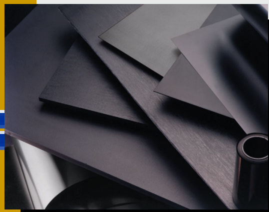
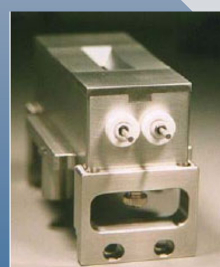


H.C. Starck

Refractory Metals

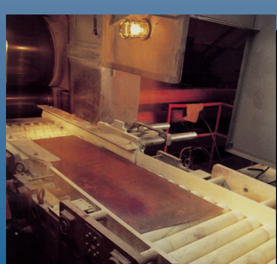
Production and Implant Applications

73
5731
3287
16.6
Ta
Tantalum
180.9479



42
4912
2890
10.2
Mo
Molybdenum
95.94

74
5828
3680
19.3
W
Tungsten
183.85



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

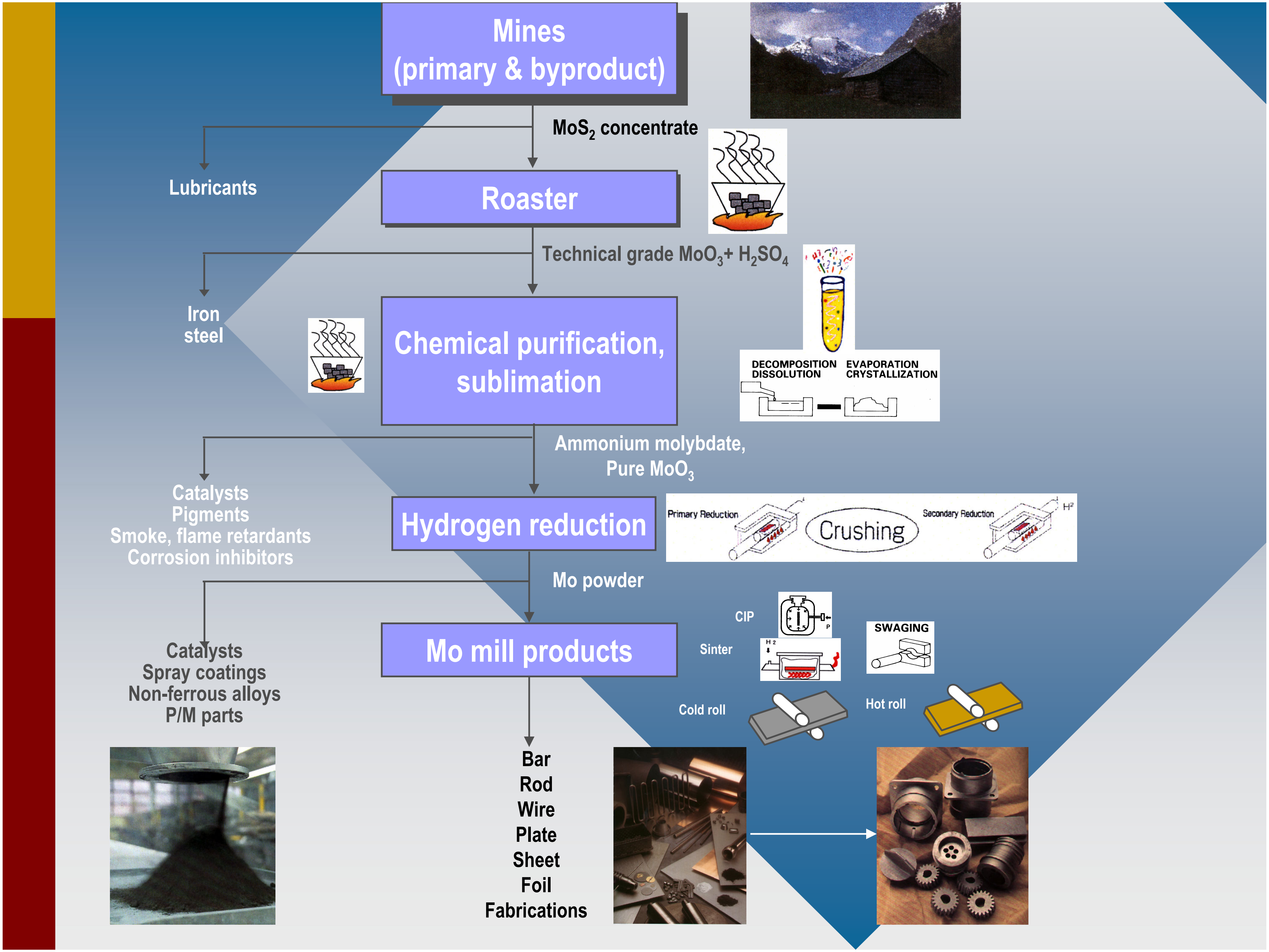
42

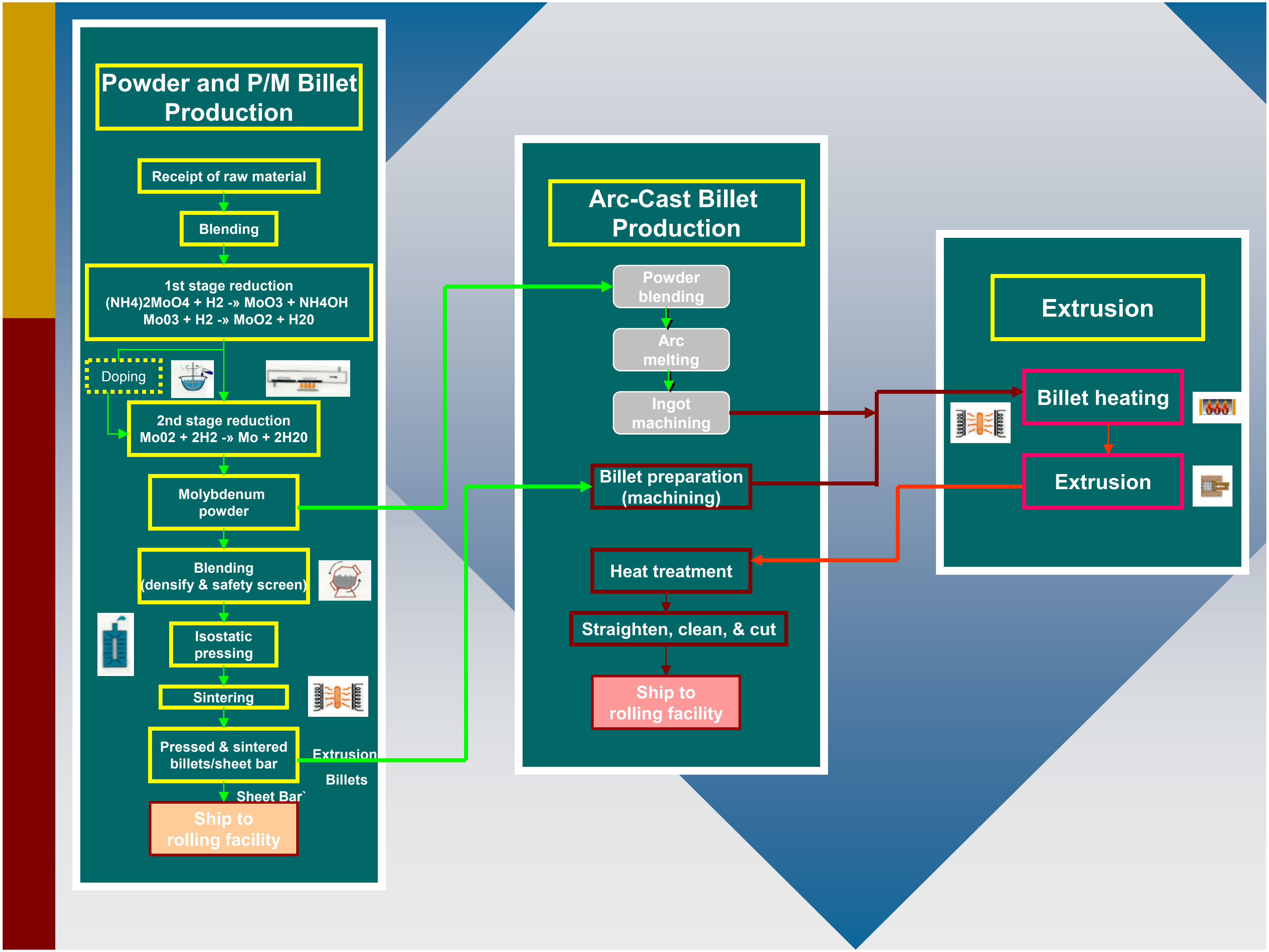
4912
2890
10.2

Mo

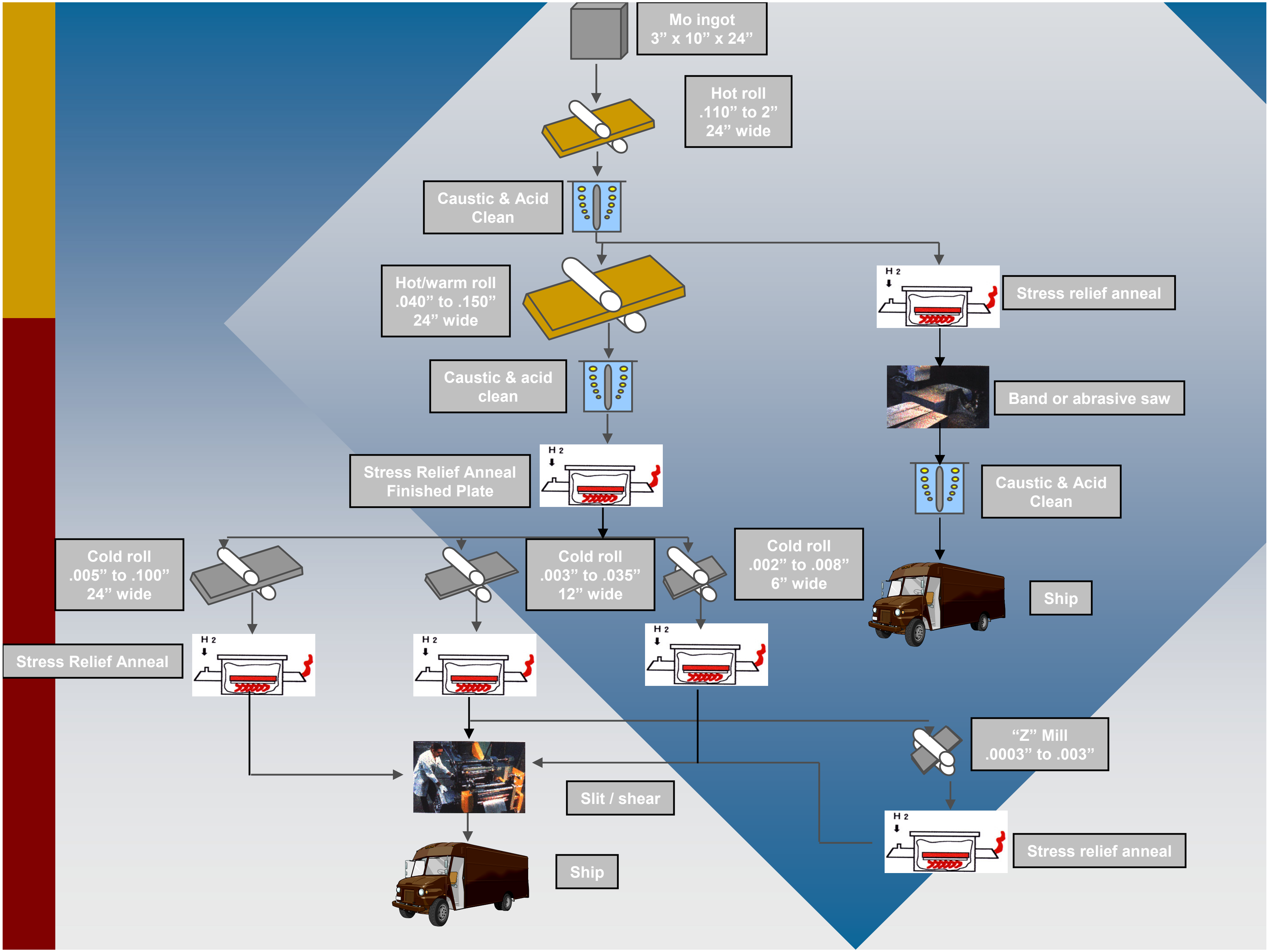
Molybdenum

95.94


Mines
(primary & byproduct)
MoS_2 concentrate
Lubricants
Roaster
Technical grade MoO_3+ H_2SO_4
Iron
steel
Chemical purification,
sublimation
DECOMPOSITION
DISSOLUTION
EVAPORATION
CRYSTALLIZATION
Ammonium molybdate,
Pure MoO_3
Catalysts
Pigments
Smoke, flame retardants
Corrosion inhibitors
Hydrogen reduction
Primary Reduction
Crushing
