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STRUCTURAL ANALYSIS AND PROPERTIES OF GRAIN BOUNDARIES IN HEXAGONAL CARBIDES

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Abstract - Grain boundaries in tungsten carbide crystals (hexagonal structure c/a = 0.976) show many coincidence orientations. The most frequent orientation has a coincidence index Σ = 2. H.R.E.M. images of such grain boundaries have been realized. These grain boundaries show a defect structure, only due to the mismatch of the a and c parameters. These defects consist of dissociated 1/6<1120> or 1/2<0001> dislocations regularly spaced. An atomic step is associated with each dislocation. This particular grain boundary can be described as a Σ = 2 (c/a = 1) grain boundary with a periodic structure of dislocations or as a Σ = 39 (c/a = 0.975) grain boundary with a 1.5° deviation to the exact coincidence orientation.

1 - INTRODUCTION

Hexagonal tungsten carbide WC (c/a = 0.976 close to 1) is the hard phase of the WC-Co composites. The microstructure of the composite is characterized by the shape of the carbide grains which appears very regular and prismatic. In consequence many grain boundaries between the carbide grains are planar boundaries. The geometric description of the grain boundaries based on the principle of the coincidence orientations has been applied to the tungsten carbide with the approximation of c/a = 1 [1,2]. Coincidence orientations have been calculated. Experimental orientation relationships between carbide grains have shown that many grain boundaries are close to very low index coincidence orientations (Σ = 2, 4, 5, 7a, 7b, 10...). These grain boundaries can be classified in three main families. The first family (Σ = 7a, ...) corresponds to rotations around the [0001] axis and therefore is independent on the c/a ratio. In the second family (Σ = 2, 5, 10 ...) the grain boundary orientation can be described as rotations around the <1010> axis, perpendicular to the {1010} boundary plane. These grain boundaries have a symmetrical twist character. The third family (Σ = 4, 7b ...) corresponds to rotations around the <1120> axis. These grain boundaries have an asymmetrical tilt character with a boundary plane parallel to the (0001) plane for one crystal [3]. The nature of these grain boundaries is very important with respect to the cobalt segregation in grain boundaries [4-6] and mechanical properties [7-11] of tungsten carbide. Concentration profiles of cobalt carried out on several precise types of grain boundaries with energy dispersive X-rays (E.D.X.) analysis have shown that there is no cobalt
segregation on grain boundaries with an orientation relationship near coincidence orientations. These data are in very good agreement with the high temperature properties of tungsten carbide. High resolution electron microscopy (H.R.E.M.) may complement the E.D.X. microanalysis and can detect segregation phenomenon. In this paper observations by H.R.E.M. concerning the structure of two Σ = 2 and one Σ = 28 grain boundaries are reported and the precise defect structure of the interface have been analyzed in one case.

EXPERIMENTAL PROCEDURE

Slices of WC-Co materials containing 25 wt% cobalt were mechanically ground and polished to a thickness of 80 μm. Discs of 2.3 mm in diameter were ion-milled (Ar+, 6KV) for T.E.M. observations. JEOL 120 CX and H.R.E.M. 200 CX were used.

STRUCTURAL CONSIDERATIONS

Tungsten carbide has a hexagonal structure (Fig. 1a) with c/a = 0.976, space group P6₃m2 with tungsten and carbon atoms in the following positions: 1 (a) 000 and 1 (f) 2/3 1/3 1/2 respectively. The lattice parameters are a = 0.2906 nm and c = 0.2837 nm.

In order to describe a grain boundary in a hexagonal material by a coincidence orientation two integers have been introduced [12]. These parameters describe the case of an ideal structure for which the c/a ratio is such as μ/ν = (c/a)² has a rational value. Consequently the experimental orientation is characterized by a near coincidence orientation when it is compared to the exact three dimensional coincidence size lattice. In a first approximation, μ/ν = (c/a)² = 1 value has been chosen to describe the coincidence orientation relationship in tungsten carbide. In this case, the Σ = 2 orientation corresponds to a 90° rotation around the <1010> direction. Fig. 1b and 1c show two crystals in this orientation. This orientation is frequently observed in tungsten carbide and the usual boundary plane is found parallel to the (1010) common plane. Fig. 1c is a schematic drawing of an exact coincidence Σ = 2 grain boundary. The boundary is perpendicular to the drawing. There is a perfect continuity of the crystal planes across the boundary plane for example (1120)₁ and (0001)₁ or (0001)₂ and (1120)₂.

