Fabrication, Microstructures, Properties and Applications of W/(TiC,ZrC) Composites

Yu ZHOU, Yujin WANG, Guiming SONG, Taiquan ZHANG

Institute for Advanced Ceramics
School of Materials Science and Engineering
Harbin Institute of Technology
1. Introduction
2. Design and Fabrication
3. Microstructures
5. High Temperature Deformation Behaviors and Strengthening Mechanisms
6. Thermophysical Properties
7. Thermal Shock and Ablation Performances
8. Applications
9. Conclusions and Outlooks
Solid rocket motor throats

Problems of throats (W-Cu):

- High thermal conductivity
- High specific weight
- Poor dimensional stability

Performance requirement:

- Low thermal conductivity
- Low specific weight
- Thermal shock resistance
- Ablative resistance

New materials
## Properties of materials those melting points are above 2500ºC

<table>
<thead>
<tr>
<th></th>
<th>Melting point [ºC]</th>
<th>Density g/cm³</th>
<th>Strength (R.T.) MPa</th>
<th>Antioxidant</th>
<th>Thermal expansion coefficient 10^-6/K</th>
<th>Thermal conductivity W/(m-K)</th>
<th>Thermal shock resistance</th>
<th>Corrosion resistance</th>
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<tr>
<td><strong>Metal</strong></td>
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<tr>
<td>Nb</td>
<td>2468</td>
<td>8.57</td>
<td>345(T)</td>
<td>general</td>
<td>7.1</td>
<td>52.7</td>
<td>good</td>
<td>good</td>
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<tr>
<td>Mo</td>
<td>2623</td>
<td>10.2</td>
<td>620(T)</td>
<td>bad</td>
<td>4.9</td>
<td>135</td>
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<td>good</td>
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<tr>
<td>Ta</td>
<td>2996</td>
<td>16.6</td>
<td>551(T)</td>
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<td>6.6</td>
<td>54.4</td>
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<tr>
<td>W*</td>
<td>3410</td>
<td>19.3</td>
<td>360~490(F)</td>
<td>bad</td>
<td>4.5</td>
<td>160</td>
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<tr>
<td><strong>Oxide</strong></td>
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<tr>
<td>ThO₂</td>
<td>3050</td>
<td>9.69</td>
<td>95(F)</td>
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<td>10.1</td>
<td>4.7</td>
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<tr>
<td>MgO</td>
<td>2800</td>
<td>3.58</td>
<td>70~340(F)</td>
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<td>15.0</td>
<td>37.7</td>
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<tr>
<td>HfO₂</td>
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<td></td>
<td></td>
<td>good</td>
<td>--</td>
<td>--</td>
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<tr>
<td>ZrO₂</td>
<td>2700</td>
<td>5.6</td>
<td>143</td>
<td>good</td>
<td>10.1</td>
<td>1.96</td>
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<td>BeO</td>
<td>2570</td>
<td>3.02</td>
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<td>170~180</td>
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<td><strong>Carbide</strong></td>
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<td>HfC</td>
<td>3890</td>
<td>12.6</td>
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<td>6.3</td>
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<td>14.5</td>
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<td>22.2</td>
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<td>good</td>
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<tr>
<td>ZrC</td>
<td>3530</td>
<td>6.74</td>
<td>1636.6(F)</td>
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<td>6.74</td>
<td>20.5</td>
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<td>6.5</td>
<td>24.7</td>
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<tr>
<td>TiC</td>
<td>3250</td>
<td>4.93</td>
<td>1352(F)</td>
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<td>7.74</td>
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<tr>
<td>SiC*</td>
<td>2600</td>
<td>3.21(α-SiC)</td>
<td>2205(F)</td>
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<td>4.7</td>
<td>41.9(β-SiC)</td>
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<td><strong>Graphite</strong></td>
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<tr>
<td>(KS-8*)</td>
<td>(3600)</td>
<td>2.26</td>
<td>35.3(//)</td>
<td>general</td>
<td>1.53(//)</td>
<td>121.4(/)</td>
<td>good</td>
<td>general</td>
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*SiC* data for polycrystalline material.
### Properties comparison between W, TiC and ZrC

