Analysis of WC with Increased Ta Doping

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Abstract

Tungsten and tantalum metal powders were co-carburized to yield a mixture of cubic and hexagonal carbide. The carburization was made through a two-step carburization process with (W,Ta)\textsubscript{2}C powder as an intermediate product. X-ray diffraction analysis showed that the lattice parameters of the hexagonal phase in the fully carburized powder were larger than those of pure WC indicating the formation of a mixed crystal carbide, (W,Ta)C. The powder with the largest lattice parameters was investigated in detail. A method to produce atom probe tomography specimens of this powder was developed. The atom probe tomography measurement showed the Ta solubility expressed as Ta/(Ta+W) to be as high as 0.086 (i.e. about 8.6 at%). In addition, it was found with electron backscatter diffraction that the (W,Ta)C grains had a large fraction of Σ2 grain boundaries as well as a small fraction of what was suggested as Σ4 grain boundaries.

Keywords

APT, XRD, EBSD, scanning electron microscopy, SEM

Introduction

In the cemented carbide production process, the solubility of transition metal atoms in WC is generally neglected on the assumption that it is small. Mo is known to be an exception with the possibility to form a continuous solid solution of MoC in WC below 1170°C [1]. However, atom probe tomography has recently shown that the transition metal solubility in the WC phase in cemented carbides can actually be substantial [2]. In a comparison between the solubility of Ti, V, Cr, Mn, Co, Zr, Nb and Ta in WC, Ta was observed to have the highest solubility in liquid phase sintered cemented carbides. Expressed as Ta/(Ta+W), the measured solubility in WC was 0.959 ± 0.009 atomic % for a WC-TaC-Co material with 16.20 mass% Ta and 5.51 mass% Co [2].

The powder production route plays an important role for the solubility in WC. It has been shown [3] that it is possible to produce a WC powder with up to 20 atomic % Cr, i.e. a (W\textsubscript{0.8}Cr\textsubscript{0.2})C powder in a two-step carburization process starting from a W + Cr\textsubscript{3}C\textsubscript{2} + C mixture. By contrast, a heat treatment of WC +
Cr₃C₂ + C showed that Cr will not dissolve into the WC structure unless the temperature is in the range of 2000 °C. Even then, the solubility is very low.

It is reasonable to believe that the production route is also important for other additions, such as Ta. In the phase diagrams for the W-Ta-C system, it can be seen that the Ta solubility in W₂C is about 12 atomic % at 1500 °C, and about 15 % at 1750 °C [4]. The solubility of Ta in WC is on the other hand just in the atomic % range (~1 %) [4].

An increased solubility of Ta in the WC structure should have an effect on the lattice parameters just as an increased solubility of Cr in WC has [3]. The usage of X-ray diffraction (XRD) should therefore be a good indicator for the possible success of an increased Ta solubility. However, a quantitative measurement of the chemical composition of a powder must also be made in order to relate it to differences in lattice parameters from pure WC. As the powders will be in the micron or submicron size range, energy dispersive X-ray spectroscopy (EDX) in a scanning electron microscope is a poor choice since the interaction volume will be too large. The similarity of Ta and W makes even EDX in a transmission electron microscope a bad choice as a proper quantification will be impossible. Instead, atom probe tomography is considered to be the most suitable method of investigation. In order to use this technique, a method for producing specimens out of WC powder first has to be developed.

**Experimental**

A mixture of tantalum and tungsten powder in the atomic ratio 2:3, as indicated by point 1 in Fig. 1, was milled in argon atmosphere. The mixture was heated at 1500 °C for three hours and then milled for a second time. This procedure was made in order to increase the homogeneity of the metal powder mixture and, if possible, create in the following a (W,Ta) mixed crystal. The metal powder mixture was milled with carbon in the carbon to metal atomic ratio 0.5:1 (point 2). Based on the phase diagram this should produce a subcarbide with Ta dissolved in the W₂C phase as indicated by point 3 in Fig. 1. The powder mixture was carburized at 1630 °C. The carbon content of the produced subcarbide powder was measured to 2.44 wt%, i.e. the carbon to metal atomic ratio was 0.38:1. Then, carbon was added to the subcarbide so that the final carbide would have the carbon to metal atomic ratio 1.2:1 (point 4). Based on the phase diagram, this should create hexagonal (W,Ta)C (point 5), cubic (Ta,W)C₁₋ₓ (point 6) and a minor amount of excess C. This mixture was milled in argon atmosphere and carburized at 1450, 1630 or 1950 °C resulting in powders P1, P2 and P3.

