SYNTHESIS AND FABRICATION OF Cu–W COMPOSITES COMBINING SHS AND HEC TECHNOLOGIES

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W-Cu pseudoalloys

1) significant difference in lattice parameters of metals (a(W) = 0.316 nm, a(Cu) = 0.361 nm)

2) the high difference of melting points of copper and tungsten
   $T_Cu = 1083^\circ C$, $T_W = 3422^\circ C$

3) W and Cu insolubility in both solid and liquid states

   they form a material with absolutely new structure which is therefore rather a metal matrix composite (MMC) instead of a true alloy or solid solution.
**W-Cu pseudoalloys**

- high thermal and electrical conductivity
- low thermal expansion

**Applications**
- High-power device
- LED
- Heat sink
- Golf Weight Attachment
- Electrode
**Aim**

To develop a new way to fabricate W-Cu composites of various compositions directly from the oxide/salt precursors by combining energy efficient combustion synthesis method and HEC technology.

**Approach**

To perform joint reduction of oxide/salt in controlled combustion mode using the coupling of low exothermic reduction reactions (MeO+C) with a high-energetic one (MeO+Mg)

**Investigated systems**

CuO - WO$_3$ - Mg - C  
CuWO$_4$ - Mg - C
Precursors preparation

Mixing of WO$_3$, CuO

Making a salt by co-precipitation or calcination

SHS co-reduction by (Mg+C) mixture

W-Cu powders HEC consolidation

W-Cu powders and billets physicomechanical characterization

Technical approach and methodology
Coupling approach in SHS

\[
\begin{align*}
WO_3 + 3Mg, & \quad T_{ad} = 3500 \text{ K}, \quad \Delta H = -840 \text{ kJ/mol} \\
CuO + Mg, & \quad T_{ad} = 3100 \text{ K}, \quad \Delta H = -162 \text{ kJ/mol} \\
WO_3 + 3C, & \quad T_{ad} = 320 \text{ K} \\
CuO + C, & \quad T_{ad} = 830 \text{ K}
\end{align*}
\]

\( \text{Explosive reactions} \)

\( \text{Low exothermic reaction} \)

\( \text{No combustion} \)

\( CuO - WO_3 - Mg - C, \quad T_{ad} = 1000 - 2500 \text{ K} \)
Thermodynamics of the WO$_3$-CuO-$y$Mg-$x$C system, including the formation of tungsten carbides.
Thermodynamics of the WO$_3$-CuO-$y$Mg-$x$C system, excluding the formation of tungsten carbides

\[ P_{(N2)} = 0.3 - 0.5 \text{ MPa} \]
Combustion parameters and phase composition vs. carbon content $x$ of WO$_3$-CuO-1.3Mg-xC mixtures

$P_{(N2)}=0.3-0.5$ MPa
XRD pattern, SEM image and EDS analysis of W-Cu composite powder after acid treatment

\[ \text{WO}_3 + \text{CuO} + \text{Mg} + \text{C} \rightarrow \text{Cu} + \text{W} + \text{MgO} + \text{CO}_2 + \text{CO} \]

\[ \text{MgO} + 2\text{HCl} = \text{MgCl}_2 + \text{H}_2\text{O} \]

Spot 1 Cu:W = 1.0:1.14
Spot 2 Cu:W = 1.0:1.29
Spot 3 Cu:W = 1.12:1.0
Spot 4 Cu:W = 1.29:1.0
Experimental Results in Copper Wedge

XRD patterns of quenched products

1. Initial mixture
2. I stage - Carbothermic reduction
3. II stage - Magnesiothermic reduction
HSTS analysis of the CuO-WO$_3$-xMg-yC system

CuO-WO$_3$-1.4Mg-2.5C mixture

V$_h$ $\sim$ 300 $^\circ$/min

T$_{\text{max}}$ $\sim$ 1300 $^\circ$C
REDUCTION MECHANISM IN THE WO₃-CuO-Mg-C SYSTEM

I step
CuO + C → Cu + CO(CO₂) and
WO₃ + C → WO₂.₉(WO₂.₇₂) + CO(CO₂)
WO₂.₉(WO₂.₇₂) + C → WO₂ + CO(CO₂)

