Effect of Ni addition on microstructure, mechanical and high temperature behavior of mechanically alloyed W-Nb

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ABSTRACT

The present investigation comprises the fabrication of tungsten (W) based alloys with nominal composition of W₇₀Ni₂₀Nb₁₀ (alloy A), W₇₅Ni₁₅Nb₁₀, (alloy B) (all in wt.%) by mechanical alloying (MA) in a planetary ball mill followed by sintering at 1500°C for 2 h in Ar atmosphere. The milled powders and the consolidated products have been investigated by X-ray diffraction (XRD), Scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS). Minimum crystallite size and maximum lattice strain of 45 nm and 0.42% respectively is achieved in alloy B. Maximum sinterability, hardness of 90.5%, 4.58 GPa (at 50g) respectively is achieved in alloy B due to finer crystallite size, higher surface energy and shorter atomic diffusion distance whereas maximum compressive strength of 2.14 GPa and minimum wear rate is achieved in alloy A owing to the formation of higher fraction of hard NbNi intermetallic phase. High temperature oxidation study at 900°C for 10 h reveals that lower oxidation rate is achieved in alloy A owing to lesser weight fraction of W and higher propensity of protective NiWO₄ scale formation.

Keywords: W based alloy; Mechanical alloying; Strength; Oxidation.
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BRIEF OUTLINE

• Aims and Objective
• Introduction & Background
• Materials and Method
• Result & Discussions
• Conclusions
• References
Aims and Objective

• To fabricate W based alloys through pressure less liquid phase sintering.

• Investigate the physical, mechanical and high temperature behavior of the fabricated alloys.
Introduction & Background

- Extreme temperature (~1000-1500°C)
- High strain rate ($10^6$ s$^{-1}$) and
- Hydrostatic pressure (2–6 GPa)

Introduction & Background

➢ Any other application?
   1. Radiation Shielding
   2. Aviation counterweights
   3. High rigidity tooling components

Radiation Shielding

Aviation counterweights
Introduction & Background

Why Tungsten?

Pros..

- High Melting point (3420°C).
- High hardness (9.8 GPa), MOE=407 GPa.
- Good thermal conductivity (1.74 W/cm K), low coefficient of thermal expansion.
- Low-activating metal in radiation environment with low sputtering yield.

(W.F. Smith, McGraw-Hill, 1993)

Cons. with Tungsten

High ductile brittle transition temperature (200-500°C).

Introduction & Background

Why alloy addition?

- To improve fabricability and effective utilization of Tungsten.
- Ni imparts liquid phase sintering (if sintering temp is higher than m.p. of Ni) and improve plastic flow properties.
- To improve the high temperature strength and lower the DBTT of W by Nb addition.

Introduction & Background

G. D. Samolyuk et. al Fusion Reactor Materials Program (2011)
Binary alloy phase diagrams of (a) W-Nb [P. Franke et al. 2006], (b) W-Ni [T. B. Massalski et al. 1990]
Introduction & Background

Why Nanostructuring?

- To lower the sintering temperature.

- To improve the mechanical properties.
Materials & Methods

Elemental powders (W, Ni, Nb)

High Energy Ball-Mill (20 h)

Nanostructured Alloy Powder

Characterization (XRD, SEM)

Pressureless sintering (1500°C, 2 h holding)

Characterization [XRD, SEM, Density, Hardness, Strength, Wear, Oxidation]
Materials & Methods

Mechanical Alloying

Mechanism of MA

FRISTSCH planetary ball mill, steel vials and 10 mm chrome steel balls

300 rpm, 10:1 (ball to powder weight). Wet milling with toluene (Process control agent to prevent particle agglomeration)

- Elemental powders of W, Ni, Nb (purity 99.5%, Sigma Aldrich)
  initial particle of 100-150 µm

Alloy Composition (wt.%)

<table>
<thead>
<tr>
<th>Alloy</th>
<th>W</th>
<th>Ni</th>
<th>Nb</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alloy A</td>
<td>70</td>
<td>20</td>
<td>10</td>
</tr>
<tr>
<td>Alloy B</td>
<td>75</td>
<td>15</td>
<td>10</td>
</tr>
</tbody>
</table>
Materials & Methods

**Compaction**
500 MPa pressure
5 min dwell time

**(a) Conventional Sintering Furnace**
(1500°C for 2 h)
(Ar flow rate: 100 ml/min)

**(b) Conventional Sintering Cycle**
Results and discussion

- W and Nb: unlimited solid solubility (similar crystal structure (BCC) and small difference between atomic radius (W: 193 pm, Nb: 198 pm)

- W and Ni: limited solid solubility (different crystal structure (Ni: FCC) and wide difference between atomic radius (W: 193 pm, Ni: 149 pm)

XRD pattern of alloy B mechanically alloyed at various time (0, 5, 10, 20 h).
Results and discussion

Variation of crystallite size and lattice strain of alloy A and alloy B with milling time

$$\beta \cos \theta = \frac{0.94 \lambda}{D} + 4\eta \sin \theta,$$

where, $\beta$ is the full width half maxima (FWHM), $D$ is the crystallite size and $\eta$ is the lattice strain.
\[ \rho_d = 2\sqrt{3} \frac{(\varepsilon^2)^{1/2}}{D \times b} \]

b is the burgers vector of dislocations, \( b = (a\sqrt{3})/2 \) for the bcc structure, \( a \) = cell parameter = lattice parameter, \( D \) = crystallite size, \( \varepsilon \) = lattice strain

Results and discussion

SEM micrograph of powder of alloy B at (a) 0 h, (b) 5 h, (c) 10 h and (d) 20 h of mechanical alloying.
Particle size distribution of 20 h milled alloy A and alloy B.

