Microstructure Formation Pathways in Tantalum Carbides

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Microstructure Formation Pathways in Tantalum Carbides

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The Attributes of Tantalum Carbides

An ultrahigh melting temperature!\[ T_m (TaC) \approx 4000^\circ C; \]

Plasticity behavior at elevated temperature

Phase content controlled microstructures
“The $\text{Ta}_6\text{C}_{5\pm x}$ phase is the only ordered phase of nonstoichiometric cubic tantalum carbide $\text{TaC}_y$. Incommensurate ordered phase similar to known $M_6\text{C}_5$ superstructures is formed in nonstoichiometric cubic tantalum carbide $\text{TaC}_y$. To produce ordered phase $\text{Ta}_6\text{C}_{5\pm x}$ the samples synthesized were annealed at a temperature 1600 K with following slow cooling to 750 K at a rate of 0.15–0.25 K min$^{-1}$ (≈ 1 K/6 minutes!).

$\text{Ta}_6\text{C}_5$

Monoclinic or Trigonal?

$\text{Ta}_2\text{C}$

Trigonal (often shown in a hexagonal setting)
Processing Route for Ta-C

**Hot Isostatic Pressing (HIP)**

- Powder mixture in vacuum sealed Ta can
- ‘can’ HIP
- Remove Ta can to reveal > 98% dense $\text{Ta}_x\text{C}_{1-x}$

**Ta powder** - *large powder size*
- $48 \, \mu\text{m} \pm 25 \, \mu\text{m}$
- Wide distribution

**TaC powder** - *small powder size*
- $2.7 \, \mu\text{m} \pm 0.7 \, \mu\text{m}$
- Narrow distribution

*Ratio of Ta and TaC powder determine the final composition.*
Variation of microstructure with carbon content (phase)

Resultant microstructures

→ Equiaxed TaC
→ Equiaxed TaC + Ta₄C₃ (Ta₂C)
→ Acicular TaC + Ta₄C₃ + Ta₂C
→ Equiaxed Ta₂C

Grain Size of the Resultant Carbides Trended with Starting, Blended Powder Sizes

Powder size increasing (TaC ~ 3μm + Ta ~ 50μm)

Grain size increasing

56Ta44C

58Ta42C

60Ta40C

68Ta32C
The Precipitation of Multiple Phases Changes the Grain Morphology

*How and Why?*

**Answer - The Reaction Diffusion Couple**

R. Morris et. al Act Materialia 60 (2012) 139-148
EDS Line Profile of Diffusion Couple

The EDS line profile:

1. Steady decrease in the carbon content 50Ta:50C to 56Ta:44C.
2. Steady state composition of the $\text{Ta}_{66}\text{C}_{33}$ ($\text{Ta}_2\text{C}$).
3. Oscillatory carbon signal that varied between $\text{Ta}_{66}\text{C}_{33}$ and $\text{Ta}_{90}\text{C}_{10}$, which corresponded to grains of either $\text{Ta}_2\text{C}$ or Ta.

R. Morris et al. *Act Materialia* 60 (2012) 139-148
The Reaction Zone Phases and Morphologies

TaC

Ta₂C

Ta₂C + Ta

Acicular TaC + Ta₂C/Ta₄C₃

Equiaxed Ta₂C

Acicular Ta₂C

STEM-HAADF

TaC + Ta₄C₃

Ta₄C₃ + Ta₂C

100 µm

20 µm

6 µm
TEM of TaC side of diffusion couple

OR: \{111\}_TaC/\{0001\}_Ta4C3; [110]_TaC//[10-10]_Ta4C3

Towards Reaction zone

STEM-HAADF Micrograph; laths fully extended across the grain

STEM-HAADF Micrograph (brighter features are Ta-rich phases)

Equiaxed TaC grains
3D reconstruction using STEM-HAADF

Laths (thin plates) are non-continuous and form on different planes of TaC

TaC + Ta₄C₃

High Angle Annular Dark Field or Z-contrast imaging

Ta₄C₃ laths are very thin – 2D SEM/TEM images are a projected surface area which can be misleading in assuming these phases are ‘thick’

Orientation Relationship (OR) of TaC and Ta$_4$C$_3$ phase

TaC FCC-like structure yields **FOUR** \{111\} variants – leads to equivalent precipitation habit planes for Ta$_4$C$_3$-criss-cross pattern morphology of laths
How do the laths relate to grain shape?

- **3D serial sectioning**: Repetitive removal of uniform amounts of material and image collection
- Image collection via ion contrast imaging
  - *electron emission is a function of orientations (ion channeling contrast) of the grains*
Global 3D Morphology 55Ta45C (TaC + Ta₄C₃)

- **Equiaxed** TaC grain with Ta₄C₃ laths

3D reconstruction reveal parallel laths
- Continuous and Non-continuous within grains

Lath structure at grain boundary walls – heterogeneous nucleation sites? More to come....

