Mechanism analysis of liquid - liquid doping and fabrication of high properties of W - Zr(Y)O$_2$ alloys

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Outline

- Introduction
- Mechanism of liquid-liquid doping
- Microstructure and properties of alloys
- Conclusions and perspectives
1. Introduction

Innovative oxide particles strengthened W alloys

Traditional solid-solid / liquid doping processes

1. Uneven particle distribution, larger oxide particles;
2. Low-temperature and recrystallization embrittlement.

Research objectives

1. Nanosized oxide particles (< 500 nm) uniformly distributed within W grains;
2. Low ductile-brittle transition temperature (< 150 °C) and high recrystallization temperature (> 1400 °C).
2. Mechanism of liquid-liquid doping processes

Existence forms and reaction mechanisms of polytungstate ions

<table>
<thead>
<tr>
<th>Reversible reaction equations</th>
<th>Reaction products</th>
<th>Common names</th>
</tr>
</thead>
<tbody>
<tr>
<td>[(H_2W_{12}O_{40})^{6-} + 6H^+ + 32H_2O = 12(H_2WO_4 \cdot 2H_2O)]</td>
<td>(H_2WO_4 \cdot 2H_2O)</td>
<td>Tungstic acid</td>
</tr>
<tr>
<td>[H_2W_{12}O_{40}^{6-} + H^+ = HW_{12}O_{39}^{5-} + H_2O]</td>
<td>(HW_{12}O_{39}^{5-})</td>
<td>Metatungstate</td>
</tr>
<tr>
<td>[HW_{12}O_{39}^{5-} + 2H_2O + OH^- = 2(H_3W_{6}O_{21})^{5-}]</td>
<td>((H_3W_6O_{21})^{5-})</td>
<td>Pseudo-AMT</td>
</tr>
<tr>
<td>[(H_3W_6O_{21})^{5-} + 2OH^- = (HW_6O_{21})^{2-} + 2H_2O]</td>
<td>((HW_6O_{21})^{2-})</td>
<td>Paratungstate</td>
</tr>
<tr>
<td>[(HW_6O_{21})^{2-} + 3H_2O + 7OH^- = 6[HWO_4]^- + H^+ + 7OH^- = 6WO_4^{2-} + 7H^+ + 7OH^-]</td>
<td>(WO_4^{2-})</td>
<td>Tungstate ion</td>
</tr>
</tbody>
</table>
Liquid-liquid doping techniques for preparing Zr(Y)O$_2$ doped W powders

**Hydrothermal method**
- Hydrothermal reaction: 170 °C
- Duration: 12 hours

**Azeotropic distillation method**
- Bath Temp.: 100 °C
- Dispersant: Alcohol + n-butyl alcohol

**Sol-gel method**
Morphologies of precursors synthesized by three different doping processes:

- (a) Microsphere
- (b) Loose
- (c) Angularity
- (d) Sheet
Formation mechanism of doped precursor powders

1. Synthetization analysis of h-HATB powder by hydrothermal method

Experimental observation of the synthetization of h-HATB

F. N. Xiao et al., J Alloy Compd. 843 (2020) 156059
Formation mechanism of doped precursor powders

2. Synthetization analysis of precursor powder by azeotropic method

Dispersing process
1. Alcohol removing water;
2. n-bulty covering particles;
3. Oranic chain replacing hydroxly.
Morphologies of W-Zr(Y)O$_2$ powders reduced after 900 °C for 2 h

(a) Step Hydrothermal method

(b) Composite hydrothermal method

(c) Sol-gel method

(d) Azeotropic distillation method

1. Preserving the precursor’ morphologies;

2. More uniformed – size and highly dispersed powders in Fig. b
3. Microstructure and properties of Z(Y)O₂ strengthened W alloy

Description of innovative liquid – liquid doping process with optimal parameters

Ionic reaction mechanisms:

1. \(2\text{Zr}^{4+} + \text{W}_{12}\text{O}_{40}^{8-} = 8\text{WO}_3 \downarrow + 2\text{Zr(WO}_4)_2 \downarrow\)

2. \((\text{H}_2\text{W}_{12}\text{O}_{40})^{6-} + 6\text{H}^+ + 32\text{H}_2\text{O} = 12(\text{H}_2\text{WO}_4 \cdot 2\text{H}_2\text{O})\)
Microstructure of the advanced material

1. Highly dispersed doped powders, shown in Fig. (a);
2. 90% of particles distributed within W grains, shown in Fig. (b) and (e);
3. 85% of Zr(Y)O₂ particles are less than 300 nm in size, shown in Fig. (d).

