Fabrication and characterization of nano–Y$_2$O$_3$ dispersed mechanically alloyed W-Ni-Nb for high temperature applications

R. Saxena$^a$, A. Patra$^{a,*}$, S. K. Karak$^a$, L. Ciupinski$^b$

$^a$Metallurgical and Materials Engineering Department, National Institute of Technology Rourkela, Rourkela-769008, Odisha, India.

$^b$Faculty of Materials Science and Engineering, Warsaw University of Technology, Wołoska 141, 02-507 Warsaw, Poland.

*Email: anspat.met@gmail.com

Abstract. The present research work deals with fabrication of nano-Y$_2$O$_3$ dispersed tungsten (W) based alloys with nominal composition of W$_{79}$Ni$_{10}$Nb$_{10}$(Y$_2$O$_3$)$_1$ (alloy A), W$_{78}$Ni$_{10}$Nb$_{10}$(Y$_2$O$_3$)$_2$ (alloy B) and W$_{72}$Ni$_{10}$Nb$_{15}$(Y$_2$O$_3$)$_3$ (alloy C) (all composition in wt.%) by mechanical alloying in a planetary ball mill and compaction at 500 MPa pressure followed by sintering at 1500°C for 2 h in Ar atmosphere. The milled powders at different milling time and the consolidated products have been investigated by X-ray diffraction (XRD), scanning electron microscopy (SEM), high resolution transmission electron microscopy (HRTEM) and energy dispersive spectroscopy (EDS). Minimum crystallite size and maximum lattice strain of 20.3 nm and 0.42% respectively is achieved in alloy C. Maximum sinterability, hardness, compressive strength of 93.38%, 6 GPa, 2.5 GPa with appreciable wear resistance has been achieved in alloy C owing to the lower crystallite size, presence of higher oxide dispersion (Y$_2$O$_3$) and NbNi intermetallic. High temperature behavior of the sintered alloys is studied in a raising hearth furnace at a temperature range of 800-1000°C. The activation energy of oxidation decreases with increase in Y$_2$O$_3$ content owing to higher energy of Y$_2$O$_3$ dispersoids. Alloy A shows superior oxidation resistance at 800-1000°C as compared to rest of the alloys. The investigated alloys shows superior strength and elongation as compared to recently investigated W-Y$_2$O$_3$ alloys [1, 2].

Keywords: W-Ni-Nb alloy, Mechanical alloying, Oxide dispersion strengthening, Hardness, Oxidation.


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R. Saxena, **Prof. A. Patra**, Prof. S.K. Karak
*Department of Metallurgical and Materials Engineering*
NATIONAL INSTITUTE OF TECHNOLOGY, ROURKELA
ROURKELA-769008, INDIA

Prof. L. Ciupinski
*Faculty of Materials Science and Engineering,*
WARSAW UNIVERSITY OF TECHNOLOGY, WOŁOSKA 141, 02-507 WARSAW,
POLAND.
BRIEF OUTLINE

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

• To fabricate nano $Y_2O_3$ dispersed W based alloys through pressureless sintering.

• Investigate the physical, mechanical and high temperature behavior of the fabricated alloys.
• Extreme temperature (~1000-1500°C)
• High strain rate (10⁶ 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 co-efficient 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).
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.
- Y$_2$O$_3$ addition to reduce the grain growth and improve strength and hardness and wear resistance.
Introduction & Background

- Why Nanostructuring?
  - To lower the sintering temperature.
  - To improve the mechanical properties.
Materials & Methods

Elemental powders (W, Ni, Nb, Y_2O_3)

High Energy Ball-Mill (20 h)

Nanostructured Alloy Powder

Characterization (XRD, SEM, TEM)

Pressureless sintering (1500°C, 2 h holding)

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

Mechanical Alloying Mechanism of MA

- Elemental powders of W, Ni, Nb (purity 99.5%, Sigma Aldrich)
  initial particle of 100-150 μm
- Y₂O₃ (<50 nm).

