Refractory Metals
Production and Implant Applications

Ta
Tantalum
180.9479

W
Tungsten
183.85

Mo
Molybdenum
95.94

73
5731
3287
16.6

42
4912
2890
10.2

74
5828
3680
19.3
Order of Presentation

- For each material
  - Production route: from the ground to the metal
  - Commercial alloys
    - Chemical compositions
    - Mechanical and physical properties
    - Applications
  - Relationship to ion implantation

- Summary
Acknowledgements

- Signet Corp. (implantation equipment photographs)
- H. Starck colleagues
  - Coldwater, MI (Mo purification and powder production flowsheets)
  - Cleveland, OH (Mo, W rolling flowsheets)
  - Newton, MA (Ta processing flowsheets)
- ITIA (W purification flowsheets)
- Competitor brochures (some technical data)
Molybdenum

42

Mo

Molybdenum

95.94
Mines (primary & byproduct)

MoS₂ concentrate

Roaster

Technical grade MoO₃ + H₂SO₄

Chemical purification, sublimation

Ammonium molybdate, Pure MoO₃

Hydrogen reduction

Mo powder

Mo mill products

Bar
Rod
Wire
Plate
Sheet
Foil
Fabrications

Lubricants

Iron steel

Catalysts
Pigments
Smoke, flame retardants
Corrosion inhibitors

Catalysts
Spray coatings
Non-ferrous alloys
P/M parts
Powder and P/M Billet Production

Receipt of raw material

1st stage reduction
(NH4)2MoO4 + H2 → MoO3 + NH4OH
MoO3 + H2 → MoO2 + H2O

Blending

2nd stage reduction
MoO2 + 2H2 → Mo + 2H2O

Molybdenum powder

Blending (densify & safety screen)

Isostatic pressing

Sintering

Pressed & sintered billets/sheet bar

Ship to rolling facility

Powder blending

Arc melting

Ingot machining

Billet preparation (machining)

Heat treatment

Straighten, clean, & cut

Ship to rolling facility

Arc-Cast Billet Production

Extrusion

Billet heating

Extrusion
## Mo Solid Solution Alloys

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Composition</th>
<th>Consolidation</th>
<th>Specification</th>
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</thead>
<tbody>
<tr>
<td>Mo</td>
<td>99.95% Mo</td>
<td>A/C, P/M</td>
<td>ASTM B386, ASTM B387</td>
</tr>
<tr>
<td>25 W</td>
<td>25% w</td>
<td>P/M</td>
<td>Manufacturer</td>
</tr>
<tr>
<td>30 W</td>
<td>30% W</td>
<td>A/C, P/M</td>
<td>ASTM B386, B387</td>
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<tr>
<td>5 Re</td>
<td>5% Re</td>
<td>P/M</td>
<td>Manufacturer</td>
</tr>
<tr>
<td>41 Re</td>
<td>41% Re</td>
<td>P/M</td>
<td>Manufacturer</td>
</tr>
<tr>
<td>50 Re</td>
<td>47.5% Re</td>
<td>P/M</td>
<td>Manufacturer</td>
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# Mo Carbide-Stabilized Alloys

<table>
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<tbody>
<tr>
<td>TZM</td>
<td>0.5% Ti, 0.08% Zr, 0.03% C</td>
<td>A/C, P/M</td>
<td>ASTM B386, ASTM B387</td>
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<td>TZC</td>
<td>1.2% Ti, 0.3% Zr, 0.1% C</td>
<td>P/M</td>
<td>Manufacturer</td>
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<tr>
<td>MHC</td>
<td>1.2% Hf, 0.05% C</td>
<td>P/M</td>
<td>Manufacturer</td>
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<tr>
<td>ZHM</td>
<td>0.4% Zr, 1.2% Hf, 0.12% C</td>
<td>P/M</td>
<td>Manufacturer</td>
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<tr>
<td>HWM-25</td>
<td>25% W, 1.0% Hf, 0.07% C</td>
<td>P/M</td>
<td>Manufacturer</td>
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Mo Dispersed-Phase Alloys

