In the present investigation, nano-Y$_2$O$_3$ dispersed W-Ni-Mo and W-Ni-Ti-Nb alloys with nominal composition of W$_{79}$Ni$_{10}$Mo$_{10}$(Y$_2$O$_3$)$_{1}$ (alloy A) and W$_{74}$Ni$_{10}$Ti$_{5}$Nb$_{10}$(Y$_2$O$_3$)$_{1}$ (alloy B) (all in wt.%) were synthesized by mechanical alloying (MA) for 20 h followed by spark plasma sintering (SPS) at 1000°C, 1200°C and 1400°C for alloy A and at 1400°C for alloy B, respectively for 5 min at 75 MPa pressure. Microstructure evolution and thermal behavior of milled powders and consolidated samples, were examined by scanning electron microscopy with energy-dispersive X-ray detection (SEM/EDX), high resolution transmission electron microscopy (HR-TEM), differential scanning calorimetry (DSC) and X-ray diffraction (XRD). Minimum crystallite size of 29 nm and 23 nm, and maximum lattice strain of 0.44% and 0.491% were observed for alloy A and B, respectively milled for 20 h. The dislocation density for both alloys significantly increased after 10 h of milling and marginal increase was exhibited at 20 h of milling. The density, hardness, compressive strength and wear resistance increased with increase in SPS temperature for alloy A and maximum values of 99%, 10.91 GPa, 2.24 GPa, $1.28 \times 10^{-15}$ m$^3$/N m (wear rate), respectively were obtained for 1400°C sintered sample. However, alloy B sintered at 1400°C achieved higher hardness (11.89 GPa), compressive strength (2.26 GPa) and wear resistance (wear rate: $1.14 \times 10^{-15}$ m$^3$/N m) owing to finer crystallite size and precipitation of higher volume fraction of hard NbNi and Ni$_3$Ti intermetallic phases (Fig 1. (b)) as compared to single hard MoNi intermetallic phase in alloy A (Fig. 1(a)). The hardness and strength of both the alloys are 2-3 times higher than the recently investigated W based alloys. The considerable improvement in the mechanical property for both alloys was attributed to dispersion strengthening mechanism contributed by the nano-Y$_2$O$_3$ dispersoids precipitated at the grain boundaries. The wear test results confirm that abrasive wear is the dominant wear mechanism in both the alloys. Observation of increased texture intensity as a function of SPS temperature for (110), a harder orientation, also confirmed the increase in hardness in alloy A with increase in SPS temperature. A regular decrease in residual stress with increase in SPS temperature was observed for both alloys. However, the alloy B had a higher residual stress compared to alloy A, both sintered at 1400°C.

Keywords: W based alloys, Mechanical alloying, Spark plasma sintering, Hardness, Wear, Texture.
Fabrication and characterization of nano-$Y_2O_3$ dispersed W-Ni-Mo and W-Ni-Ti-Nb alloys by mechanical alloying and spark plasma sintering

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ISMAMANAM 2016.

by

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BRIEF OUTLINE

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

• To fabricate nanostructured W based alloys through Spark Plasma Sintering (SPS).

• Investigate the physical, mechanical and texture behavior of the fabricated alloy.
• To fabricate alloy for Defense application.
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 ($3420^\circ$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.

(Anshuman Patra, Microscopy and Analysis, 26 (5), (2012))
Introduction & Background

Why alloy addition?

- To improve fabricability and effective utilization of Tungsten.
- Ni imparts liquid phase sintering and improve plastic flow properties.
- To improve the high temperature strength by Mo and Nb addition.
- Addition of Ti also contributes to enhanced densification and strength, though it increases the DBTT of W.
- 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. 
  \[ \text{(R malewar et.al, J. Mater. Res., 22 (2007))} \]

- To improve the mechanical properties. 
  \[ \text{[H. Glieter, Acta. Mater., 48 (2000)]} \]
Materials & Methods

Elemental powders (W, Ni, Mo Nb, Ti, Y₂O₃)

High Energy Ball-Mill (20 h)

Nanostructured Alloy Powder

Characterization (XRD, SEM, TEM)