The powders were analyzed with XRD using a PANalytical X’Pert PRO powder diffractometer (CuKα radiation, X’Celerator detector, Ni Kβ filter). Before analysis, the powders were mixed with a Si powder with a standardized lattice parameter. The lattice parameters of the (W,Ta)C phase were determined using the TOPAS software with Rietveld refinements having the lattice parameter of Si fixed.
All powders P1-P3 where embedded in copper. The Cu embeddings were polished with diamond spray with the smallest particle size being 1 µm. The outer surface layers were cleaned through two hours 4.0 kV Ar⁺ ion sputtering in a Gatan precision polishing system, model 691. The incident angle was 2 ° and both guns were used during the sputtering. Based on the lattice parameter results, powder P1 was chosen to be analyzed with atom probe tomography. The Cu embedment of this powder was inserted in a FEI Strata DB 235 DualBeam focused ion beam scanning electron microscope (FIB-SEM). A (W,Ta)C grain was identified in the FIB-SEM, Fig. 2a. A platinum rich gas was used to deposit a protective 2 µm thick platinum rich layer on the (W,Ta)C grain of interest. By using a 22 ° tilt from the ion column, trenches were milled on the upper and lower sides of the platinum thus creating a wedge shaped specimen held only by supporting bridges on the left and right side of the platinum, Fig. 2b. The left support was milled away and a thin needle was inserted in the FIB-SEM. This needle was welded to the wedge using the platinum rich gas, Fig. 2c. The right support was milled away and the Cu embedment was lowered thus leaving the tungsten needle with the wedge shaped specimen hanging loose, Fig. 2d. The high field needed for field evaporation of WC [5] makes the usage of silicon-based pre-sharpened micro tips inappropriate. Instead, a supporting atom probe tomography specimen was made by electropolishing of another WC-Co based cemented carbide material. The outer part of this supporting specimen was milled away and the wedge shaped specimen was welded to the supporting specimen,
Fig. 2e. The needle was cut loose and further platinum was deposited in the contact zone. The specimen was sharpened through ion milling in the FIB-SEM until the specimen had a radius below 100 nm and the platinum was removed thus leaving the (W,Ta)C grain at the apex of the tip, Fig. 2f. Further details of the specimen preparation technique are given elsewhere [6].

![SEM micrographs of the production steps of an atom probe tomography specimen of the (W,Ta)C powder.](image)

Figure 2: SEM micrographs of the production steps of an atom probe tomography specimen of the (W,Ta)C powder.

An Imago LEAP 3000X HR system was used for the atom probe analysis which was performed using 0.35 nJ laser pulsing at 200 kHz frequency with the cryostat set at 66 K. The reconstruction of the analysis was carried out using the software IVAS 3.4.3.
Scanning electron microscopy (SEM) imaging of the powders were performed with an FEI Quanta 200 FEG SEM and a Leo Ultra 55 FEG SEM. The latter instrument was equipped with a HKL electron backscatter diffraction (EBSD) system using the HKL Channel 5 software. An EBSD analysis was performed on powder P1 at 20 kV, in high current mode and using a 60 μm aperture with the specimen being tilted 70° and the camera being inserted as far in as possible in the SEM. The step size was set to 50 nm. Data was filtered using wild spikes and noise reduction level 4 one time and at least four pixels were needed to define a grain. In order to define a WC/WC grain boundary of the Σ2 type, i.e. a 90° rotation around the [10̅0] axis, a deviance of 3° was accepted. The Brandon criterion [7] would lead to an acceptance of a 10.6° deviance but we noted that the Σ2 peak was much sharper and a larger acceptance would therefore include more randomly oriented grain boundaries. The numbers for the fraction of Σ2 WC/WC grain boundaries will therefore appear smaller than those calculated using the Brandon criterion.

Results

XRD analysis of the subcarbide powder gave W (56.8), TaC (35.7), W₂C (6.4) and WC (1.1 mass %). The lattice parameters for the W₂C phase were a=0.52277 nm and c=0.47462 nm.

The XRD analysis of the carbide powders showed P1 to contain WC (56.7), TaC (42.6) and W₂C (0.7 mass %). P2 contained WC (58.5) and TaC (41.5 mass %) and P3 contained WC (53.3) and TaC (46.7 mass %). The lattice parameters of the WC phase can be seen in Fig. 3. The lattice parameters of pure WC are also included in the figure.

![Figure 3: XRD measurements of lattice parameters in WC phase for carbide powders P1-P3.](image)

The atom probe tomography reconstruction of the investigated (W,Ta)C grain from powder P1 was the shape of a 14 nm long cylinder with the largest diameter being 18 nm (Fig. 4). W, Ta and C were observed to be uniformly distributed in the volume. In addition, Ga atoms were found in the beginning of
the reconstruction. A total of 26073 C, 3056 Ga, 3573 Ta and 37993 W atoms were detected. This gives a Ta/(Ta+W) fraction of 0.08596 (i.e. about 8.6 at% Ta in WC).

All (W,Ta)C powders had the same appearance when imaged in SEM. Fig. 5 shows a SEM micrograph of the Cu embedment of powder P1.