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<th>Specification</th>
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<tr>
<td>Z-6</td>
<td>0.5 vol. % ZrO₂</td>
<td>P/M</td>
<td>Manufacturer</td>
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<tr>
<td>K-Si doped</td>
<td>150-200 ppm K, 300 ppm Si, 0-100 ppm Al</td>
<td>P/M</td>
<td>Manufacturer</td>
</tr>
<tr>
<td>La₂O₃ doped</td>
<td>0.7-1.0% La as La₂O₃</td>
<td>P/M</td>
<td>Manufacturer</td>
</tr>
<tr>
<td>Y₂O₃ doped</td>
<td>0.55% Y as Y₂O₃</td>
<td>P/M</td>
<td>Manufacturer</td>
</tr>
</tbody>
</table>
Molybdenum Physical Properties

- Moderate density (10.22 g/cc)
- High stiffness ($\approx 325 \text{ GPa}$)
- Moderate hardness (240-280 VHN)
- Low thermal expansion ($\approx 5 \times 10^{-6} \text{ C}^{-1}$)
- Intermediate thermal conductivity ($\approx 140 \text{ W/m\cdot K}$)
- Low specific heat ($\approx 270 \text{ J/kg\cdot K}$)
Annealing Response

Diagram showing the hardness-VPN response at different reheating temperatures.
Annealing Response: Effect of Alloying

Annealing Response of ODS Mo-La$_2$O$_3$ vs. P/M Mo

- P/M Molybdenum (Bianco & Buckman)
- A/C TZM (Briggs & Barr)
- Mo-2 volume %La$_2$O$_3$ (Bianco & Buckman)

Vickers hardness, VHN (kgf/mm$^2$)

One-hour annealing temperature, C
Mechanical Properties: Ductile-Brittle Transition
Mechanical Properties: Strength
Typical Mo Applications

- **Electronics**
  - Packaging & substrates (Cu-Mo-Cu)
  - Manufacturing equipment (crystal pullers, implantation)
  - Sputtering targets
  - Microwave tube components

- **Metallurgical processing**
  - Furnaces (elements, shielding, furniture)
  - Tooling (isothermal forging, extrusion, casting dies)

- **Glass melting** (electrodes, furnace components)

- **Radiation equipment** (X-ray targets, detector plates)

- **Aerospace/military** (shaped charges, rocket nozzles)
Issues for Mo in Implantation

- Purity
  - Contamination of ion beam
    - Mo is primary concern ($^{98}\text{Mo}^{2+}$ vs. $^{11}\text{B}^{19}\text{F}_2^-$)
    - Surface contamination (Fe, Ni, Cu)
    - Bulk contamination
      - Generally quite low
      - Typical levels $<100$ ppm for most
      - Probably not an issue
Issues for Mo in Implantation

• Evaporation/erosion
  – Related to $T_m$
  – Related to hardness
  – Related to atomic mass
  – Probably lower performance than W or Ta
    • M/e issues
    • Melting point
Manufacturing Costs

- Least expensive raw material
- Readily machinable with standard techniques
  - Single-point, EDM, grinding
  - Requires additional attention to technique and equipment
Tantalum

\[ \text{Atomic Number: 73} \]
\[ \text{Atomic Mass: 180.9479} \]
Sons of Gwalia Mine - Australia
Tantalite ore \((\text{Fe, Mn})(\text{Ta, Nb})_2\text{O}_6\)  
[Iron Manganese Tantalum Niobium Oxide]

- Tin slag
- Dissolve in HF
- Filter
- Solvent extraction
  - Hydrofluoniobic acid
  - Hydrofluotantalic acid
  - Reaction with potassium
    - \(\text{K}_2\text{TaF}_7\)
  - Sodium reduction
- Tantalum powder

- Recycle
- Waste

Electronic applications (capacitors)

Mill product applications  
(Pressing & sintering, EB Melting)
Process for Producing Ta Plate

1. Recycle
2. Powder
3. Electron Beam melt
4. Vacuum Arc Remelt
5. Machine
6. Forge, clean, & anneal
7. Roll
8. Trim
9. Level
10. Clean and anneal
Electron Beam Melting