SPS (1000°C, 1200°C, 1400°C, 5 min holding)

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

Mechanical Alloying

Mechanism of MA

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

<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>74</td>
</tr>
</tbody>
</table>

- FRISTSCH planetary ball mill, Tungsten carbide vials and 10 mm tungsten carbide balls
- 300 rpm, 10:1 (ball to powder weight). Wet milling with toluene (Process control agent to prevent particle agglomeration)
Materials & Methods
Spark Plasma Sintering
## Materials & Methods

<table>
<thead>
<tr>
<th>Equipment and Method</th>
<th>Parameters measured</th>
</tr>
</thead>
</table>
| XRD (X-Pert High Score, Origin, Powdill)   | 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                                       |
| Bruker D8 Advance XRD system with Co Kα radiation.  
1. Labotex 3.0  
2. Panalytical X’Pert Stress software | 1. Texture analysis.  
2. Residual stress analysis. |
Materials & Methods

Wear Measurement:

Ball on Plate Wear Tester
Results and Discussion

Fig. 1. XRD pattern of powder (alloy B) milled for different times (0, 5, 10, 20 h)
**Results and Discussion**

\[ B \cos \theta = \frac{(0.94\lambda)}{d} + \epsilon \sin \theta \quad (1), \quad d= \text{crystallite size}, \ \epsilon= \text{lattice strain}, \ B= \text{full width at half maxima.} \quad [\text{B. D. Cullity, Elements of X-ray diffraction, 1978.}] \]

\[ \rho_d = 2\sqrt{3} \frac{(\epsilon^2)^{1/2}}{D \times b} \quad (2), \quad \text{Burger Vector}, \ b = \frac{(a\sqrt{3})}{2} \ (\text{BCC}), \ D = \text{crystallite size}, \ \epsilon = \text{lattice strain}, \ a= \text{lattice parameter.} \quad [\text{Y. H. Zhao, Acta. Mater, 49 (2001)}] \]

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Milling time (h)</th>
<th>Crystallite size (nm)</th>
<th>Lattice strain (%)</th>
<th>Dislocation density ((10^{16}/\text{m}^2))</th>
<th>Lattice Parameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Alloy A</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>103.2</td>
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<td>0.31645</td>
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<tr>
<td>5</td>
<td>60.1</td>
<td>0.26</td>
<td>5.47</td>
<td>0.31653</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>44.6</td>
<td>0.36</td>
<td>10.19</td>
<td>0.31656</td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>34.8</td>
<td>0.4</td>
<td>14.53</td>
<td>0.31636</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>29.4</td>
<td>0.44</td>
<td>18.93</td>
<td>0.31630</td>
<td></td>
</tr>
<tr>
<td><strong>Alloy B</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>75.8</td>
<td>0.15</td>
<td>2.50</td>
<td>0.31645</td>
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<td>5</td>
<td>55.7</td>
<td>0.27</td>
<td>6.12</td>
<td>0.31658</td>
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<tr>
<td>10</td>
<td>46.1</td>
<td>0.39</td>
<td>10.69</td>
<td>0.31660</td>
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<tr>
<td>15</td>
<td>33.1</td>
<td>0.46</td>
<td>17.57</td>
<td>0.31637</td>
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<tr>
<td>20</td>
<td>23.2</td>
<td>0.49</td>
<td>26.71</td>
<td>0.31627</td>
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</table>
Fig. 2. 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.
Fig. 3. (a) Bright Field TEM image of 20 h milled alloy B (b) corresponding SAD pattern.
Fig. 4. Thermal analysis of 20 h milled powder a) alloy A b) alloy B

Activation energy (Q)= 110.13 KJ/mol

Activation energy (Q)= 95.44 KJ/mol
Results and Discussion

Formation of Hard Brittle intermetallic MoNi in alloy A, NbNi, Ni₃Ti in alloy B

Fig. 5. XRD pattern for a) alloy A and b) alloy B milled for 20 h and spark plasma sintered at different temperature for 5 min.
Fig. 6. FE-SEM micrographs of a) alloy A and b) alloy B, SPS at 1400°C for 5 min.
Results and Discussion