II step
WO₃ + Mg → W + MgO
WO₂ + Mg → W + MgO

At insufficient amount of reducers
WO₃ + MgO → magnesium tungstate

At excess amount of carbon (& long duration)
WO₂ + C → W (W₂C, WC) + CO(CO₂) and
W + C → W₂C, WC
Hot Explosive Consolidation (HEC)

Cylindrical steel tubs containers, ampoules with upper cork (115x22x3mm)

Explosive predensification of W/Cu composite powder with W:Cu=1:1 at room temperature pressure 10 GPa
Hot Explosive Consolidation (HEC)

Cylindrical HEC billets of Cu:W=1:1 composite after 2 stage loading (5GPa) at 700, 930 and 1000°C
Microstructure of HEC consolidated sample, 700°C

The temperature dependence of Young modulus (E) and internal friction Q-1(T)

Microhardness measurements for different sections after two-stage HEC of W-Cu=1:1 composite, 10 & 5 GPa

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<tr>
<th>Sample</th>
<th>Temperature, °C</th>
<th>Microhardness, kg/mm²</th>
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<tbody>
<tr>
<td>1</td>
<td>700</td>
<td>274</td>
</tr>
<tr>
<td>2</td>
<td>930</td>
<td>297</td>
</tr>
<tr>
<td>3</td>
<td>1000</td>
<td>383</td>
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Conclusions

1. Combustion synthesis of W-Cu composite was performed directly from oxides via reaction’s coupling approach. Optimum conditions of target nanocomposite (W-Cu) SHS synthesis were found.

2. The reduction mechanism was proposed due to copper wedge technique and HSTS method. It was shown that firstly reacts weak reducer (carbon), then stronger one (Mg).

3. Explosive consolidation of fine W-Cu precursors allows to fabricate high dense cylindrical billets near to theoretical density without cracks and uniform distribution of consisting phases.
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PARTICIPATING INSTITUTES

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Microhardness kg/mm²
measured on a PMT-3 at P = 100g

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<th>According to the formula</th>
<th>Tabular results</th>
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<tr>
<td>1</td>
<td>Cu : W = 1 : 1&lt;br&gt;t = 1000°C</td>
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<td></td>
<td>129.76&lt;br&gt;206.97&lt;br&gt;277.88&lt;br&gt;179.59&lt;br&gt;241.28&lt;br&gt;102.50&lt;br&gt;169.42&lt;br&gt;442.03&lt;br&gt;291.95&lt;br&gt;307.12&lt;br&gt;291.95&lt;br&gt;350.47</td>
<td>128&lt;br&gt;206&lt;br&gt;274&lt;br&gt;181&lt;br&gt;236&lt;br&gt;100&lt;br&gt;170&lt;br&gt;464&lt;br&gt;297&lt;br&gt;297&lt;br&gt;297&lt;br&gt;350</td>
</tr>
<tr>
<td>2</td>
<td>Cu : W = 1 : 1&lt;br&gt;t = 930°C</td>
<td>297&lt;br&gt;135&lt;br&gt;193&lt;br&gt;193&lt;br&gt;193&lt;br&gt;151&lt;br&gt;170&lt;br&gt;30.5&lt;br&gt;87.6&lt;br&gt;181&lt;br&gt;116</td>
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<td>307.12&lt;br&gt;136.46&lt;br&gt;198.52&lt;br&gt;198.52&lt;br&gt;190.58&lt;br&gt;148.95&lt;br&gt;166.29&lt;br&gt;30.38&lt;br&gt;86.79&lt;br&gt;176.07&lt;br&gt;117.69</td>
<td>Khrushchev-Berkovich method&lt;br&gt;H = (1854x100)/C² kg/mm²&lt;br&gt;where C is diagonal of impression of micrometer eyepiece.</td>
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<tr>
<td>3</td>
<td>Cu : W = 1 : 1&lt;br&gt;t = 700°C</td>
<td>383</td>
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<td></td>
<td>392.27&lt;br&gt;595.82&lt;br&gt;536.47&lt;br&gt;186.85&lt;br&gt;186.85&lt;br&gt;183.11&lt;br&gt;125.54&lt;br&gt;70.31&lt;br&gt;110.56&lt;br&gt;381.32&lt;br&gt;119.55&lt;br&gt;428.95&lt;br&gt;57.67</td>
<td>383</td>
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Microstructures of the Cu-20%W composite consolidated at 900°C