Electron Beam Gun

Electrode (Rotating)

Focus & Aiming Coils

Vacuum

Molten Pool

Water Cooled Crucible

Ingot
Vacuum Arc Remelting

- Vacuum
- Consumable Electrode
- Water Cooling
- Copper Crucible
- Arc
- Molten Pool
- VAR Ingot
# Tantalum Alloys

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Composition</th>
<th>Consolidation</th>
<th>Specification</th>
</tr>
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<tbody>
<tr>
<td>Ta</td>
<td>99.9% Ta</td>
<td>EB/VAR, P/M</td>
<td>ASTM B364, B365, B521, B708</td>
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<tr>
<td>Ta 2½W</td>
<td>2.5% W</td>
<td>EB/VAR</td>
<td>ASTM B364, B365, B521, B708</td>
</tr>
<tr>
<td>Ta 10W</td>
<td>10% W</td>
<td>EB/VAR</td>
<td>ASTM B364, B365, B521, B708</td>
</tr>
<tr>
<td>Ta 40 Nb</td>
<td>40% Nb</td>
<td>EB/VAR</td>
<td>ASTM B364, B365, B521, B708</td>
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<tr>
<td>TA-111</td>
<td>8.0% W, 2% Hf</td>
<td>EB/VAR</td>
<td>Manufacturer</td>
</tr>
<tr>
<td>TA-222</td>
<td>10.0% W, 2.5% Hf, 0.01% C</td>
<td>EB/VAR</td>
<td>Manufacturer</td>
</tr>
</tbody>
</table>
Tantalum Physical Properties

- High density (16.6 g/cc)
- Moderate stiffness ($\approx 185$ GPa)
- Low hardness (75-100 VHN)
  - Most material sold in recrystallized condition
- Low thermal expansion ($\approx 6.6 \times 10^{-6}$ C$^{-1}$)
- Low thermal conductivity ($\approx 62$ W/m$\cdot$K)
- Low specific heat ($\approx 150$ J/kg$\cdot$K)
Ductile-Brittle Transition

- Tantalum has none
- Ductile behavior to very low temperatures
- Atypical for BCC metals
- Lower handling risks in recrystallized condition
Typical Ta Applications

- Chemical processing (vessel linings, rupture discs, sheaths, HX tubing)
- Electronics
  - Manufacturing equipment (crystal pullers, implantation)
  - Sputtering targets
  - Capacitors
- Furnaces (elements, shielding, furniture)
- Aerospace/military (shaped charges)
Issues for Ta in Implantation

• Purity
  – Contamination of ion beam
    • M/e problems do not affect performance
    • Surface contamination less of an issue than for Mo
  – Volatile elements efficiently removed by EB/VAR process
    • High $T_m$ elements (Nb, W, Mo) remain behind
    • 100-500 ppm residuals
    • More atoms/vol. than Mo because of density difference
  – P/M alloys can contain 100-300 ppm O, C, N
  – Are these really problems? Probably not
Issues for Ta in Implantation

- Evaporation/erosion
  - Evaporation is less of a problem than for Mo, not as good as W
  - Erosion/sputtering a smaller effect due to atomic mass
Manufacturing Costs

• Expensive material
  – Base price ≈10x that of Mo
  – Recent availability issues

• Readily machinable
  – Requires experience because of softness
  – Problems opposite those of Mo, W
Tungsten

Tungsten

74  5828
   3680
   19.3

W

Tungsten
183.85
**Typical Wolframite Upgrading Process**

- **Mining**
- **Scaling / Crushing**
- **Hand Picking**
  - Optical or Gravity Sorting
- **Grinding / Milling**
- **Jig**
- **Classifier**
- **Table Flotation**
- **Drying**
- **Magnetic Separation**