Fig. 1 a) Hexagonal structure of WC.
   b) Two crystals in a Σ = 2 orientation with c/a = 1. The two crystals are schematized by two hexagonal cells.
   c) Projection of two crystals in a Σ = 2 orientation in a plane perpendicular to the grain boundary plane. Atomic positions of W and C are denoted on the drawing.
HREM OBSERVATIONS OF GRAIN BOUNDARIES IN TUNGSTEN CARBIDE

Fig. 2a, and b, are different parts of the same boundary. These images show clearly the orientation of the two crystals. If the white dots represent tungsten atomic columns, it can be seen that the two crystals have been rotated by 90° around the [1010] common direction. A defect structure appears in the boundary plane. It

![Image of HREM observations of grain boundaries in tungsten carbide](image)

Fig. 2a) Example of a Σ = 2 grain boundary between two tungsten carbide grains. The H.R.E.M. image shows clearly the relationship between the two grains. The two crystals have been rotated by 90° around the [1010] common direction. The grain boundary has been indicated by a dashed line on the micrograph. A defect structure appears in the interface. It consists of single steps along the boundary plane. They have been denoted by an arrow. The number of (0001) planes for the crystal 1 and (1120) planes for the crystal 2 have been indicated. There is an extra (0001) plane due to the difference between the a and c values. It is consistent with the relation:

\[ 41. a = 42. c \]

There are four steps for 84 (0001) planes.

b) Another part of the same grain boundary. Two steps are associated with this part of the grain boundary. In this case the steps have two opposite orientations.
consists of steps: 4 in Fig. 2a and 2 in Fig. 2b. In Fig. 2b steps have two opposite
directions. In comparison with Fig. 1c there is no perfect continuity between the
most compact planes across the interface. A mismatch of these planes is due to the
slight difference between the a and c parameters. If the rotation angle is exactly
90° as it is observed in Fig. 2, an extra (0001) plane appears in crystal 1. Each
extra plane is separated by a distance equal to 41 a or 42 c (11.9 nm).

Fig. 3a and b represent enlarged parts of two different steps observed in this
boundary plane. Steps which have been arrowed in Fig. 2a and b are of the type of the
single step shown in Fig. 3a. If a Burgers circuit is drawn around this step
and then in a perfect Σ = 2 grain boundary (Fig. 3c) a dislocation is found to be
associated with the step and has a Burgers vector equal to 1/6 [1120] or
1/2 [0001] parallel to the boundary plane. If the same procedure is made around the
step shown in Fig. 3b) which is a double step more occasionally observed, the dislo-
cation associated with this step has a 1/3 [1120] or [0001] Burgers vector.

These results clearly demonstrate that the mismatch introduced in the boundary plane
due to the particular tungsten carbide structure can be accommodated by 1/6 [1120],
or 1/2 [0001] dislocations with a separation distance equal to 5.95 nm. This
calculated value is in good agreement with the experimental mean value corresponding
to the separation distance between two single steps (5.5 nm).

2 - Near Σ = 2 grain boundary

Fig. 4 is a H.R.E.M. observation of a near Σ = 2 grain boundary. In this case there
is a small deviation to the exact Σ = 2 orientation. As it is indicated on the
micrograph it can be evaluated by the angular difference between the (1010) planes
in the two crystals, found exactly parallel in the precedent case. The measured
deviation is equal to 5° and corresponds to a small supplementary rotation around the
[1120] or [0001] directions. Due to this small deviation the boundary plane be-
comes asymmetrical, parallel to the (1010) and (1012) planes. The well defined
defect structure described in the precedent case is now destroyed.