**Ta₄C₃ Lath Formation**

“deck of cards sliding”

- Energy surfaces show it takes significantly less energy to shear Ta-Ta layers than Ta-C
Similarly for Ta$_2$C (from TaC)

Remove every other carbon plane, for correct chemistry

Shear to have stacking sequence correct

Note, the TaC lattice parameter has not been allowed to relax after shearing in model above
Carbon Loss and Phase Stability

When the local carbon content drops to ~10/12 or $\text{Ta}_6\text{C}_5$, the $\text{Ta}_4\text{C}_3$ stacking sequence becomes energetically favorable.
Anisotropy based precipitate growth

Plate-like growth if:
\[
\frac{\partial I}{\partial V}_{r} \geq \frac{\partial I}{\partial V}_{h} \Rightarrow \frac{\gamma_s}{\gamma_b} \geq \frac{2r}{h}
\]
Change in interfacial energy by changing the height. \( \gamma_s \) greater than the change in \( \gamma_b \) by changing the radius.

Cylinder like growth if:
\[
\frac{\partial I}{\partial V}_{r} \leq \frac{\partial I}{\partial V}_{h} \Rightarrow \frac{\gamma_s}{\gamma_b} \leq \frac{2r}{h}
\]
Change in interfacial energy by changing the radius. \( \gamma_b \) is greater than the change in \( \gamma_s \) by changing the height.
Interfacial Energy: Side Walls

- Transformation is a prismatic dislocation shear loop (bounding conditions)

\[ E_s = \frac{G b_s^2 r}{2(1 - \nu)} \ln \left( \frac{2r}{r_0} \right) = 2\pi h \gamma_s \]

**Total energy dislocation**

\[ E_s = 9.454 \times 10^{-9} \times r \ln(4 \times 10^9 \times r) \]

**circular shear loop**

\[ \gamma_s = 8.3169 + 0.372 \ln(r) \]

**Inputs:**
- \( \nu = 0.21 \)
- \( G(111) = 260 \text{ GPa} \)
- \( b = 0.25 \text{ nm} \)
- \( r_0 = 0.50 \text{ nm (disl core radius)} \)
- \( r = 30 \text{ nm (size of plate – more to come)} \)
- \( h = 1 \text{ nm (~ 4 Ta layers)} \)

\[ \gamma_s = \frac{1.8731 J}{m^2} \]

Value seems a little high...continuing to work to refine energies
Interfacial Energy: Top Surface

- If the Ta₄C₃ is 3 units high (or 12 Ta layers), it has perfect registry with the TaC ‘above’ and ‘below’. If it is 1 unit high, a dislocation shear loop is needed to “restore” the ordering sequence → prismatic loop

![Ta₄C₃ loop](image)

**TaC {111} plane**

**Total energy dislocation**

\[
E_t = \frac{Gb^2 r}{2(1-\nu)} \left( 1 - \frac{\nu}{2} \right) \ln\left( \frac{2r}{r_0} \right) = 2\pi r^2 \gamma_t
\]

**Circular shear loop**

\[
\gamma_t = 6.046 \cdot 10^{-10} \cdot r \ln\left( \frac{2r}{r_0} \right)
\]

**Inputs:**
\[
\nu = 0.21 \\
G(111) = 207 \text{ GPa} \\
b = 0.18 \text{ nm} \\
r_0 = 0.50 \text{ nm (disl core radius)} \\
r = 30 \text{ nm (size of disc)}
\]

**Very low value!**

\[
\gamma_t = \frac{0.0965 J}{m^2}
\]
Lack of c-axis coarsening

Energy of side wall very high and contributes to lack of coarsening the lath’s thickness
Lath Spacing

• Interlayer distance near the shifted layer
  – layers near shifted area are compressed

• Strain energy (Volume)
  – 1% reduction in c-cell parameter with loss of C layer. Yields a strain energy term that must be overcome to precipitate lath... working to determine if significant

• Depletion region
  – vacancy depletion zone

\[\begin{array}{|c|c|}
\hline
& \text{A} & \text{B} \\
\hline
\text{A} & -0.02711 & \text{0.121623} \\
\text{B} & -0.02686 & 0.073748 \\
\text{C} & -0.11079 & -0.13283 \\
\text{A} & \text{0.13283} & -0.11079 \\
\text{B} & 0.073748 & -0.02686 \\
\text{C} & -0.02711 & \text{0.121623} \\
\text{B} & 0.071614 & \\
\hline
\end{array}\]
Critical Radius

\[ \Delta E = \text{Energy gain from transformation (V*G_v) + Energy cost of new interfaces (S*\gamma) + Energy cost of applied strain (V*G_s)} \]

\[ \Delta G = \pi r^2 h(\Delta G_v + \Delta G_s) + E_s + E_b \]

Solve for \( \frac{d\Delta G}{dr} = 0 \)

\[ \Delta G_v = -5.18 \times 10^8 \frac{J}{m^3} \]

\[ \Delta G_s = 1.34 \times 10^8 \frac{J}{m^3} \]

r critical = 32.5 nm

\[ \Delta G = 8.225e-16 \text{ J} \]

Homogenous nucleation barrier is very large...

likely looking for heterogeneous nucleation at grain boundaries, etc. which are defect structures that are fast diffusion paths.
Ta₂C/Ta Reaction Interface

- Limited solubility of carbon in Ta results in precipitation of Ta₂C phases when carbon reaches Ta grains.
- Grain size is comparable for both phases.