Fig. 7. EDS pattern of a) Alloy A  b) Alloy B milled for 20 h and SPS at 1400°C for 5 min.
Fig. 8. Bright Field HRTEM image of alloy B milled for 20h and SPS at 1400°C for 5min.
Results and Discussion

Fig. 9. (110) pole figure of alloy A and alloy B at different SPS temperatures: (a, b & c) Alloy A sintered at 1000°C, 1200°C & 1400°C respectively; (d) Alloy B sintered at 1400°C. The contour levels are at 0.8, 1.0, 1.5, 2.0, 2.2 and 2.4 times random.
Results and Discussion

Fig. 10. Residual stress developments in alloy A and alloy B at different SPS temperatures.
Results and Discussion

Measurement of Sinterability for alloy A and alloy B

\[ \rho_s = \frac{W_a}{W_{sat} - W_{susp}} \times \rho_w \, \text{gm/cm}^3 \]  \hspace{1cm} (3)

\( W_a \): weight of the sintered sample in air. \( W_{sat} \): weight of the sample with all the open porosity saturated with water, \( W_{susp} \): weight suspended in water. \( \rho_w \): density of water.  \[ \text{[N. Ozkan et al., J. Eur. Ceram. Soc., 14 (1994)]} \]

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Temperature (°C)</th>
<th>Weight of sample in air (gm)</th>
<th>Soaked weight (gm)</th>
<th>Suspended weight (gm)</th>
<th>Sintered density (gm/cm³)</th>
<th>Theoretical density (gm/cm³)</th>
<th>% Sinterability</th>
</tr>
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<tbody>
<tr>
<td>Alloy A</td>
<td>1000</td>
<td>2.03</td>
<td>2.04</td>
<td>1.907</td>
<td>15.263</td>
<td>15.65</td>
<td>97.53</td>
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<tr>
<td></td>
<td>1200</td>
<td>1.23</td>
<td>1.24</td>
<td>1.160</td>
<td>15.375</td>
<td>15.65</td>
<td>98.24</td>
</tr>
<tr>
<td></td>
<td>1400</td>
<td>1.23</td>
<td>1.25</td>
<td>1.171</td>
<td>15.569</td>
<td>15.65</td>
<td>99.48</td>
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<tr>
<td>Alloy B</td>
<td>1400</td>
<td>1.47</td>
<td>1.49</td>
<td>1.38</td>
<td>13.364</td>
<td>13.43</td>
<td>99.51</td>
</tr>
</tbody>
</table>
Results and Discussion

Fig. 11. Variation of hardness of SPS treated alloy A and alloy B


Fig. 12. Compressive stress strain curve of alloy A spark plasma sintered at 1000°C, 1200°C, 1400°C and SPS treated alloy B at 1400°C for 5 min.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>SPS Temp (°C)</th>
<th>Compressive strength (max) (GPa)</th>
<th>%Elongation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alloy A</td>
<td>1000</td>
<td>2.19</td>
<td>19.63</td>
</tr>
<tr>
<td></td>
<td>1200</td>
<td>2.21</td>
<td>21.74</td>
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<tr>
<td></td>
<td>1400</td>
<td>2.24</td>
<td>23.95</td>
</tr>
<tr>
<td>Alloy B</td>
<td>1400</td>
<td>2.26</td>
<td>23.07</td>
</tr>
</tbody>
</table>
Results and Discussion

Fig. 13. FE-SEM micrograph of compression tested fracture surface of (a) alloy A (1000°C SPS), (b) alloy A (1200°C SPS), (c) alloy A (1400°C SPS) d) alloy B (1400°C SPS).
Results and Discussion

\[ \text{Sliding Distance (S. D)} = \left( \frac{R}{60} \right) \times t \times 2\pi r \]  \hspace{1cm} (4)

Fig. 14. Variation of Wear depth with sliding distance of SPS treated alloys A and B.
Results and Discussion

Fig. 15. SEM of worn surface of (a) alloy A (1000°C SPS),
(b) alloy A (1200°C SPS), (c) alloy A (1400°C SPS) d) alloy B (1400°C SPS).
## Results and Discussion