3 - Σ = 28 grain boundary

Fig. 5 is an example of a grain boundary formed by a rotation around a [1120] axis.
The precedent studies [9] have shown that this type of grain boundary has an asymme-
trical tilt character. The grain boundary of the Fig. 5 corresponds to a rotation of
20° and has a Σ value equal to 28 (calculated rotation angle value is equal to 21°79
with c/a = 1). The boundary plane is faceted and one facet (crystal 1) is vertical
and parallel to the (0001) plane. Others facets are not vertical and a contrast of
moire fringes appears.

DISCUSSION AND CONCLUSION

A defect structure has been observed in a Σ = 2 grain boundary. It consists of two
perpendicular 1/6 [1120], or 1/2 [0001] edge dislocations. One family can be imaged
in HREM. The two families of dislocations accommodate the mismatch between the a
and c parameters in two perpendicular directions. Dislocation cores appear as single
step and more rarely as double step with a total Burgers vector 1/3 [1120] or
[0001]. The geometric description of this grain boundary based on the principle of
coincidence orientation demonstrates that other values can be attributed in the
present case by changing the u/v ratio. For example, the Σ = 39 description (u/v =
19/20 c/a = 0.975) is obtained with a 88°53 rotation around the <1010> axis (table I).
It is the best value to describe the experimental case in the real material. It
exists a small deviation (1°5) because the experimental rotation value is found
exactly 90°. The Fig. 5 represents the three descriptions (Σ = 2, c/a = 1 ; Σ = 39,
c/a = 0.975 (rotation angle 88°53) and Σ = 39 ; c/a = 0.975 with a rotation angle
equal to 90°). This supplementary rotation is the necessary condition to accommodate
the mismatch between the two a and c parameters by two families of edge disloca-
tions. From this drawing (Fig. 6) the most favorable coincidence orientation
Fig. 3  a) Single step with a $\frac{1}{6} [11\bar{2}0]_1$ or $\frac{1}{2} [0001]_2$ dislocation associated
b) Double step in the same grain boundary
c) Schematic drawing of the two Burgers circuits denoted in Fig. 3a, and b.

Fig. 4 Near $\Sigma = 2$ grain boundary. The boundary plane is asymmetrical.

Fig. 5 $\Sigma = 28$ grain boundary. The rotation axis is parallel to the boundary plane.
description seems to be the near coincidence orientation $\Sigma 39$. It appears that in this well defined grain boundary plane no cobalt segregation has been observed. The two other grain boundaries which have been observed in HREM studies have a more complicated grain boundary structure.

![Diagram](image_url)

Fig. 6 Schematic drawing of the $a$ and $c$ positions in two crystals for $\Sigma = 2$ (a), $\Sigma = 39$ (b) with a $88^\circ 53'$ rotation angle, $\Sigma = 39$ (c) with a $90^\circ$ rotation angle (Deformation has been exaggerated).

<table>
<thead>
<tr>
<th>$c/a$</th>
<th>$\Sigma$</th>
<th>$\mu/\nu$</th>
<th>Rotation angle around $&lt;10\bar{1}0&gt;$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.968</td>
<td>31</td>
<td>15/16</td>
<td>88°15</td>
</tr>
<tr>
<td>0.970</td>
<td>33</td>
<td>16/17</td>
<td>88°26</td>
</tr>
<tr>
<td>0.972</td>
<td>35</td>
<td>17/18</td>
<td>88°36</td>
</tr>
<tr>
<td>0.973</td>
<td>37</td>
<td>18/19</td>
<td>88°45</td>
</tr>
<tr>
<td>0.975</td>
<td>39</td>
<td>19/20</td>
<td>88°53</td>
</tr>
<tr>
<td>1</td>
<td>2</td>
<td>1</td>
<td>90°</td>
</tr>
</tbody>
</table>

Table I: Different coincidence orientations near $\Sigma = 2$ for different $\mu/\nu$ ratio

REFERENCES