Secondary Reduction
Mo powder
CIP
Sinter
SWAGING
Catalysts
Spray coatings
Non-ferrous alloys
P/M parts
Mo mill products
Cold roll
Hot roll
Bar
Rod
Wire
Plate
Sheet
Foil
Fabrications



Powder and P/M Billet Production
Receipt of raw material
Blending
1st stage reduction
(NH4)2MoO4 + H2 -» MoO3 + NH4OH
Mo03 + H2 -» MoO2 + H20
Doping
2nd stage reduction
Mo02 + 2H2 -» Mo + 2H20
Molybdenum powder
Blending (densify & safety screen)
Isostatic pressing
Sintering
Pressed & sintered billets/sheet bar
Extrusion
Billets
Sheet Bar`
Ship to rolling facility
Arc-Cast Billet Production
Powder blending
Arc melting
Ingot machining
Billet preparation (machining)
Heat treatment
Straighten, clean, & cut
Ship to rolling facility
Extrusion
Billet heating
Extrusion


Mo ingot
3” x 10” x 24”
Hot roll
.110” to 2”
24” wide
Caustic & Acid
Clean
Hot/warm roll
.040” to .150”
24” wide
Stress relief anneal
Band or abrasive saw
Caustic & acid
clean
Caustic & Acid
Clean
Stress Relief Anneal
Finished Plate
Ship
Cold roll
.005” to .100”
24” wide
Cold roll
.003” to .035”
12” wide
Cold roll
.002” to .008”
6” wide
Stress Relief Anneal
“Z” Mill
.0003” to .003”
Slit / shear
Stress relief anneal
Ship

Mo Solid Solution Alloys

Alloy	Composition	Consolidation	Specification
Mo	99.95% Mo	A/C, P/M	ASTM B386, ASTM B387
25 W	25% w	P/M	Manufacturer
30 W	30% W	A/C, P/M	ASTM B386, B387
5 Re	5% Re	P/M	Manufacturer
41 Re	41% Re	P/M	Manufacturer
50 Re	47.5% Re	P/M	Manufacturer

Mo Carbide-Stabilized Alloys

Alloy	Composition	Consolidation	Specification
TZM	0.5% Ti, 0.08% Zr, 0.03% C	A/C, P/M	ASTM B386, ASTM B387
TZC	1.2% Ti, 0.3% Zr, 0.1% C	P/M	Manufacturer
MHC	1.2% Hf, 0.05% C	P/M	Manufacturer
ZHM	0.4% Zr, 1.2% Hf, 0.12% C	P/M	Manufacturer
HWM-25	25% W, 1.0% Hf, 0.07% C	P/M	Manufacturer