- FRISTSCH planetary ball mill, WC vials and 10 mm chrome steel balls
- 300 rpm, 10:1 (BPR).
- Toluene (PCA)

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Composition (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>W</td>
</tr>
<tr>
<td>Alloy A</td>
<td>79</td>
</tr>
<tr>
<td>Alloy B</td>
<td>78</td>
</tr>
<tr>
<td>Alloy C</td>
<td>72</td>
</tr>
</tbody>
</table>
Materials & Methods

Sintering Cycle

- Heating Rate: 3°C/min up to 1500°C
- Heating Rate: 4°C/min up to 1200°C
- Heating Rate: 5°C/min up to 1000°C
- Cooling rate is same as heating rate up to the temperature points mentioned
- 1500°C (2 h)
## Materials & Methods

<table>
<thead>
<tr>
<th>Equipment and Method</th>
<th>Parameters measured</th>
</tr>
</thead>
</table>
| XRD (X-Pert High Score, Origin, PowdII)       | 1. Crystallite size, Lattice strain, Lattice parameter, Dislocation density, phase evolution of milled powder  
|                                               | 2. phase evolution in sintered product.                                             |
| SEM/TEM                                       | 1. Morphology, compositional, indexing of milled and consolidated product.           |
| Archimedes’s principle                        | Density/porosity measurement, Sartorius Density Measuring Kit                       |
| Hardness                                      | Hardness and Elastic Modulus evaluation (MTS)                                       |
| Ball on plate wear tester                     | Wear study (load = 20 N, time = 10 mins, speed= 25 r.p.m)                           |
| Instron-SATEC KN600                           | Compressive strength study at room temperature                                      |
| Raising Hearth Furnace                        | High temperature behavior.                                                          |
Materials & Methods

Wear Measurement:

Ball on Plate Wear Tester
Results and Discussion

XRD pattern of powder milled for different times (0, 5, 10, 20 h)

- Ni solubility with W (0.3 at.% at 1495°C) solubility decreases with decrease in Temperature.
Results and Discussion

\[ B \cos \theta = \frac{(0.94\lambda)}{d} + \epsilon \sin \theta \]  
(1), \( d = \) crystallite size, \( \epsilon = \) lattice strain, \( B = \) full width at half maxima. [B. D. Cullity, Elements of X-ray diffraction, 1978.]
SEM micrograph of powder morphology of alloy A at different milling time (a) 0 h, (b) 5 h, (c) 10 h, and (d) 20 h.
SEM micrograph of powder morphology of alloy B at different milling time (a) 0 h,  (b) 5 h, (c) 10 h, and (d) 20 h.
Results and Discussion
Results and Discussion

XRD of Sintered of alloys A through C
Results and Discussion

SEM Sintered of alloys A through C
Results and Discussion

TEM image of sintered alloy C (3%Y₂O₃)
Results and Discussion

- Surface energy increases, GB area increased, diffusion distance decreases with reduction in crystallite size.
- Improved GB diffusion enhances sintering kinetics and superior densification.

Microhardness

%Densification
The interdiffusion co-efficient for W-Nb system increases with decrease in W content.

Wear Results

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

Finer grains/particles : Strengthening
Coarser grains : Yielding


\[ \Delta \sigma = 2G\varepsilon f \]

\( \Delta \sigma = \) increase in yield stress, \( G = \) shear modulus, \( \varepsilon = \) measurement of strain field, \( f = \) volume fraction of dispersed particles.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Compressive strength (max) (GPa)</th>
<th>%Elongation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alloy A</td>
<td>1.82</td>
<td>13.86</td>
</tr>
<tr>
<td>Alloy B</td>
<td>2.35</td>
<td>19.43</td>
</tr>
<tr>
<td>Alloy C</td>
<td>2.54</td>
<td>19.55</td>
</tr>
</tbody>
</table>

Lesser brittle W content
FRACTOGRAPHY

- Deformation mismatch between matrix and particle, large stress concentrations.