Main characteristic of the advanced W alloys

1. The oxide particle are **smallest**;
2. More oxide particles distributed within W grains;
3. The distribution of oxide particles are **more uniform**.

References

(a) Present work;
(b) C. J. Wang, J. Refract. Met. Hard Mater. 84 (2020) 105082;
(c) Y. Shen, J. Nucl. Mater. 455 (2014) 234-241;
## Comparison of microstructure and properties of ODS-W alloys

<table>
<thead>
<tr>
<th>Doping process</th>
<th>Sintering Process</th>
<th>Alloy</th>
<th>W grain size (μm)</th>
<th>Oxide size (μm)</th>
<th>Relative density (%)</th>
<th>Microhardness /HV</th>
<th>Refs.</th>
</tr>
</thead>
<tbody>
<tr>
<td>L - L</td>
<td>SPS</td>
<td>W-6vol% Al₂O₃</td>
<td>3.64</td>
<td>&gt;1.0</td>
<td>94.96</td>
<td>347.39</td>
<td>[35]</td>
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<td></td>
<td>SPS</td>
<td>W-2.5%ZrO₂</td>
<td>4.65</td>
<td>2.5</td>
<td>99.6</td>
<td>480</td>
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<td>VD</td>
<td>W-2.5%ZrO₂</td>
<td>40-80</td>
<td>1.5</td>
<td>98.7</td>
<td>-</td>
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<tr>
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<td>VD</td>
<td>W-La₂O₃</td>
<td>50</td>
<td>3</td>
<td>-</td>
<td>-</td>
<td></td>
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<tr>
<td>L - S*</td>
<td>SPS</td>
<td>W-0.9wt%La₂O₃</td>
<td>-</td>
<td>2</td>
<td>94</td>
<td>406</td>
<td>[39]</td>
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<tr>
<td></td>
<td>SPS</td>
<td>W-1.0%Y₂O₃</td>
<td>2.3</td>
<td>Nanosize (Uneven)</td>
<td>92</td>
<td>423</td>
<td>[40]</td>
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<tr>
<td></td>
<td>HIP</td>
<td>W-1%La₂O₃</td>
<td>-</td>
<td>&gt;5</td>
<td>90.6</td>
<td>-</td>
<td>[41]</td>
</tr>
<tr>
<td>S - S</td>
<td>HIP</td>
<td>W-Ti-0.5%Y₂O₃</td>
<td>2-5</td>
<td>&gt;1.5</td>
<td>-</td>
<td>-</td>
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<tr>
<td></td>
<td>SPS</td>
<td>W-5%HfO₂</td>
<td>11.6</td>
<td>&gt;5</td>
<td>94.5</td>
<td>440</td>
<td>[43]</td>
</tr>
</tbody>
</table>

**Novel process**

| HIP            | W-0.5%Zr(Y)O₂    | 4.67 ± 0.5 | 0.25 ± 0.05 | 96.7 ± 0.2 | 472 ± 10 | Present |

### Conclusion

1. Smallest particles size;
2. Medium properties.
1. The oxide particle are smaller;
2. Most Zr(Y)O₂ distributed within W grains;
3. The distribution of oxide particles are more uniform.

Main characteristic of my prepared heavy W alloy

References
(a) Present work;
## Comparison of microstructure and properties of ODS-heavy W alloys

