates the results of EBSD analysis of samples E and F.

If platelet structures occur in a particle a common characteristic was found in all samples: W2C in between WC platelets always has the same orientation with regard to their tungsten atom sub lattices, meaning that they form a special WC/W2C phase boundary.

### 4. Discussion and conclusion

A metallographic technique was developed as an easy way to distinguish between WC and W2C within a growing WC particle: When using OP-S suspension with additions of NH3 and H2O2 for final metallographic preparation, W2C was preferentially leached out of the material leaving behind empty spaces where W2C had formerly been.

Comparison of samples obtained by carburization on graphite plates emphasize the importance of hydrogen for a homogenous carbon distribution during carburization. In the presence of hydrogen, carbon can be transported in the form of hydrocarbons over a distance of several millimeters up to centimeters. If the carburization is performed in vacuum, the carbon transport is limited to very short distances resulting in WC formation only in direct contact with the solid carbon source (Fig. 6). Furthermore, if no direct contact of solid carbon with tungsten powder exists (as in case of a straight vapor transport reaction) it is impossible to observe the formation of a closed WC rim at the beginning of carburization as described in literature [3] [4].

In the transition area W2C → WC, WC crystals grow in the form of platelets into the W2C matrix. Moreover, WC is not uniformly growing into W2C, instead some fast-growing WC platelets can be found forming big WC grains inside the polycrystalline particles. Such phenomenon occurs independently of the carburization temperature, however, particle size and size of platelets increase with increasing temperature (Fig. 11).

Detailed observations of EBSD results indicate the existence of special WC/W2C phase boundaries with deviation angle < 3°. The nature of such phase boundaries seem to result from the densely-packed tungsten basal plains of both the growing WC and the adjacent W2C grain. The share of special phase boundaries of the total WC/W2C phase boundary length is about 15%.

Most of such special phase boundaries can be found in the platelet WC structures growing into the W2C grain. More precisely, they are those phase boundaries parallel to the WC platelets (Fig. 12). As a consequence, the tungsten sublattice of WC platelets and the W2C in between have the same orientation. The only difference is that the stacking sequence of W layers in W2C is ABAB whereas AAA in WC. In both cases C atoms are distributed within the vacancies between the W layers (either octahedrally or prismatically coordinated).

It is our working-theory that carbon diffusion occurs faster along the densely packed tungsten layers. During the transition of W2C to WC the inter-diffusing carbon atoms lead to an expansion of the respective W layers resulting in a change of the W layer sequence from ABAB in W2C to AAA in WC, and to the change in chemical composition.

This preferential growth of particular WC grains into the W2C particle is driven by the preferential diffusion path of carbon atoms along with W layers in the WC structure. Therefore, a orientation relationship of a WC grain relative to the adjacent W2C grain must exist. Finally, the supply of carbon atoms into the WC lattice on the particle surface is crucial. Consequently, carburization in atmospheres able to transport carbon via gaseous species is required.

Experimental observations suggests that occurrence of fast growing WC platelet structures during carburization of tungsten metal powder might be caused by the change in density from 17.34 g/cm³ to 15.77 g/cm³ during the transformation W2C → WC. This expansion induces stress in the material which is believed to impede the uniform growth of
WC along the preferred orientation (Fig. 12). As a result, thin platelets are formed. By now, in the literature no reference on this process can be found. With ongoing carburization the remaining W₂C “slits” transform into WC. Upon completion, no further platelets can be found in the fully carburized powders. However, it is very likely, that lattice defects remain.

EBSD measurements also demonstrated that Σ2 WC/WC coincidence grain boundaries are formed in the growing WC particles, and that their occurrence is quite high (> 30%). Reports on WC powders indicate a portion of 15 to 40% [5] [14].

**In conclusion,** the formation of the substructure of WC powder particles is strongly related to the oriented growth of WC grains into the W₂C matrix. Preferred diffusion of carbon along certain crystal planes can be assumed to be the underlying mechanism. Platelet-like growth of the WC grains is observed which might indicate that the growth is also affected by stresses, originating from density differences (W₂C → WC) within the growing particle. The share of Σ2 WC/WC coincidence grain boundaries was shown to be high. This might indicate that residual stresses influence the formation of coincidence boundaries and therefore such boundaries can be regarded as “growth defects” related to the

---

**Fig. 9.** EBSD investigation of sample D: above: phases by color and Σ2 WC/WC grain boundaries in white; below: W₂C/WC phase boundaries with deviation angle 0–3° (between (0 0 1) plain in WC and (0 0 1) plain in W₂C) in red, the rest in cyan. Step size: 50 nm. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

**Fig. 10.** EBSD investigation of sample E (right) and sample F (left): phases by color superimposed by image-quality, special W₂C/WC phase boundaries in white, Σ2 WC/WC grain boundaries in cyan, example lattice orientations are included. Step size: 70 nm (left), 150 nm (right). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
growth of WC grains into the solid W₂C matrix.

Acknowledgment

The authors would like to thank Stefan Mitsche for help with the EBSD analysis at FELMI-ZFE Graz. Also, we would like to thank Edward Sachet for valuable discussion.

Funding

This work was supported by the Austrian Research Promotion Agency FFG.

References


Georg Mühlbauer was born in 1981 and studied chemistry at the Vienna University of Technology. He did his doctoral thesis with Professor Schubert on Carburization of tungsten carbide at the Institute of Chemical Technologies and Analytics. Since 2012 he works at Wolfram Bergbau and Hütten AG. After focusing on the recyling of Wolfram he is now contributing in the group for the powder technology of tungsten and the department for technical customer service.

Gabriele Kremser was born in 1982 and studied Chemistry at Graz University of Technology. After her doctoral theses on thiophene derivates she moved to tungsten industry. Her main focus at R&I at Wolfram Bergbau und Hütten AG is on properties of tungsten carbides related to their production conditions and the resulting microstructure in cemented carbides.
Andreas Bock, born in 1966, studied chemistry in the Vienna University of Technology. His doctoral thesis with Professor Lux focused on ultrafine grained cemented carbides.

In 1998 he joined WOLFRAM Bergbau und Hütten AG and held various positions in R&D and technical customer service. Since 2011 he manages the company as vice president technology.

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 associate professor at Chalmers. His main interest is on characterization of the microstructure of metallic materials with a special focus on cemented carbides. Jonathan has > 20 publications in refereed journals and was awarded with the 2015 Sawamura Award from the Iron and Steel Institute of Japan.

Wolf-Dieter Schubert was born in Vienna in 1951. He is professor at the Institute of Chemical Technologies and Analytics at Vienna University of Technology. He is head of a research group focused on the metallurgy of less common metals. His main expertise is on refractory metals and cemented carbides.

> 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.