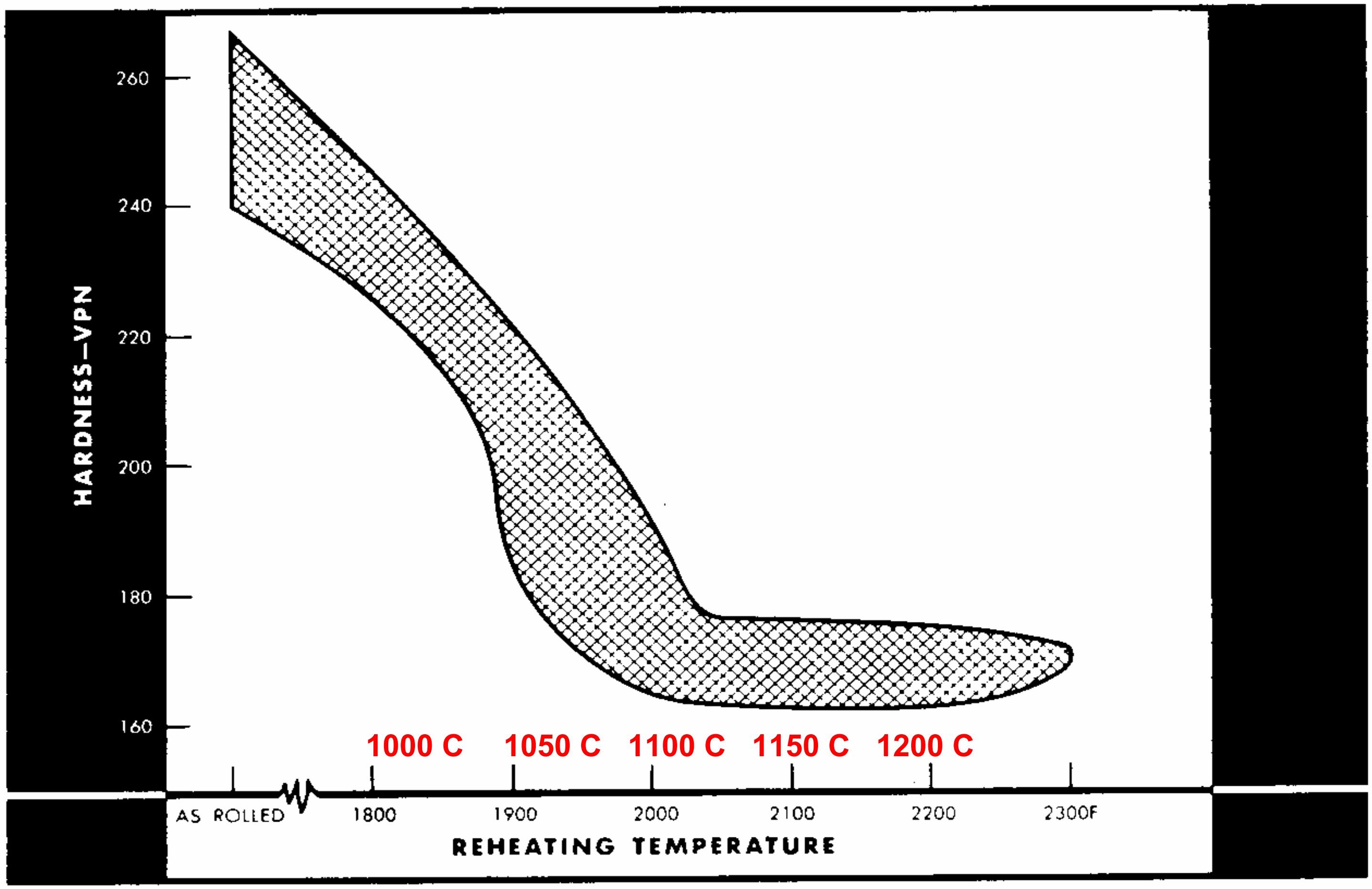
Mo Dispersed-Phase Alloys

Alloy	Composition	Consolidation	Specification
Z-6	0.5 vol. % ZrO_2	P/M	Manufacturer
K-Si doped	150-200 ppm K, 300 ppm Si, 0-100 ppm Al	P/M	Manufacturer
La_2O_3 doped	0.7-1.0% La as La_2O_3	P/M	Manufacturer
Y_2O_3 doped	0.55% Y as Y_2O_3	P/M	Manufacturer

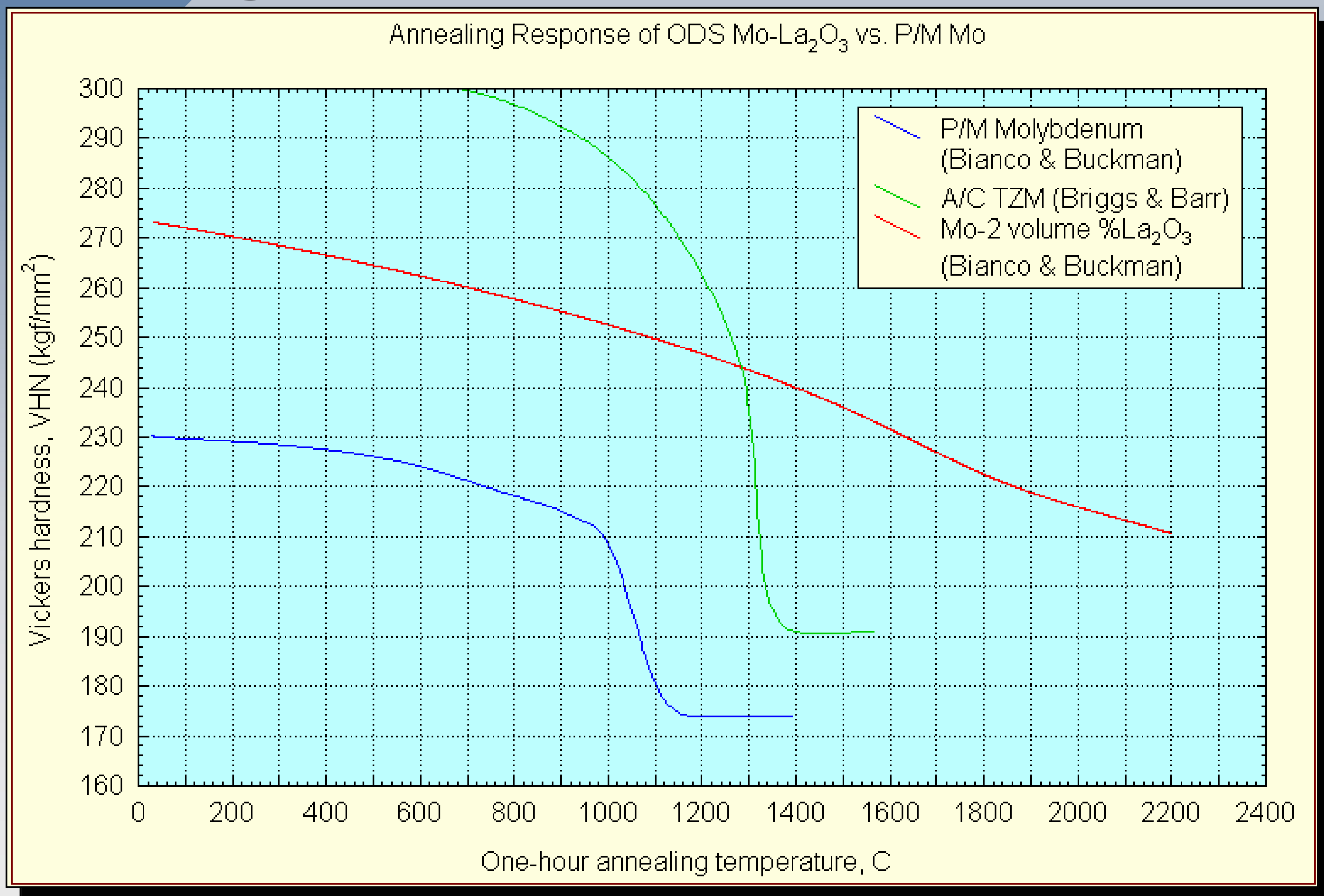
Molybdenum Physical Properties

- Moderate density (10.22 g.cc)
- High stiffness (≈325 GPa)
- Moderate hardness (240-280 VHN)
- Low thermal expansion (≈5 x 10^{-6} C^{-1})
- Intermediate thermal conductivity (≈140 W/m·K)
- Low specific heat (≈270 J/kg·K)