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<thead>
<tr>
<th>Properties</th>
<th>W</th>
<th>TiC</th>
<th>ZrC</th>
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<tbody>
<tr>
<td>Density, g/cm³</td>
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<td>4.93</td>
<td>6.63</td>
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<td>Lattice constant, nm</td>
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<td>0.4320</td>
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<td>Melting point, °C</td>
<td>3410</td>
<td>3250</td>
<td>3530</td>
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<tr>
<td>Elastic modulus, GPa</td>
<td>390~410</td>
<td>450</td>
<td>345~400</td>
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<td>Hardness, GPa</td>
<td>□ 4</td>
<td>32</td>
<td>29</td>
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<td>Ultimate tensile Strength, MPa</td>
<td>980</td>
<td>114</td>
<td>90</td>
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<td></td>
<td>□ 980°C</td>
<td>□ 980°C</td>
<td>□ 980°C</td>
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<td>Thermal expansion coefficient, ×10⁻⁶K⁻¹</td>
<td>4.5</td>
<td>7.7</td>
<td>4.0</td>
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<tr>
<td>Thermal conductivities, W/(m.K)</td>
<td>105</td>
<td>24</td>
<td>40</td>
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<tr>
<td>Electrical resistivity, ×10⁻⁶ohm. m</td>
<td>55</td>
<td>52.5</td>
<td>78</td>
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</table>
Properties comparison between W, TiC and ZrC

W
- High melting point
- Good high temperature plasticity
- Good thermal shock resistance

Carbide
- High melting point
- Low specific weight
- Good high temperature strength
- Low thermal conductivity
- Good ablative resistance

TiC_p/W
ZrC_p/W
<table>
<thead>
<tr>
<th>Materials</th>
<th>Fabrication process</th>
<th>Authors</th>
<th>Country</th>
<th>Year</th>
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<tr>
<td>ZrC-W</td>
<td>Hot-pressing</td>
<td>G. V. Samsonov</td>
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<td></td>
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<td>V. S. Neshpor</td>
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<td>G. M. Song</td>
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<td>Displacive Compensation of Porosity</td>
<td>K. H. Sandhage</td>
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<td>Reactive pressureless sintering</td>
<td>S. C. Zhang</td>
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<td>Plasma Spraying</td>
<td>P. Ctibor</td>
<td>Czech</td>
<td>2009</td>
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<td>G. M. Song</td>
<td>China</td>
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<td>TaC-W</td>
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<td>G. E. Hilmas</td>
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<td>ZrC-Mo</td>
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<td>G. V. Samsonov</td>
<td>Russia</td>
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<td>S. Hanada</td>
<td>Japan</td>
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</table>
1. Introduction
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Compositional design of composites

<table>
<thead>
<tr>
<th>Samples</th>
<th>W (vol%)</th>
<th>TiC (vol%)</th>
<th>ZrC (vol%)</th>
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<tr>
<td>W</td>
<td>100</td>
<td>0</td>
<td>0</td>
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<td>10TiC&lt;sub&gt;P&lt;/sub&gt;/W</td>
<td>90</td>
<td>10</td>
<td>0</td>
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<tr>
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<td>80</td>
<td>20</td>
<td>0</td>
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<td>10ZrC&lt;sub&gt;P&lt;/sub&gt;/W</td>
<td>90</td>
<td>0</td>
<td>10</td>
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<td>20ZrC&lt;sub&gt;P&lt;/sub&gt;/W</td>
<td>80</td>
<td>0</td>
<td>20</td>
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<td>30ZrC&lt;sub&gt;P&lt;/sub&gt;/W</td>
<td>70</td>
<td>0</td>
<td>30</td>
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<tr>
<td>40ZrC&lt;sub&gt;P&lt;/sub&gt;/W</td>
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<td>50ZrC&lt;sub&gt;P&lt;/sub&gt;/W</td>
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Materials preparation and test methods

W powder

TiC, ZrC

Ball-milling 24h

Hot press sintering
2000-2200 °C /20MPa /1.3 × 10^{-3}Pa/1h

TiC_p/W, ZrC_p/W

Microstructures analysis

Properties measurement

Numerical simulation
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Density

Density

Relative density

Carbide content, %

Density g/cm³

Relative density, %

Carbide content, %

TiCₚ/W

ZrCₚ/W

TiCₚ/W

ZrCₚ/W
Microstructures of (a) W2000; (b) W2200
Microstructures of ZrC\textsubscript{p}/W composites with different ZrC\textsubscript{p} contents

SEM morphologies of (a), (d) 10ZW; (b), (e) 20ZW; (c), (f) 30ZW; (a), (b), (c) polished surfaces; (b), (e), (f) etched surfaces
Fracture morphologies of TiC\textsubscript{p}/W composites (R.T.)