Enhanced Bimodality represent superior particle packing during compaction.
Results and discussion

Peak Shift in (110) diffraction plane of 20 h milled W to higher angle in sintered alloys (alloy A: from 40.29° to 46.97°, alloy B: from 40.31° to 47.20°)

XRD pattern of alloy A and alloy B mechanically alloyed for 20 h and sintered at 1500°C for 2 h.
Results and discussion

SEM micrograph of sintered (a) alloy A, (b) alloy B

Histogram of sintered (a) alloy A, (b) alloy B
Results and discussion

\[ \rho_s = \frac{W_a}{(W_{sat} - W_{sus})} \times \rho_w \]

\( W_a \) is weight of the sintered sample in air.
\( W_{sat} \) is the weight of the sample with all the open porosity saturated with water,
\( W_{sus} \) is the weight suspended in water. \( \rho_w \) is the density of water.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Dry Weight (gm)</th>
<th>Soaked Weight (gm)</th>
<th>Suspended Weight (gm)</th>
<th>Theoretical Density (gm/cm(^3))</th>
<th>Sintered Density (gm/cm(^3))</th>
<th>%Sinterability</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>2.07</td>
<td>2.08</td>
<td>1.92</td>
<td>14.82</td>
<td>12.94</td>
<td>87.31</td>
</tr>
<tr>
<td>B</td>
<td>1.67</td>
<td>1.69</td>
<td>1.56</td>
<td>14.19</td>
<td>12.85</td>
<td>90.56</td>
</tr>
</tbody>
</table>

- Superior particle bimodality in 20 h milled powder of alloy B.
- Low crystallite size → enhanced surface energy → improved mass transport
Results and discussion

- Enhanced density, Finer microstructure
- Smaller indentation at reduced loads (ISE)
- Stress field-dislocation core interaction

\[ HV = 1.8544 \frac{P}{d^2} \]
Results and discussion

True- stress- strain curve under Compressive loading

- Higher hard brittle NbNi in alloy A. (high strength-low %strain to failure) than alloy A

(strain rate: 10^{-1}/min)

Results and discussion

Fractographic study of (a) alloy A and (b) alloy B

Particle shearing
Results and discussion

Higher fraction of hard NbNi particles strongly restrict the dislocation motion which results in lower wear depth in alloy A.

Sliding Distance (S.D) = \( \left( \frac{N}{60} \right) \times t \times 2\pi r \)

Test condition: 30 N load, 25 rpm, track diameter: 4 mm, time: 10 min.
Results and discussion

SEM micrograph of wear track of (a) alloy A, (b) alloy B milled for 20 h and sintered at 1500°C for 2 h at 30 N load.
Results and discussion

Weight change with exposure time of alloy A and alloy B during oxidation in furnace, (b) XRD pattern of alloys A and alloy B subjected to oxidation at 900°C for 10 h.
Results and discussion

\[
\left( \frac{\Delta m}{A} \right)^2 = Kt + C
\]


<table>
<thead>
<tr>
<th>Oxides</th>
<th>( \Delta G_f^\circ ) (KJ mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>WO(_3)</td>
<td>-349.3</td>
</tr>
<tr>
<td>Nb(_2)O(_5)</td>
<td>-539.5</td>
</tr>
<tr>
<td>TiO(_2)</td>
<td>-688.69</td>
</tr>
<tr>
<td>NiO</td>
<td>-192.2</td>
</tr>
</tbody>
</table>

Molar volume of WO\(_3\), WO\(_2\), Nb\(_2\)O\(_5\) is 31.76 cm\(^3\), 19.57 cm\(^3\), 58.30 cm\(^3\) respectively whereas the molar volume of impervious NiWO\(_4\) is 38.56 cm\(^3\)
Conclusions

- Nanostructured novel W-Ni-Nb alloy powders are produced by mechanical alloying. Minimum crystallite size of W and maximum lattice strain is achieved in $W_{75}Ni_{15}Nb_{10}$ alloy at 20 h of milling.

- The lattice parameter of W in all alloys expanded at 10 h of milling due to hydrostatic pressure exerted by the nanocrystals and contraction at 20 h of milling owing to formation of solid solution.

- Presence of NbNi intermetallic is evident in the sintered alloys due to Ni rich liquid phase formation at the selected sintering temperature.

- The % densification and hardness of $W_{75}Ni_{15}Nb_{10}$ alloy is higher as compared to $W_{70}Ni_{20}Nb_{10}$ alloy.

- $W_{70}Ni_{20}Nb_{10}$ shows higher strength and low % strain to failure as compared to $W_{75}Ni_{15}Nb_{10}$. 
Conclusions

- Minimum wear depth is recorded in alloy A due to higher presence of NbNi intermetallic phase.

- High temperature oxidation behavior shows superior oxidation resistance of $W_{70}\text{Ni}_{20}\text{Nb}_{10}$ alloy as compared to $W_{75}\text{Ni}_{15}\text{Nb}_{10}$ due to lower W content and quick formation of more stable and impervious NiWO$_4$ oxide scale.