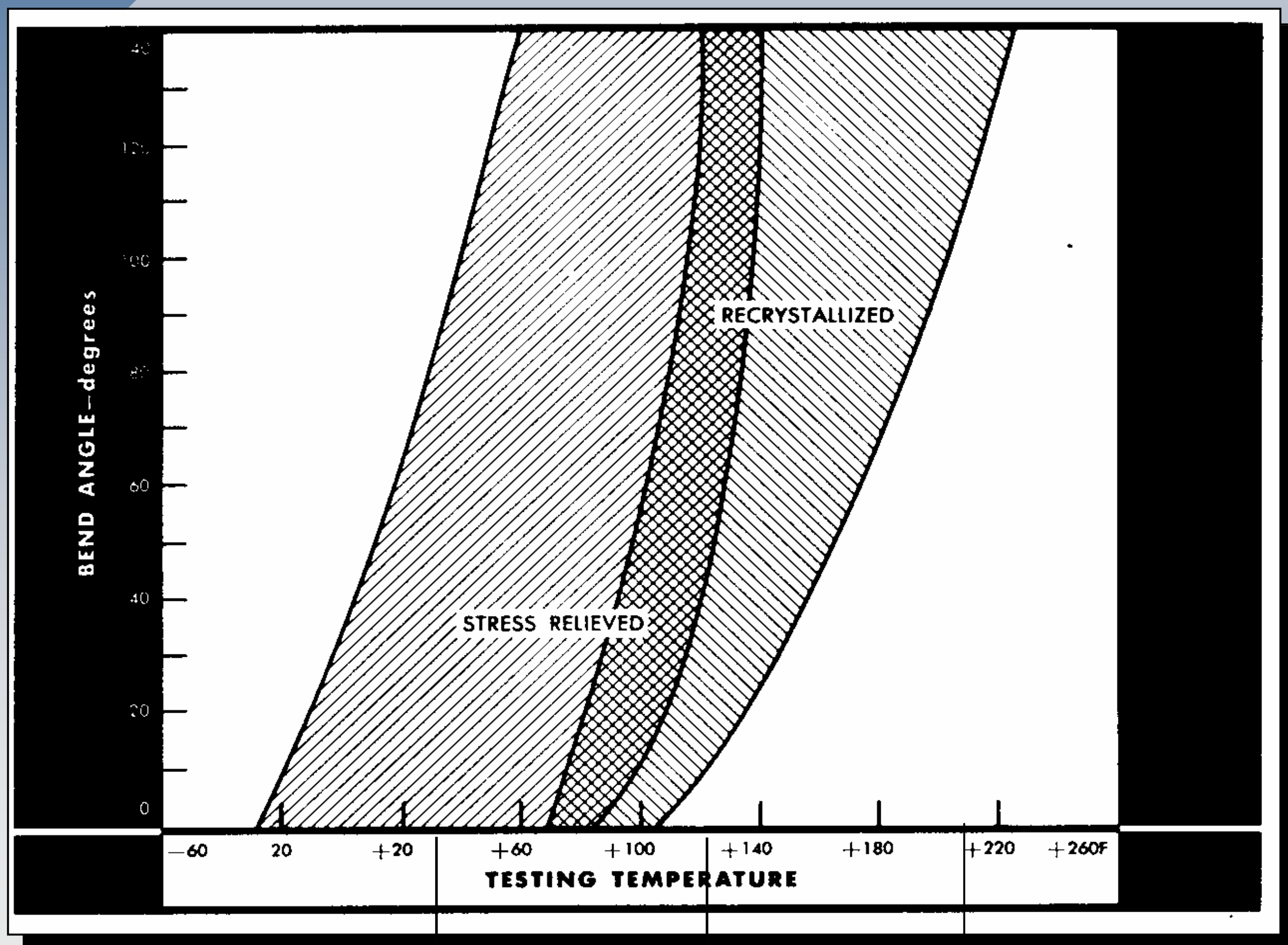
Annealing Response



Annealing Response: Effect of Alloying

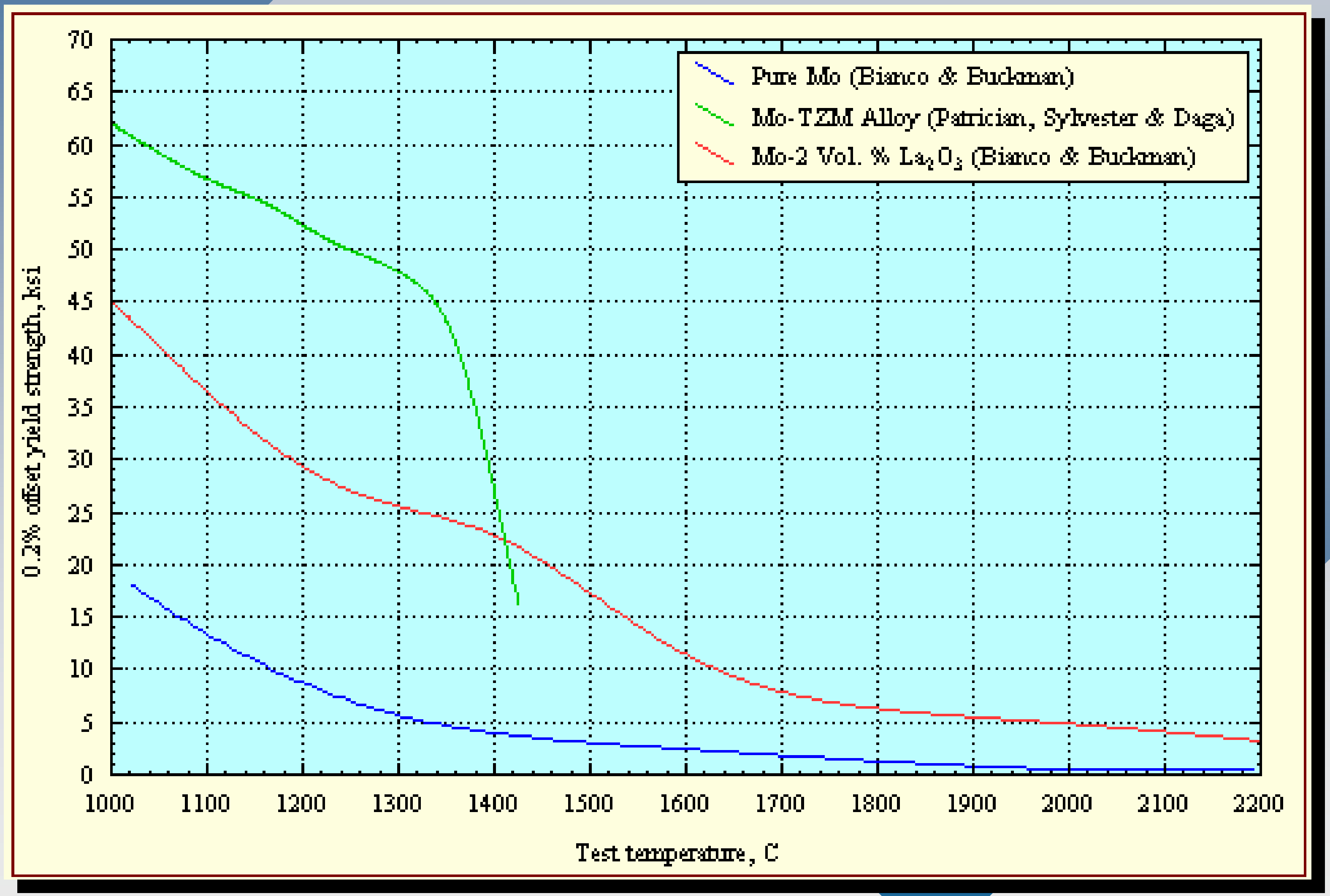


Mechanical Properties: Ductile-Brittle Transition



0 C
50 C
100 C

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 ($^{98}Mo^{2+}$ vs. $^{11}B^{19}F_2^-$)
    - 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