Pure W  10TiC\textsubscript{p}/W  30TiC\textsubscript{p}/W
XRD patterns of composites before and after sintering

20TiC\textsubscript{p}/W

30ZrC\textsubscript{p}/W
Changes of lattice parameters of carbide before and after sintering (nm)

<table>
<thead>
<tr>
<th>Planes</th>
<th>TiC</th>
<th>ZrC</th>
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<tr>
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<td>(111)</td>
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<td>(200)</td>
<td>(200)</td>
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<td>(220)</td>
<td>(220)</td>
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<table>
<thead>
<tr>
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<th>Before sintering</th>
<th>After sintering</th>
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<tr>
<td></td>
<td>0.2499</td>
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<td>0.2167</td>
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<tr>
<td></td>
<td>0.1532</td>
<td>0.1524</td>
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</table>

| ZrC                  |                  |                 |
|                      | 0.2712           | 0.2680          |
|                      | 0.2347           | 0.2322          |
|                      | 0.1659           | 0.1646          |

TiC $\rightarrow$ (W, Ti)C
ZrC $\rightarrow$ (W, Zr)C

$W+ZrC \rightarrow (W_x,Zr_{1-x})C$
TEM morphologies and the EDS analysis of interface

Element relative content, at%

Distance from the TiCp/W interface, nm

Distance from the ZrCp/W interface, nm
TEM images and HREM images of ZrCp/W interface

(a) TEM image showing the ZrCp/W interface with labeled distances 0.23 nm and 0.24 nm. (b) HREM image with labeled ZrC and W phases. (c) Electron diffraction pattern showing [001]_W and [011]_ZrC.
Precipitated phase and interface EDS analysis in a ZrC grain

![Image of ZrC grain with precipitated phase and interface analysis](image)

**Graphical Analysis**

- **X-axis:** Distance from interface, nm
- **Y-axis:** Element content, at.%
- **Lines:**
  - **Zr** (blue)
  - **W** (pink)

**Legend:**
- **ZrC matrix**
- **Precipitated phase**
- **Interface**

**Image Details**

- **Scale Bar:** 200nm

---

**Note:**

- The analysis shows a sharp change in element content at the interface, indicating a clear boundary between the ZrC matrix and the precipitated phase.
- The precipitated phase contains a significant amount of W, suggesting a complex interaction at the interface.

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**Additional Observations**

- The precipitated phase appears as dark spots in the ZrC grain, indicative of a different chemical composition.
- The interface analysis confirms the presence of Zr and W, crucial for understanding the mechanical properties of the material.

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**References**

HREM images of Precipitated phase

HREM image of interface between precipitated phase W and ZrC
a) TEM image of precipitated phase W, b) diffraction pattern of ZrC/W interface, c) HREM image of ZrC/W interface
a) TEM image of precipitated phases, b) diffraction pattern of ZrC along [011] direction, c) HREM image of W$_2$C, d) diffraction of W$_2$C along [110] direction calculated according to the W$_2$C PDF cards
Formation mechanism of precipitated phase

- Formation of \( \text{ZrC} \) and \( \text{(W,Zr)C} \)
- Diffusion of \( \text{W} \)
- Growth of \( \text{W}_2\text{C} \)
- Resolve of \( \text{(W,Zr)C} \)
- Long-range diffusion of \( \text{W} \)
- Short-range diffusion of \( \text{W}_2\text{C} \)
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Hardness and Modules

TiC<sub>p</sub>/W

ZrC<sub>p</sub>/W
Flexural strength and fracture toughness (R.T.)

**Flexural strength**

- **TiC<sub>P</sub>/C**
- **ZrC<sub>P</sub>/C**

**Fracture toughness, MPa.m<sup>1/2</sup>**

- **TiC<sub>P</sub>/W**
- **ZrC<sub>P</sub>/W**
Stress-deflection curve (R.T.~1200 ℃)

30TiCp/W

30ZrCp/W
Cracks initiation and propagation of 30TiCp/W composite (1000 ☏)
Cracks initiation and propagation of 30ZrC$_p$/W composite (1000×)
Flexural strength at high temperature

**TiC\(_p\)/W**

**ZrC\(_p\)/W**
Fracture morphology of $30\text{TiC}_p/W$ composite under different temperature

- **R.T.**
- **800°C**
- **1000°C**
- **1200°C**
Fracture morphology of 30ZrCₚ/W composite under different temperature.
Tensile properties at high temperature