  - Slimes
  - Tails

**Wolframite Concentrate**

Grade 0.5% WO₃

Grade 1.0% WO₃

**Concentrates Processing**

- **Low Grade and Mixed Ore or Residues**
  - Soda Roast & Leach
  - Purification
  - CaWO₄ Precipitation
  - Decomposition to Tungstic Acid
  - Dissolution in Ammonia Solution
  - Crystallization
  - Ammonium Paratungstate (APT)

- **High Grade Ore or Oxidized Scrap**
  - Soda or Caustic Autoclave Leach
  - Purification
  - Liquid or Solid Ion Exchange
  - Crystallization
  - Ammonium Paratungstate (APT)
Wingot
1.675" x 10" x 24"

Hot roll
24" wide

Caustic & Acid
Clean

Hot/warm roll
24" wide

Caustic & acid
Clean

Stress Relief Anneal
Finished Plate

Cold roll
12" wide

Stress Relief Anneal

Cold roll
6" wide

Band or abrasive saw

Stress relief anneal

Caustic & Acid
Clean

Shipping

“Z” Mill
<0.003"

Slitting / shearing

Shipping

Stress relief anneal
# Tungsten Alloys

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<tr>
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<tbody>
<tr>
<td>W</td>
<td>99.95%</td>
<td>P/M</td>
<td>ASTM B760</td>
</tr>
<tr>
<td>W 3Re</td>
<td>3% Re</td>
<td>P/M</td>
<td>Manufacturer</td>
</tr>
<tr>
<td>W 5Re</td>
<td>5% Re</td>
<td>P/M</td>
<td>Manufacturer</td>
</tr>
<tr>
<td>W ThO₂</td>
<td>1%-3% ThO₂</td>
<td>P/M</td>
<td>Manufacturer</td>
</tr>
<tr>
<td>K/Si doped W</td>
<td>50-100 ppm K, 30-50 ppm Si</td>
<td>P/M</td>
<td>Manufacturer</td>
</tr>
</tbody>
</table>
Tungsten Physical Properties

- High density (19.3 g/cc)
- High stiffness (≈410 GPa)
- High hardness (400-500 VHN)
- Low thermal expansion (≈4.4 x 10^-6 C⁻¹)
- High thermal conductivity (≈155 W/m·K)
- Low specific heat (≈140 J/kg·K)
Strength of W vs. Temperature

Figure 1. Typical Tensile Strength Ranges of Tungsten Flat-Rolled Products
DBTT Behavior of W
Typical W Applications

- Electronics
  - Packaging (WCu)
  - Manufacturing equipment (implantation)
  - Sputtering targets
- Radiation equipment
  - Shielding (heavy metal)
  - Detector plates
- Furnaces (elements, shielding, furniture)
- Aerospace/military (green bullets)
Issues for W in Implantation

- **Purity**
  - Contamination of ion beam
    - M/e problems do not affect performance
    - Surface contamination is less of an issue than for Mo
    - Bulk contamination is similar to Mo, though atoms/vol. are double at equivalent wt. % levels

- **Evaporation/erosion**
  - Evaporation problems are least
  - Erosion/sputtering also are least
Manufacturing Costs

- Very difficult to machine
  - Single-point techniques are used by only a few
  - Grinding is typical
  - EDM is possible
- Raw material costs between Mo and Ta
Evaporation of Refractory Metals
<table>
<thead>
<tr>
<th>Material</th>
<th>Material Cost</th>
<th>Manufacturing Costs</th>
<th>Performance Issues</th>
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<tbody>
<tr>
<td>Mo</td>
<td>Lowest</td>
<td>Lowest</td>
<td>Highest ( P_v )</td>
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<td></td>
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<td>M/e problems,</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>embrittlement with use</td>
</tr>
<tr>
<td>Ta</td>
<td>Highest</td>
<td>Intermediate</td>
<td>( P_v \ll Mo ),</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>no M/e problems,</td>
</tr>
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<td></td>
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<td>remains ductile w/ use</td>
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<tr>
<td>W</td>
<td>Intermediate</td>
<td>Highest</td>
<td>( P_v \ll\ll Mo ),</td>
</tr>
<tr>
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<td>no M/e problems,</td>
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<tr>
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<td>embrittlement with use</td>
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