73

5731
3287
16.6

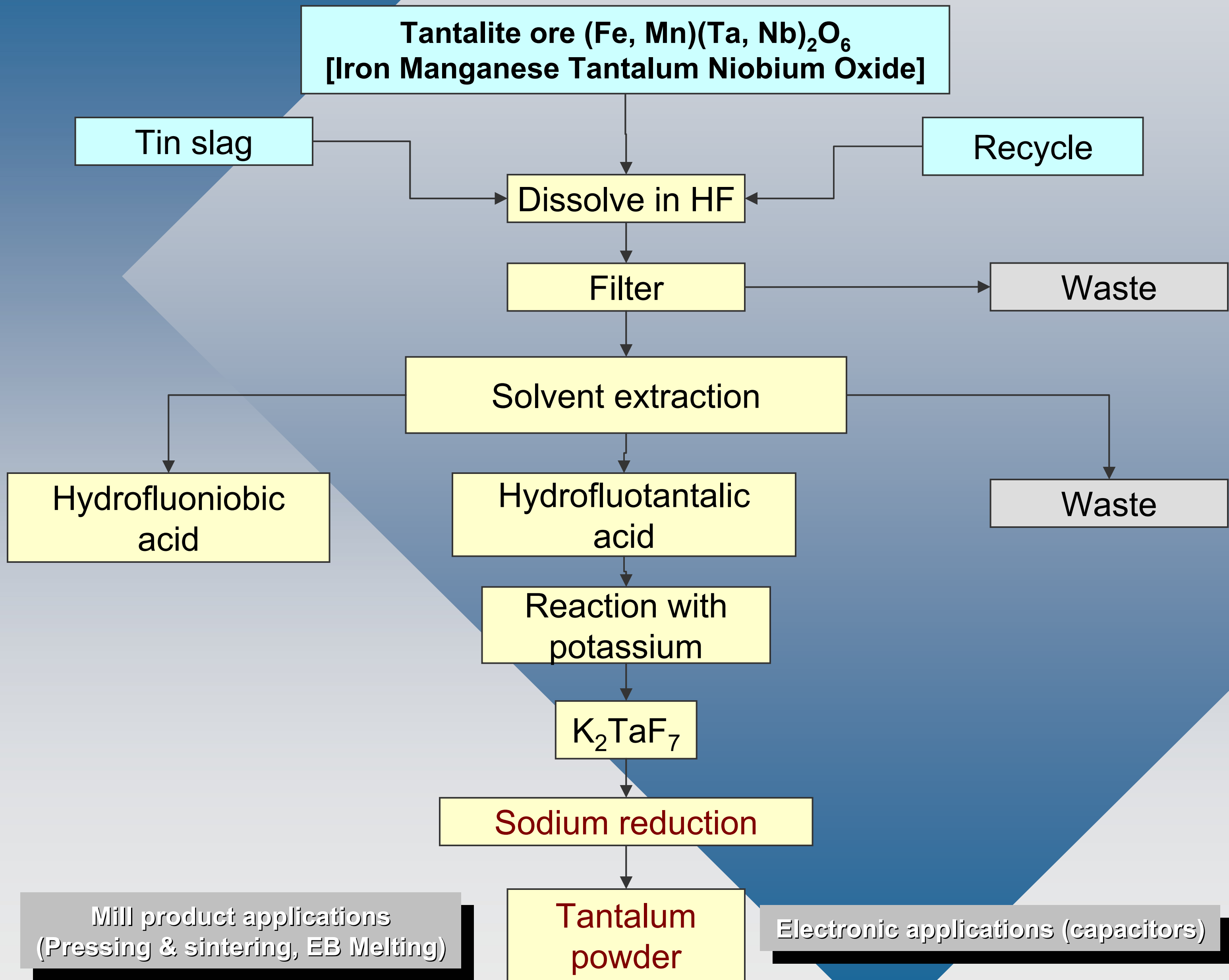
Ta

Tantalum

180.9479

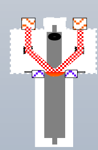
Sons of Gwalia Mine - Australia

Tantalum Separation - Powder



Process for Producing Ta Plate

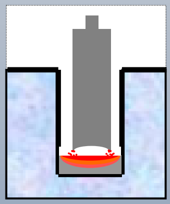
Recycle → Powder



Electron Beam melt

↓

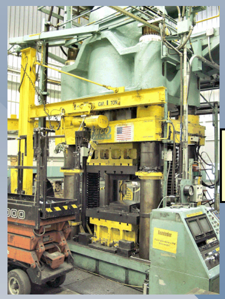
Vacuum Arc Remelt



↓

Machine

↓



Forge, clean, & anneal

↓

Roll

↓

Trim

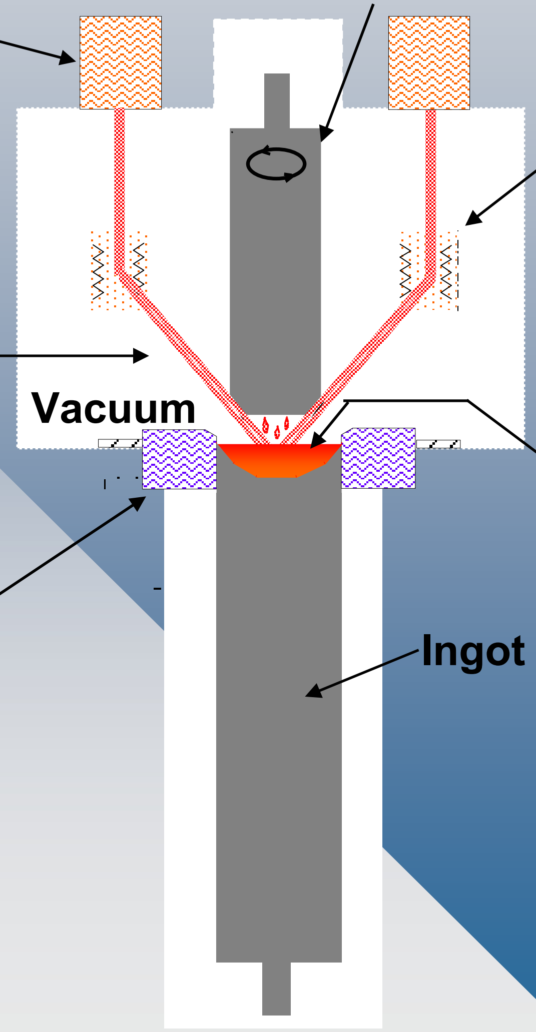