<table>
<thead>
<tr>
<th>Materials</th>
<th>R.T.</th>
<th>800°C</th>
<th>1000°C</th>
<th>1200°C</th>
<th>1400°C</th>
<th>1600°C</th>
<th>1880°C</th>
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<td>511</td>
<td>543</td>
<td>480</td>
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Tensile stress - strain behavior of 30ZrCp/W composite
Stress-strain curves of ZrCp/W composites with different ZrCp contents under 1400 °C
Tensile fracture morphology of 30ZrCp/W composite
Tensile fracture morphology of ZrCp/W composite (1400 ×)

20ZrCp/W

30ZrCp/W

40ZrCp/W

50ZrCp/W
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(a) Shape and (b) size and tolerance of the compressive specimens

Test conditions

- Temperature: RT~1600°C
- Strain rate: 10^{-3}~1/s

Schematic representation of the core part of Gleeble-1500D equipment.
Compressive true stress-strain curves of ZrC_p/W composites with various ZrC_p contents at (a) RT; (b) 600ºC; (c)1100ºC
Compressive yield strengths of ZrCp/W composites with various ZrCp contents at different temperatures
Effect of temperature on compressive deformation behavior of ZrCp/W composites

Effect of temperature on high temperature compressive deformation behavior of ZrCp/W composites
(a) 10ZW; (b) 20ZW; (c) 30ZW
Relationships between compressive yield strengths and deformation temperature

High temperature compressive yield strengths of ZrC\textsubscript{p}/W composites

Temperature ranges:
(a) RT~600ºC
(b) 600~1100ºC yield platform
(c) >1100ºC

Plastic deformation of W
Fracture of ZrC grains
Compressive true stress-strain curves of ZrCp/W composites under various temperatures
The effect of temperature and strain rate on the serrated deformation

The serrated true stress-strain curves (a), (b), and (c) and corresponding to micrographs (d), (e), and (f)
The fracture of ZrC particles: (a) the collapse of ZrC agglomerations in compressed composite at 1400°C and 10⁻³/s strain rate; (b) the fracture of the single ZrC particle in compressed composite at 1600°C and 10⁻³/s strain rate
The process of serrated deformation

An amplified schematic diagram of the serration formation process
Regions I: elasticity deformation stage; II: yielded; III: a slight decrease of the stress caused by the ZrC agglomerations collapse; IV: an increase of the stress caused by the mutual extrusion of ZrC particles; V and VI: repetitious process.
Deformed microstructures of 30ZrCp/W

Microstructures of 30ZW composite deformed at 10\(^{-3}\)/s strain rate and various temperatures (a) 1400\(^\circ\)C; (b) 1500\(^\circ\)C; (c) 1600\(^\circ\)C

**Deformation mechanisms**

(a) W grains deformation
(b) ZrC grains rotation
(c) ZrC grains boundary sliding
(d) ZrC grains fracture
Fracture strain of 30ZW composite in 1300~1600°C and 10^{-3}~1/s strain rates
Deformation activation energy of 30ZW

\[ \delta = AF(\sigma) \exp(-Q/RT) \]

\[ F(\sigma) = \begin{cases} 
\sigma^n & \text{if } \alpha\sigma < 0.8, \\
\exp(\alpha\sigma) & \text{if } \alpha\sigma > 1.2, \\
[\sinh(\alpha\sigma)]^n & \text{for all values of } \sigma 
\end{cases} \]

\[ \ln(\text{strain rate}) \text{ vs. } \ln[\sinh(\alpha\sigma_{0.2})] \text{ for 30ZW composite at various temperatures} \]

\[ \ln[\sinh(\alpha\sigma_{0.2})] \text{ vs. } 1/T \text{ for 30ZW composite deformed at various strain rates} \]
Deformation activation energy = 344 kJ/mol;
Stress exponent = 17.6

Some data of activation energy of tungsten at high temperatures

<table>
<thead>
<tr>
<th>Activated energy</th>
<th>Pipe diffusion</th>
<th>Lattice diffusion</th>
<th>Self diffusion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Values (kJ/mol)</td>
<td>378</td>
<td>585</td>
<td>650</td>
</tr>
</tbody>
</table>

The stress exponent of tungsten alloy is 5 ~ 7 at 1300~2200°C, so for the deformation mechanism of ZrCp/W composite, except for the deformation of tungsten matrix, it also include ZrC particles fracture, grain boundary sliding.
Deformation, boundary slip and interface slip of ZrC grains

A schematic diagram of plastic deformation mechanisms for the composite loaded by a compressive stress: (a) an ideal microstructure of the composite; (b) grains deformation in the W matrix, showing a slight rotating for the ZrC particles (shown by numeral); (c) grain boundary slip or failure in the ZrC particles; (d) interface slip or failure
Microstructures of ZrC/W composite deformed under various temperature
Dynamic recovery and re-crystallization of W matrix in the process of deformation

1200°C, dislocation arrays

1500°C, dislocation nets

1600°C, Recrystallization
Effect of temperature on the morphology of dislocations in ZrC grains.