EBSD analysis of powder P1 showed the powder to be a mixture of a hexagonal phase identified as (W,Ta)C and a face-centered cubic phase identified as (Ta,W)C1-X. Fig. 6 shows the grain orientations (Euler angles) of the two phases. Fig. 7 shows the grain boundary misorientation profile of powder P1.
Apart from the $\Sigma 2$ (W,Ta)C/(W,Ta)C grain boundaries at 90 °, a smaller peak can also be seen at 60 °. The $\Sigma 2$ boundaries correspond to 57.9 % of the total (W,Ta)C/(W,Ta)C grain boundary length and the peak at 60 ° to 1.2 %.

Figure 6: Euler angles representation of EBSD analysis of powder P1. (a) Hexagonal (W,Ta)C  (b) Cubic (Ta,W)C$_{1-X}$.

Figure 7: Grain boundary distribution for (W,Ta)C/(W,Ta)C grain boundaries in powder P1.

Discussion

The co-existence of W, TaC, W$_2$C and WC in the subcarbide powder shows the difficulty in the production of a homogeneous powder mixture. On the other hand, the lattice parameters of the W$_2$C phase is an indication that a substantial amount of Ta exists in the structure. Based on the literature [8], the $a$ lattice parameter leads to about 21 at% Ta in the structure while the $c$ lattice parameter gives about 13 at%. This margin arises from the uncertainty in the lattice parameter and uncertainty in the measurement from the literature [8]. Based on knowledge from earlier experiments, we estimate the uncertainty in the lattice parameter to be in the range of ±0.00005-0.0001 nm.

For the mono carbide powders, all lattice parameters are larger than those for pure WC. This is interpreted as Ta being dissolved in the WC structure. At higher temperatures during the second carburization step less Ta is dissolved in the WC structure, analogous to what was obtained in case of both (W,Mo)C [1] and (W,Cr)C [3].
In the atom probe tomography measurement of a (W,Ta)C grain in powder P1, the Ga atoms detected were implanted by sputtering during specimen preparation. This does not therefore reflect the true composition of the material. The Ga sputtering will preferentially decrease the concentration of light elements, i.e. C, in the volume at the tip of the specimen. The Ga concentration will be decreased further down the specimen but as the analyzed volume was small (largest diameter 18 nm, length 14 nm), we cannot exclude this part. It is also known that generally there is a carbon deficiency in the analysis of carbides [9]. Despite these issues, there is no reason to expect the calculated Ta/(Ta+W) ratio (0.086) to be wrong. Comparing this result with the study where the Ta content of a WC grain in a cemented carbide material was measured [2], we have now detected about nine times more Ta. If the Ta content relates to the lattice parameter linearly, every pm deviance from the a lattice parameter of pure WC would correspond to 0.020 % Ta dissolved in the structure expressed as Ta/(Ta+W). For the c lattice parameter, the corresponding value is 0.021 % Ta. This means that the changes in both lattice parameters are approximately the same. This also means that WC in powder P2 is estimated to contain 3.9-6.6 % Ta and WC in powder P3 to contain 2.0-4.8 % Ta. The relatively large intervals are due to the uncertainty of the measurement which has a bigger impact for smaller deviances.

It is known that Σ2 WC/WC grain boundaries found in cemented carbides are produced already during the WC powder production process and not during sintering in the cemented carbide production process [10]. Calculations predict that this CSL boundary is stable and strong and that it will not be penetrated by Co during the cemented carbide sintering [11]. The carburization was performed at a relatively low temperature which means that the entropy is low and it is therefore easy to understand that the chance for formation of a special low energy boundary is high. The presence of a peak in the WC/WC grain boundary misorientation profile at 60 ° is believed to be due to a Σ4 grain boundary. Lay and Loubradou conclude that a 60 ° rotation around the [2̅2̅0] axis results when two WC grains with different Σ2 relationships to a third grain are in contact with each other [12]. We expect this Σ4 grain boundary to exist for a low temperature carburization where the same argumentation as in the case of Σ2 grain boundaries can be used.

It is of interest to produce cemented carbides from Ta doped WC powder as this potentially could have a solid solution hardening effect. The production route and temperature play an important role for the phase formation and tantalum to be dissolved in the tungsten carbide lattice. Low temperatures of course may lead to a powder with a large amount of Σ2 grain boundaries. If a fine grained material is desired and if the Σ2 grain boundary causes the two adjacent WC grains to behave as only one, this is in support of having a higher carburization temperature.

**Conclusion**

A hexagonal (W,Ta)C carbide powder has been produced by making the carburization of W in two steps with Ta being present. XRD measurements indicate that Ta exists already in the W2C grains. XRD also indicates that Ta remains after the second carburization, and the lower carburization temperature, the more Ta remains. A method to produce atom probe tomography measurements of carbide powders has been developed. For a powder produced at 1450 °C, the Ta/(Ta+W) ratio was determined with atom probe tomography to be 0.086. The powder had a high fraction of Σ2 grain boundaries as well as a small fraction of what was suggested to be Σ4 grain boundaries.


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