↓

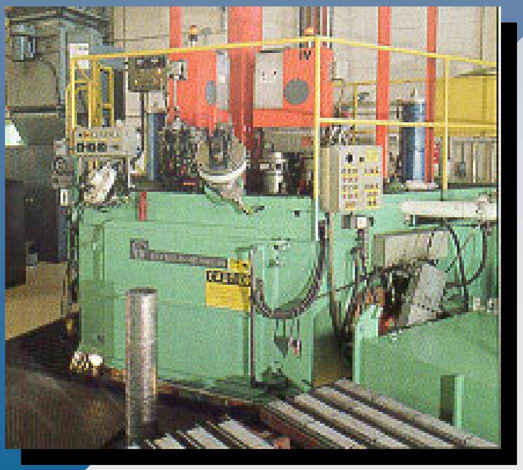
Level

↓

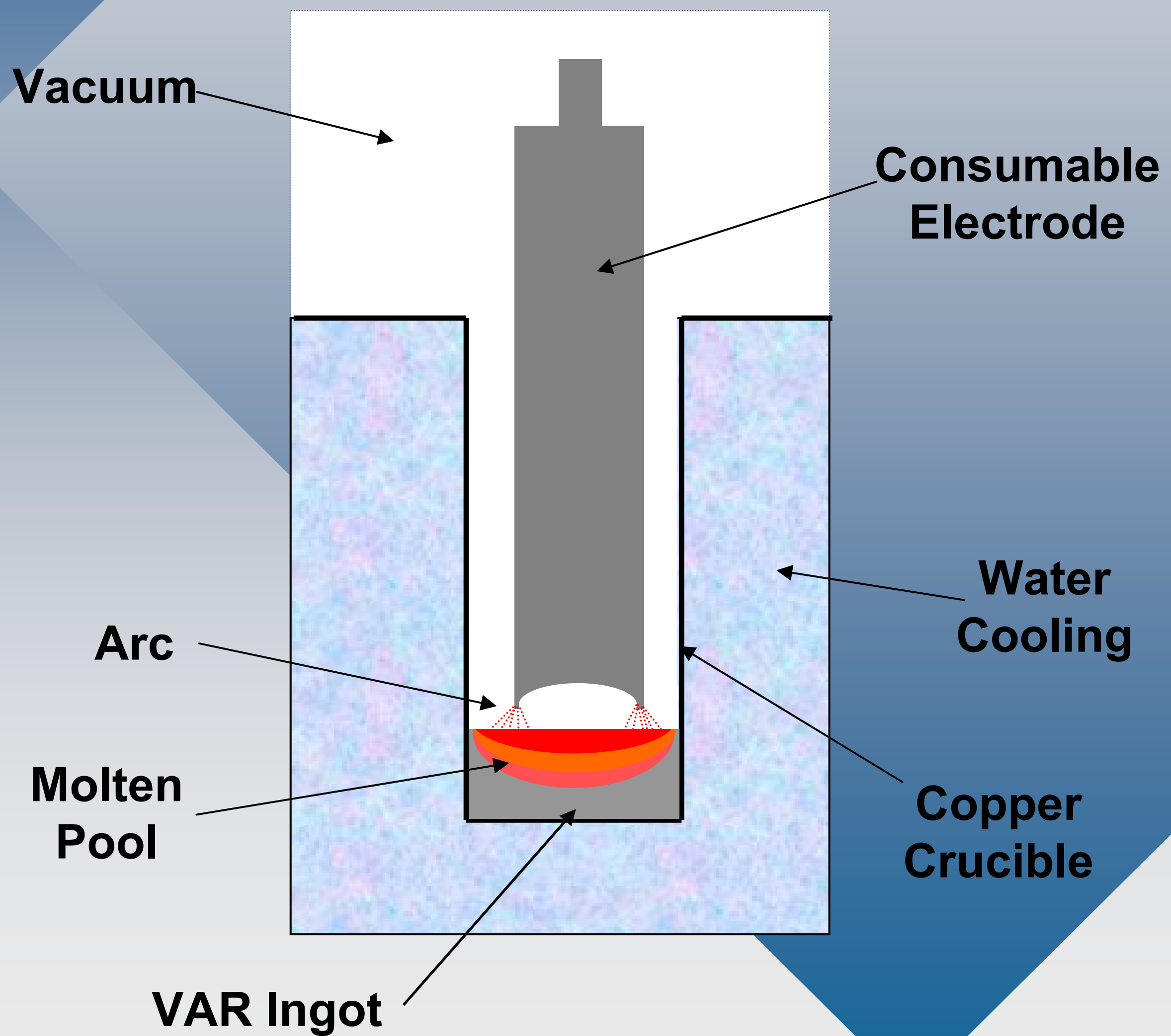
Clean and anneal

Electron Beam Melting





Vacuum Arc Remelting



Tantalum Alloys

Alloy	Composition	Consolidation	Specification
Ta	99.9% Ta	EB/VAR, P/M	ASTM B364, B365, B521, B708
Ta 2½W	2.5% W	EB/VAR	ASTM B364, B365, B521, B708
Ta 10W	10% W	EB/VAR	ASTM B364, B365, B521, B708
Ta 40 Nb	40% Nb	EB/VAR	ASTM B364, B365, B521, B708
TA-111	8.0% W, 2% Hf	EB/VAR	Manufacturer