Dislocation behaviors in ZrC particles during the composite deformed at $10^{-3}$/s strain rate and (a) 1200°C; (b) 1500°C; (c) 1600°C.

T>1200°C dislocation glide begin in lots of ZrC grains.
Sub-grain boundary of ZrC particles

Pure tilt boundary in ZrC particles during the composite deformed at $10^{-3}$/s strain rate and (a) 1500°C, dislocation arrays; (b) 1500°C, dislocation array and hexagonal; (c) 1600°C, dislocation array deriving from pores
Effect of strain rate on the morphology of dislocations in ZrC grains

$\varepsilon = 5\%$  $\varepsilon = 20\%$  $\varepsilon = 50\%$

$30\text{ZrCp/W}, 1200^\circ\text{C}, \dot{\varepsilon} = 10^{-3}/\text{s}$
Interaction of dislocations in ZrC particles during the composite deformed at 1300°C and 10^{-3}/s strain rate.

(a) Kinetics jogs; (b) thermodynamics jogs; in ZrC particles.

Schematic diagram:
- Kink on (111)
- B = 1/2 <110>
- Vacancy emission
- Jog
- Bowing on (111)
Dislocation curving in ZrC particles during the composite deformed at 1600°C and 10^{-3}/s strain rate, and some thermodynamic jogs also shown by arrows.
Dislocation initiating from (a) W/ZrC interface; (b) ZrC/W/ZrC interface triple point in ZrC particles during the composite deformed at (a) 1500°C and 10⁻³/s strain rate; (b) 1600°C and 10⁻¹/s strain rate
Schematic diagram of the dislocation nucleation in ZrC particles: (a) no dislocation nucleation due to not satisfy the CRSS law; (b) dislocation nucleation due to satisfy the CRSS law by rotating ZrC particles for accommodating the plastic deformation of the W matrix

Notions: P-{111} slip plane; N-normal direction; R-rotating

\[ \tau = \sigma \cos \phi \cos \lambda \]

(1) Work hardening
(2) Fracture of ZrC particles
Macro-cracks of 30ZrCp/W specimens

Photographs of 30ZW specimens compressed at 1500 ºC under
(a) 10^{-3}/s; (b) 10^{-2}/s; (c) 10^{-1}/s; (d) 1/s strain rates

Photographs of 30ZW specimens compressed at 10^{-3}/s strain rate under
(a) 1300ºC; (b) 1400ºC; (c) 1500ºC; (d) 1600ºC
Macroscopic fracture mechanism under compressive loading

- **Shear zone**
- **Tension zone**
- **Pressure direction**
- **Friction direction**
- **Fracture direction**

**L/D ≤ 1**

**L/D ≥ 1**
Microstructure at 45° direction of II and III regions in the deformed specimen
Microcosmic fracture process of composites

Microstructures in a compressed specimen at 1300°C and 10⁻³/s strain rate:
(a) voids at ZrC and W gain boundaries triple points;
(b) voids at ZrC particle tips
(c) failure at ZrC/ZrC boundaries
Shear and trans-crystalline rupture of ZrC grains

Microstructures of ZrC particles:
(a) ZrC/ZrC boundary in as-sintered composite;
(b) ZrC/ZrC boundary slipping or shear fracture;
(c) cleavage failure of ZrC particles
Schematic expression of microcosmic fracture process

(a) microstructure in the composite;
(b) voids initiating from ZrC and W grain boundaries triple points;
(c) microcrack propagating along ZrC/ZrC boundaries
Fracture on ZrC/W interface

The microcracks at the ZrC/W interface shown by the arrows in the specimen deformed at 1600°C and 10^{-2}/s strain rate
Grain refinement of W matrix

Grain sizes of pure tungsten and tungsten matrix in ZrCp/W composites

<table>
<thead>
<tr>
<th>Materials</th>
<th>W2000</th>
<th>W2200</th>
<th>10ZW</th>
<th>20ZW</th>
<th>20ZW</th>
<th>20ZW</th>
<th>30ZW</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZrC particle size (µm)</td>
<td>-</td>
<td>-</td>
<td>2.5</td>
<td>1.25</td>
<td>1.7</td>
<td>5</td>
<td>2.5</td>
</tr>
<tr>
<td>Grain size (µm)</td>
<td>10.41</td>
<td>18.3</td>
<td>4.16</td>
<td>2.96</td>
<td>3.79</td>
<td>4.96</td>
<td>2.06</td>
</tr>
</tbody>
</table>