<table>
<thead>
<tr>
<th>Diameter (µm)</th>
<th>(1) Ta₂C sidec</th>
<th>(2) Middle</th>
<th>(3) Ta Sidec</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ta</td>
<td>9 ± 4.1</td>
<td>11 ± 3.5</td>
<td>17 ± 6.9</td>
</tr>
<tr>
<td>Ta₂C</td>
<td>15 ± 5.5</td>
<td>10 ± 4.7</td>
<td>6 ± 2.0</td>
</tr>
</tbody>
</table>

Ta$_2$C Phase Region

- Ta$_2$C found to have parallel banded structure (HAADF-STEM and SEM)
- SAED indentified as only Ta$_2$C phase

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Acicular Grain Morphology

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Acicular Grain Morphology

laths appear to be continuous across the grain

- OR: \( \{0001\}_{Ta2C} \parallel \{0001\}_{Ta4C3} \) : \( \langle 11-20 \rangle_{Ta2C} \parallel \langle 11-20 \rangle_{Ta4C3} \)

Laths span major axis of the acicular grains

Matrix phase

Ta\(_2\)C hcp-like structure has only ONE close packed plane – hence all phases are aligned parallel in the grain

Secondary phase

STEM-HAADF \( \langle 110 \rangle \)

10 nm

10 μm
Refined, equaxed grains @ interface - TaC/Ta₂C

At the interface, refined equiaxed grains Ta₂C grains

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Summary: Consequences of Precipitation Sequence on Grain Morphology

Carbon is lost on TaC closed packed planes – multiple variants of \{111\} yields cross-hatched encasement of Ta$_2$C/Ta$_4$C$_3$ in various directions.

Formation of Ta$_2$C has only one closed packed plane variant \{0001\}. As carbon continues into Ta$_2$C and precipitates Ta$_4$C$_3$, the phase laths are parallel and acicular in grain shape.

Low energy interfaces can/will drive microstructure morphology!
Precipitation sequence is paramount!
Please visit De Leon et al. Poster #13

"Deformation Mechanisms in Ta₂C"
Ta$_x$C$_{1-x}$ Phases and Microstructures Processed by Vacuum Plasma Spraying (VPS)

Deposit molten powder mixture on graphite mandrel

Sinter to in graphite furnace to densities > 95+%

‘can-less’ HIP to further improve densification > 98%
VPS As-Sprayed Condition

• Bimodal distribution of grain sizes
  ➢ (±μm) in size and (sub-μm) in size

• TaC grains larger than Ta$_2$C grains

• Topographical difference because of different hardness values between the phases

Microstructure Evolution with VPS-based Processing

Processing Steps
→ Spraying
→ Sintering
→ "Canless" HIP’ing

As-sprayed

Sintered

HIP’ed

5 µm 5 µm 5 µm
Defect and Inclusion Characterization

Starting Powders produced using carbo-thermal reduction of Ta$_2$O$_5$

Ta$_2$O$_5$+7C $\rightarrow$ 2TaC+5CO

- Oxygen content (LECO analysis) determined to be $\sim$1300 ppm
- Oxide phase(s) was not observed XRD of powder

EDS Spectral map showed powders contain oxygen
Post-VPS processing

- Multiphase microstructures
  - TaC, Ta$_2$C, Ta$_4$C$_3$ phases present
- No oxide peaks detected in XRD spectrum
- Acicular Microstructure

Post-VPS processing

EDS Mapping of post VPS processed Ta-C specimen containing oxide inclusions

Ta$_2$O$_5$ phase identification

EDS

Composition (at%) vs. Distance (nm)

- Ta
- O

View direction <112>

FFT

β- Ta$_2$O$_5$
Monoclinic space group C 2/c
$T_m$: 1872 °C

Ta$_x$C$_{1-x}$

Ta$_2$O$_5$
3D Characterization of Oxide Inclusion

- SEM and TEM imaging techniques only yield a 2D perspective on the microstructure.

- The oxides are rounded, globular and interconnected as one large feature.

\[ \beta-\text{Ta}_2\text{O}_5 \]
\[ T_m: 1872 \, ^\circ\text{C} \]

Porosity analysis

- Porosity randomly distributed both at the grain boundaries and within the grains.
  - Suggest pores *formed during initial spraying* and remained during processing.
- The presence of pores suggests *difficulty to fully consulate the material*.
  - Result of extremely high melting temperature (~4000 °C) and the inability to provide adequate temperature and/or pressure during processing of the carbides.

Average pore volume = 0.046 ±0.134 μm³
Majority pore volume less than 0.04 μm³
Total pore volume = 5 μm³ (~ 2%); \( r_{avg} \sim 0.5 \mu m \)

Where are we going?

Atom probe tomography, where do the impurities segregate....

Atom Probe Technique

Image courtesy of M.K. Miller, ORNL
Thank you – questions?