Table 3. Variation of wear rate with composition and SPS temperature

\[
\text{wear rate (K)} = \frac{\text{wear volume (Q)}}{\text{(Applied load} \times \text{sliding distance)}}
\]

<table>
<thead>
<tr>
<th>Alloy</th>
<th>SPS Temperature (°C)</th>
<th>Load (N)</th>
<th>Maximum wear depth (µm)</th>
<th>Sliding Distance (m)</th>
<th>Track radius (mm)</th>
<th>Wear Volume (m$^3$) $\times 10^{-12}$</th>
<th>Wear rate (m$^3$/Nm) $\times 10^{-15}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1000</td>
<td>30</td>
<td>247.53</td>
<td>3.12</td>
<td>4</td>
<td>8.60</td>
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<td>125.85</td>
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<td>4</td>
<td>2.24</td>
<td>2.10</td>
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<td>30</td>
<td>98.06</td>
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<td>4</td>
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<td>1.28</td>
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<tr>
<td>B</td>
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<td>23.92</td>
<td>3.12</td>
<td>4</td>
<td>1.21</td>
<td>1.14</td>
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</tbody>
</table>
Conclusions

- Minimum crystallite size of 23 nm, maximum lattice strain and dislocation density of 0.49%, \(26.71 \times 10^{16}/m^2\) respectively has been achieved in 20 h milled \(W_{74}Ni_{10}Nb_{10}Ti_{5}(Y_2O_3)_{1}\) alloy.

- The lattice parameter of W in all the alloys expands at 10 h of milling owing to severe stress assisted plastic deformation and contract beyond 10 to 20 h of milling due to atomic diffusion of the solute elements to lesser or higher extend.

- The activation energy for recrystallization is lower in 20 h milled \(W_{74}Ni_{10}Nb_{10}Ti_{5}(Y_2O_3)_{1}\) alloy owing to higher deformation during milling as compared to \(W_{79}Ni_{10}Mo_{10}(Y_2O_3)_{1}\) alloy.

- Texture intensity increases with increase in SPS temperature and Ti addition. Texture for both alloys is harder in (110) orientation of W as compared to other orientation.
Conclusions

- The % densification of $W_{74}\text{Ni}_{10}\text{Nb}_{10}\text{Ti}_{5}(\text{Y}_2\text{O}_3)_1$ and $W_{79}\text{Ni}_{10}\text{Mo}_{10}(\text{Y}_2\text{O}_3)_1$ alloy is comparable and increases with increase in SPS temperature in $W_{79}\text{Ni}_{10}\text{Mo}_{10}(\text{Y}_2\text{O}_3)_1$ alloy due to enhanced interparticle bonding at higher temperature.

- The higher hardness (11.89 GPa), strength (2.26 GPa) of $W_{74}\text{Ni}_{10}\text{Nb}_{10}\text{Ti}_{5}(\text{Y}_2\text{O}_3)_1$ alloy is attributed to finer crystallite size and superior sinterability and higher content of hard intermetallic phases.

- Ti and Mo addition increases and decreases the DBTT of W respectively and results in reduced elongation of $W_{74}\text{Ni}_{10}\text{Nb}_{10}\text{Ti}_{5}(\text{Y}_2\text{O}_3)_1$ alloy as compared to SPS treated $W_{79}\text{Ni}_{10}\text{Mo}_{10}(\text{Y}_2\text{O}_3)_1$ alloy at 1400°C.

- The wear rate of $W_{74}\text{Ni}_{10}\text{Nb}_{10}\text{Ti}_{5}(\text{Y}_2\text{O}_3)_1$ alloy is substantially lower as compared to $W_{79}\text{Ni}_{10}\text{Mo}_{10}(\text{Y}_2\text{O}_3)_1$ alloy due to superior hardness, strength of the surface layers and predominant hindrance of dislocation movement by NbNi, Ni$_3$Ti intermetallic phases.
Acknowledgements

• The research work was supported by TEQIP II NIT Rourkela.

• I am thankful Prof. T. LAHA, and Mr. P. Karmakar, Metallurgical and Materials Engineering, IIT Kharagpur for helping in spark plasma sintering of the alloy.

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