When the deformation of polycrystalline materials happened under high temperature, there was no doubt that in Hall-Petch relation, friction stress and the pinning constant were all the function of temperature. Thus, Hall-Petch relation can be rewritten as:

\[
\sigma_m(T) = \sigma_0(T) + k(T)d^{-1/2}
\]  
(6-4)

\[
\sigma_0(T) = \alpha_1 \times 10^{(\beta_1/T)}
\]  
(6-5)

\[
k(T) = \alpha_2 + \beta_2 \log\left(\frac{1}{T}\right)
\]  
(6-6)
Comparison of the experimental results of high temperature compressive yield strength of pure tungsten with the calculated results

\[
\sigma_m (T) = 22.9 \times \exp\left(\frac{1055.5}{T}\right) + \left[5041.5 + 619.5 \times \ln\left(\frac{1}{T}\right)\right] \times d^{-1/2}
\]  
(6-7)
To metal matrix composite material, the yield strength can be divided into two parts: (1) without strengthening phase (fibers or particles), only the strength of metal matrix; (2) Added the strengthening phase, the resulting intensity increment. Therefore, the yield strength of composites can be expressed as:

\[
\sigma_{\text{MMC}} = \sigma_m + \Delta\sigma
\]  

(6-8)

The strengthening of metal-matrix composites are to achieve directly or indirectly, by increasing the dislocation density or impede dislocation movement. Therefore, to the particles reinforced metal-matrix composites, when the deformation happened under high temperature, changes of the dislocation density can be expressed as follows:

\[
\rho_{\text{total}} = \rho_s + \rho_g + \rho_h - \rho_r
\]  

(6-9)
Under the applied compressive loading, resulted in a strain $\varepsilon$, and as the different of elastic modulus between the metal matrix and the enhanced particles, in the matrix around the particles, it produced in a large number of geometrically necessary dislocations, the density can be expressed as:

$$
\rho_g = \frac{6V_p}{bD} \varepsilon
$$

(6-12)
Dislocations strengthening model and its mathematical expression

For \( \rho_h - \rho_r \), it can be attributed to the metal matrix dislocation density changes at high temperature deformation when there are no parties to strengthen, that is, its contribution to the strength of the metal matrix. When the composite material has high temperature deformation, it is clear that the metal matrix strength and elastic modulus is a function of temperature, the compressive yield strength of composites at elevated temperature can be expressed as:

\[
\sigma_{MMC}(T) = \sigma_m(T) + \sqrt{3\alpha G(T)}b\sqrt{\rho_g} \tag{6-11}
\]
Dislocations strengthening model and its mathematical expression

As long as knowing the changes of tungsten matrix yield strength and shear modulus with changed temperature, the yield strength of the composite material can be calculated. Studies have shown that the shear modulus of tungsten with temperature as the following relations:

\[
G_m(T) = 1.5893 \times 10^5 - 1.4733 \times 10^1 \times (T - 273) - 2.448 \times 10^{-1} \times (T - 273)^2 \text{ MPa} \quad (6-13)
\]
The calculation results of compressive yield strength

The calculated high temperature compressive yield strength of \( \text{ZrC}_p/\text{W} \) composites with (a) various volume fractions of \( \text{ZrC} \) particles; (b) various \( \text{ZrC} \) particle sizes by strain gradient strengthening model.
Characteristics of loading transition strengthening

loading transition strengthening conditions:
(1) interface strengthening;
(2) no brittle phase formed at interface

The fracture and dislocation slip in the ZrC particles clearly showed that stress can be well delivered to the ZrC particles

The stress at ZrC/W interface in the deformed ZrC_p/W samples: (a) 10ZW-2.5 at RT and 10^{-3}/s strain rate; (b) 20ZW-1.7 at 1200°C and 10^{-3}/s strain rate
The composite strength can be obtained by the fracture strength of ZrC, and also, through the strength of the composites, it can be inversed the temperature of ZrC particles occurred to dislocation slip.
Model of loading transition strengthening

According to the dislocation pile-up model, assuming that $n$ generated dislocations accumulated at the interface, then, in the end of the dislocation accumulation, that is, the shear stress generated at the interface can be expressed as:

$$\tau_0 = n\tau$$ \hspace{1cm} (6-14)