<table>
<thead>
<tr>
<th>Heavy W alloy</th>
<th>Sintering process</th>
<th>RD/%</th>
<th>Grain size/μm</th>
<th>Particle size/μm</th>
<th>Hardness/ HV</th>
<th>Refs.</th>
</tr>
</thead>
<tbody>
<tr>
<td>W–Ni–Fe–0.3PSZ</td>
<td>1480 °C (1h)</td>
<td>-</td>
<td>18</td>
<td>0.8</td>
<td>-</td>
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<tr>
<td>W–Ni–Fe–1Al₂O₃</td>
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<td>98.3</td>
<td>36.8</td>
<td>7</td>
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<tr>
<td>W–Ni–Fe–xY₂O₃</td>
<td>1485 °C (1h)</td>
<td>99.1</td>
<td>19.5</td>
<td>0.6 - 1.3</td>
<td>-</td>
<td>[10]</td>
</tr>
<tr>
<td>W-Ni-ZrO₂</td>
<td>1500 °C (1h)</td>
<td>93.5</td>
<td>~25</td>
<td>3 - 5</td>
<td>333</td>
<td>[50]</td>
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<tr>
<td>W-Ni-Fe-Co-Y₂O₃</td>
<td>1450 °C (1h)</td>
<td>94.1</td>
<td>12</td>
<td>&gt;0.6</td>
<td>425</td>
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<tr>
<td>94W–4.56Ni–1.14Fe–Y₂O₃</td>
<td>1485 °C (1h)</td>
<td>99.0</td>
<td>15</td>
<td>0.65</td>
<td>-</td>
<td>[53]</td>
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<tr>
<td>Previous W-ODS</td>
<td>SPS/HIP</td>
<td>&lt;99.9</td>
<td>&lt;10</td>
<td>1 - 5</td>
<td>406 - 480</td>
<td>[27]</td>
</tr>
<tr>
<td>93W–4.9Ni–2.1Fe–Zr(Y)O₂</td>
<td>1520 °C (2.5h)</td>
<td>99.2</td>
<td>26</td>
<td>0.2 - 1</td>
<td>402 ± 10</td>
<td>[47]</td>
</tr>
<tr>
<td>WHA₀.75</td>
<td>1400° C (2.5h)</td>
<td>99.2 ± 0.1</td>
<td>25 ± 2</td>
<td>0.2 - 1</td>
<td>402 ± 10</td>
<td>Present</td>
</tr>
</tbody>
</table>

### Conclusion

1. Finer particles;
2. Larger grain size;
3. Limited grain refinement.
TEM analysis of HIP sintered W-Ni-Fe-ZrO$_2$ alloys

Conclusion:
1. Cubic structure of Zr(Y)O$_2$;
2. Well-bonded interface.
Comparison of properties with state-of-the-art review

**W-Zr(Y)O₂ alloy in fig (a, b)**

1. High compressive strength;
2. High critical failure strain;
3. Higher than published alloys.

**93W-Zr(Y)O₂ alloy in fig (c, d)**

1. Higher tensile strength;
2. Compressive strength.
Objective: Arrhenius model was used to identify the compressive behaviours of the W-Zr(Y)O₂ alloy.

\[
Z = A \left[ \sinh(\alpha \sigma) \right]^n
\]

\[
\ln Z = \ln A + n \ln \left[ \sinh(\alpha \sigma) \right]
\]

\[
\ln \dot{\varepsilon} = \ln A + n \ln \left[ \sinh(\alpha \sigma) \right]
\]

\[
AARE = \frac{1}{N} \sum_{i=1}^{N} \left| \frac{\sigma_e^i - \sigma_p^i}{\sigma_e^i} \right| \times 100\%
\]

\[
\alpha = A_0 + A_1 \varepsilon + A_2 \varepsilon^2 + A_3 \varepsilon^3 + A_4 \varepsilon^4 + A_5 \varepsilon^5 + A_6 \varepsilon^6
\]

\[
n = B_0 + B_1 \varepsilon + B_2 \varepsilon^2 + B_3 \varepsilon^3 + B_4 \varepsilon^4 + B_5 \varepsilon^5 + B_6 \varepsilon^6
\]

\[
\ln Z = C_0 + C_1 \varepsilon + C_2 \varepsilon^2 + C_3 \varepsilon^3 + C_4 \varepsilon^4 + C_5 \varepsilon^5 + C_6 \varepsilon^6
\]

- $Z$ is Zener-Hollomon parameter;
- $\varepsilon$ is strain;
- $\dot{\varepsilon}$ is strain rate;
- $A$, $n$ and $\alpha$ are material constants.

Conclusion: The average relative error (AARE) = 3.6 % was calculated to investigate the good prediction accuracy.
Conclusions

1. Investigation of reaction mechanism and formation mechanism of doped W precursor powders;

2. Development of an innovative liquid – liquid hydrothermal doping process;

3. Fabrication of W alloys having ZrO₂ particles (< 300 nm) within grains;

4. Fabrication of the advanced W alloys with high strength and critical failure strain.
1. **Tensile and bending** tests at various temperatures (100 ~ 500 °C);

2. Compressive tests at high temperatures (1000 ~ 1400 °C);

3. **Thermomechanical behaviour** of the elaborated W alloys and numerical modelling;

4. Extension of the developed method for $\text{Y}_2\text{O}_3$, $\text{La}_2\text{O}_3$ and $\text{CeO}_2$ strengthened W alloy.
Thank you for your attention!