- Stress Concentration at GB → Localize strain → cracking under deformation.
Results and Discussion

TEM image of sintered alloy C


Increased Y$_2$O$_3$ content at GB $\rightarrow$ Increased Coalescence of particle $\rightarrow$ enhanced intense stress/strain concentration.

TEM image of sintered alloy C
High temperature oxidation behavior

Alloy A

Alloy B

Alloy C
<table>
<thead>
<tr>
<th>Oxides</th>
<th>Molar Vol (cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>WO$_3$</td>
<td>31.5</td>
</tr>
<tr>
<td>WO$_2$</td>
<td>19.99</td>
</tr>
<tr>
<td>Nb$_2$O$_5$</td>
<td>58.3</td>
</tr>
<tr>
<td>NiWO$_4$</td>
<td>38.56</td>
</tr>
<tr>
<td>YNbO$_4$</td>
<td>44.05</td>
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</table>
# Activation energy for Oxidation

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Oxidation Temp (T)°C</th>
<th>I/T (K)</th>
<th>Oxidation rate (K)</th>
<th>ln K</th>
<th>Activation Energy (KJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alloy A</td>
<td>800</td>
<td>0.000932</td>
<td>72.52</td>
<td>4.283862</td>
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<tr>
<td></td>
<td>900</td>
<td>0.0008525</td>
<td>1682.32</td>
<td>7.427929</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1000</td>
<td>0.0007855</td>
<td>3457.577</td>
<td>8.148323</td>
<td>222.80</td>
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<tr>
<td>Alloy B</td>
<td>800</td>
<td>0.000932</td>
<td>963.3957</td>
<td>6.870464</td>
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</tr>
<tr>
<td></td>
<td>900</td>
<td>0.0008525</td>
<td>3956.664</td>
<td>8.283157</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1000</td>
<td>0.0007855</td>
<td>45389.01</td>
<td>10.72303</td>
<td>216.57</td>
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<tr>
<td>Alloy C</td>
<td>800</td>
<td>0.000932</td>
<td>1306.36</td>
<td>7.175</td>
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<td>0.0008525</td>
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<td>1000</td>
<td>0.0007855</td>
<td>43739.54</td>
<td>10.68601</td>
<td>199</td>
</tr>
</tbody>
</table>

\[(\Delta m/S)^2 = K_p t + C \quad \ldots (1)\]

\[K_p = K_0 \exp \left(-\frac{Q}{RT}\right) \quad \ldots (2)\]

\[\ln (K_p) = -Q(1/RT) + C \quad \ldots (3)\]
Results and Discussion

Schematic of oxidation mechanism in W-Ni-Nb-Y$_2$O$_3$.
Conclusions

- Minimum crystallite size of 20 nm, maximum lattice strain and dislocation density of 0.42%, $27 \times 10^{16}/m^2$ has been achieved in 20 h milled $W_{72}Ni_{10}Nb_{15} (Y_2O_3)_3$ alloy.

- The % densification enhances with $Y_2O_3$ addition owing to substantial reduction in crystallite size which enhances the sintering kinetics.

- The higher hardness (6 GPa), strength (2.25 GPa) of $W_{72}Ni_{10}Nb_{15} (Y_2O_3)_3$ alloy is attributed to finer crystallite size and superior sinterability, higher content of $Y_2O_3$ dispersion.

- %Elongation increases with increase in $Y_2O_3$, however exhibit marginal increase beyond 2% $Y_2O_3$ content due to increased stress/strain concentration resulted from agglomeration of finer $Y_2O_3$ particles during sintering.
Conclusions

- Increase in $Y_2O_3$ content promotes intergranular fracture during compressive loading as coarser $Y_2O_3$ particles enhances the stress/strain and facilitates interfacial debonding.

- Superior oxidation resistance is achieved in lower Nb containing alloys and upto 2% $Y_2O_3$.

- $W_{72}Ni_{10}Nb_{15} (Y_2O_3)_3$ alloy shows poor oxidation resistance due to increased difference in molar volume and thermal expansion co-efficient of higher content of oxides which results in spallation and cracking of oxide layer.
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