For single-phase metals or alloys, it can assume the center of the grain as the dislocation source, then, the distance between dislocation slip and the grain boundary is $d/2$, $d$ is grain size. The number of accumulation of dislocation can be expressed as:

$$n = \frac{C\tau d}{Gb}$$ \hspace{1cm} (6-15)

For particle reinforced metal matrix composites, in the accumulation of the number of dislocations is associated with the particle spacing, which can be expressed as:

$$n = \frac{\pi(1 - \nu_m)\tau\lambda}{G_m b}$$ \hspace{1cm} (6-16)
Model of loading transition strengthening

If the assumed reinforced particles as sphere, the effective distance between the ZrC particles are:

\[ \lambda_e = \lambda_s - D \quad (6-17) \]

\[ \lambda_s = \left( \frac{\pi}{6V_p} \right)^{1/2} D \quad (6-18) \]

Assumed that the stress concentration at the accumulation end as the ZrC particles fracture stress, combined equation (6-14) - (6-16), the external stress can be expressed as:

\[ \tau = \left( \frac{G_m b \tau_0}{\pi(1 - \nu_m)} \right)^{1/2} \lambda_e^{-1/2} \quad (6-19) \]
Model of loading transition strengthening

When ZrCp / W composites deformed under high temperature, the ZrC particles fracture stress $\sigma_0$, tungsten matrix Poisson's ratio $\nu_m$ and shear modulus $G_m$ are all the function of temperature. The relations between the compressive yield strength of ZrCp/W composites and temperature can be expressed as:

$$\sigma_{MMC}(T) = \sigma_m(T) + m \left( \frac{G_m(T)\sigma_0(T)}{\pi(1-\nu_m(T))} \right)^{1/2} \lambda_e^{-1/2} \quad (6-20)$$

Equation (6-13) shows the relationship between shear modulus of tungsten and temperature, and Poisson's ratio with temperature is

$$\nu_m(T) = 0.28247 + 6.1902 \times 10^{-6} \times (T - 273)$$
$$+ 3.162 \times 10^{-9} \times (T - 273)^2 \quad (6-21)$$
The fracture of ZrC particles in the deformed 20ZW-1.7 samples at RT and 10^{-3}/s strain rate

The relation of flexural strength of ZrC and temperatures

\[ \sigma_f(T) = \sigma_{RT} + k_f(T - 273) \quad (RT \leq T \leq 1200^\circ C) \quad (6-22) \]

\[ \sigma_f = 45.2217 + 0.2384 \times (T - 273) - 9.94 \times 10^{-5} \times (T - 273)^2 \quad (T \geq 1200^\circ C) \quad (6-23) \]
Predicted results of ZrCp/W composites with various ZrCp sizes

Fig. 6-9 Comparison of the experimental and calculated high temperature compressive yield strength of 20vol.% ZrCp/W composites with various ZrC particle sizes by loading transition strengthening model.
Fig. 6-10 Comparison of the experimental and calculated high temperature compressive yield strength of ZrCp/W composites with various volume fractions of ZrC particles by loading transition strengthening model.
Predicted results of dislocation initiating temperature in ZrCp

Fig. 6-11 Critical resolved shear stress of ZrC particles vs. temperature
The Orowan strengthening mechanism of small particles: when the ZrC particles are as small as nano, with the nano-particles inside the grains of the tungsten, if tungsten matrix deforms plasticly, with the occurrence of dislocation slip, these nano-particles interact with dislocations, leading to Orowan strengthening.

Solid solution strengthening and bubbles strengthen of tungsten matrix: another result of the diffusion of interface atomics is the formation of dilute solid solution strengthening of tungsten matrix. In addition, because the tungsten powder used in this article is for commercial available, it contains a small amount of Na and Si elements, causd the bubble to strengthen.
Outlines

1. Introduction
2. Design and Fabrication
3. Microstructures
5. High Temperature Deformation Behaviors and Strengthening Mechanisms
6. Thermophysical Properties
7. Thermal Shock and Ablation Performances
8. Applications
9. Conclusions and Outlooks
Coefficient of thermal expansion

Temperature, °C

Coefficient of thermal expansion, $\times 10^{-6}/K$

**TiC$_p$/W**

**ZrC$_p$/W**
Specific heat (C_p)

TiC_p/W

ZrC_p/W
Thermal diffusivity

TiC_p/W

ZrC_p/W
Thermal conductivity

Thermal conductivity, W/(m·K) vs. Temperature, ℃

Thermal conductivity, W/(m·K) vs. Carbide content, vol%
Electrical resistivity

![Graph showing electrical resistivity vs. temperature for different materials.](image)
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Oxyacetylene flame ablation equipment

samples
Measured temperature curves of front and back surfaces

1- The front surface;
2- The back surface
Measured and simulated temperature curves

W, 30TiC_p/W, 30ZrC_p/W

1, 3—simulation results;
2, 4—measurement results
Ablation rate of composites measured by oxyacetylene flame

Mass ablation rate

Linear ablation rate
Ablation results of 30ZrCp/W composites measured by oxyacetylene flame

(a) Ablation surface: bubbles

(b) The microstructures of ablation surface: micro-cracks
Ablation results of 30TiCp/W composites measured by oxyacetylene flame

Thermal shock damage

The micro-cracks around the TiC particles
Ablation results of 30TiCp/W composites measured by oxyacetylene flame

(a) ablation pits on ablation surface;
(b) cross-section of the ablation surface, showing the ablation surface (S), transition zone (T), matrix (M);
(c) the erosion product of river patterns
Ablation results of 30TiCp/W composites measured by oxyacetylene flame

(d) ablation pit;
(e) ablation morphology of the cross section;
(f) porous morphology showed in the transition zone.
(a) Surface ablation morphology, showing that the ablation pit and copper leaching out the matrix and then solidified in the ablation surface;

(b) morphology of the cross-section: after copper leaked out, left the porous tungsten skeleton.
### Properties comparison of W-Cu (W75~86/Cu25-14vol%) and ZrCp/W composites

<table>
<thead>
<tr>
<th>Property</th>
<th>W-Cu</th>
<th>ZrCp/W</th>
<th>Addition (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density, g/cm³</td>
<td>~17</td>
<td>12.7~13.9</td>
<td>-17.9~25.5</td>
</tr>
<tr>
<td>Hardness</td>
<td>160~260(HB)</td>
<td>536~577(HV)</td>
<td></td>
</tr>
<tr>
<td>Modulus, Gpa</td>
<td>300~400</td>
<td>350~375</td>
<td>Match</td>
</tr>
<tr>
<td>Strength (R.T.), MPa</td>
<td>300~600(tensile)</td>
<td>497~705(bending)</td>
<td></td>
</tr>
<tr>
<td>Strength (1200 °C), MPa</td>
<td>~130</td>
<td>643~810</td>
<td></td>
</tr>
<tr>
<td>Fracture toughness, MPa·m^{1/2}</td>
<td></td>
<td>6.94~9.23</td>
<td></td>
</tr>
<tr>
<td>Thermal expansion coefficient, 10^{-6}/K</td>
<td>5.92~6.09</td>
<td>4.6~4.8</td>
<td>-15~25</td>
</tr>
<tr>
<td>Thermal conductivity, W/(m·K)</td>
<td>160</td>
<td>34~38</td>
<td>-76~79</td>
</tr>
<tr>
<td>Specific heat, 10^{-2}J/(g·K)</td>
<td>12</td>
<td>16.3~17.5</td>
<td>36~46</td>
</tr>
<tr>
<td>Linear ablation rate, 10^{-3}mm/s</td>
<td>9.4</td>
<td>1.6~3.7</td>
<td>-61~83</td>
</tr>
<tr>
<td>Mass ablation rate, 10^{-3}g/s</td>
<td>62</td>
<td>8.7~13</td>
<td>-79~86</td>
</tr>
<tr>
<td>Thermal shock resistance</td>
<td>Good</td>
<td>Good</td>
<td></td>
</tr>
</tbody>
</table>
1. Introduction
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Application on high temperature fixture

Photos of high temperature (a),(b) tensile clamp and (c) anvils of ZrC$_p$/W composite

- Application environments:
  - vacuum, inert gases
  - $1500^\circ$C long time
  - $\sim2000^\circ$C short time
Under the using conditions of 1500 °C, 200MPa and continuous using time more than 240h every once, the fixture have worked for 3 years, and the total working time is about 4780h. Compared to original fixture of tungsten alloy, the working life increased by 30 times.
Tungsten-matrix composites with high volume refractory-metal carbides exhibit the extensive applications for the components in high temperature environments because of their excellent room and high temperature mechanical properties, thermal physical properties, ablation and thermal shock resistance. It makes them as one of the most promising materials for applications in aerospace fields, such as the injector of rocket engine, and used as components in ultra-high temperature environment, such as grips, clamps and anvils, etc. Control of microstructure, electrical properties, low temperature fabrication and high temperature applications of tungsten-matrix composites need to be further studied and discussed.
Thanks for Your Attention!