TA-222	10.0% W, 2.5% Hf, 0.01% C	EB/VAR	Manufacturer

Tantalum Physical Properties

- High density (16.6 g.cc)
- Moderate stiffness (≈185 GPa)
- Low hardness (75-100 VHN)
  - Most material sold in recrystallized condition
- Low thermal expansion (≈6.6 x 10-6 C –1)
- Low thermal conductivity (≈62 W/m•K)
- Low specific heat (≈150 J/kg•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

74

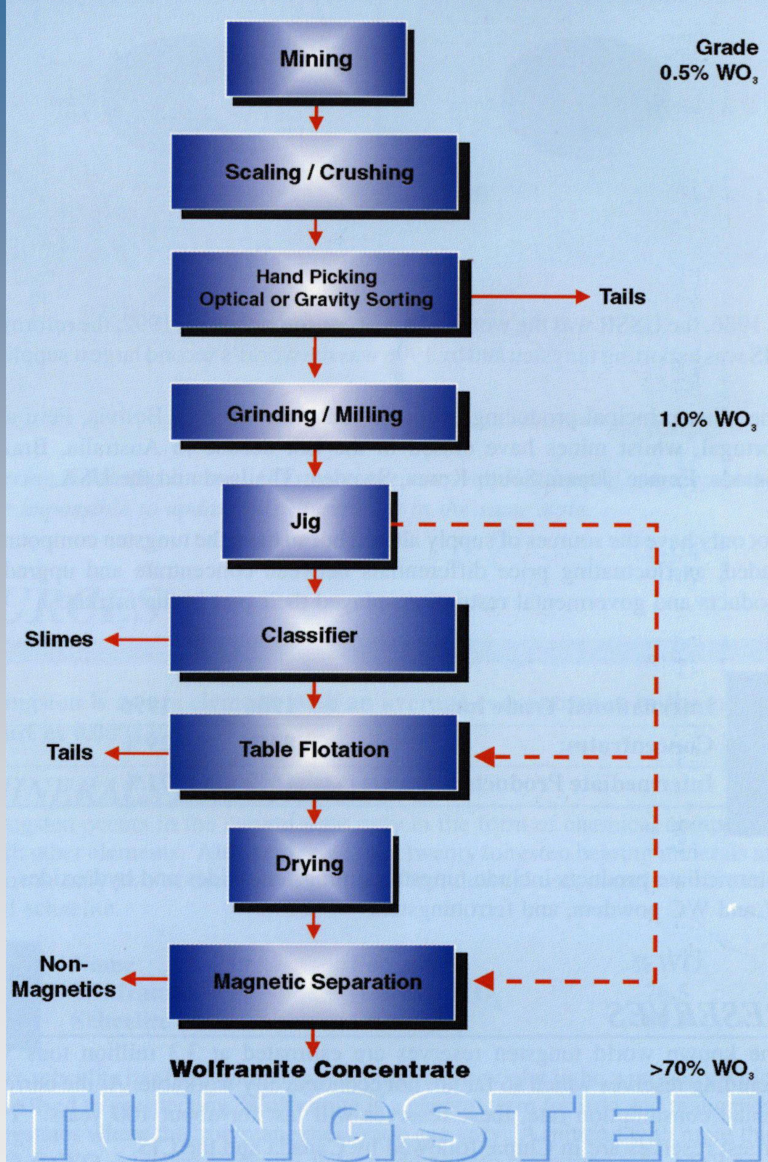
5828
3680
19.3

W

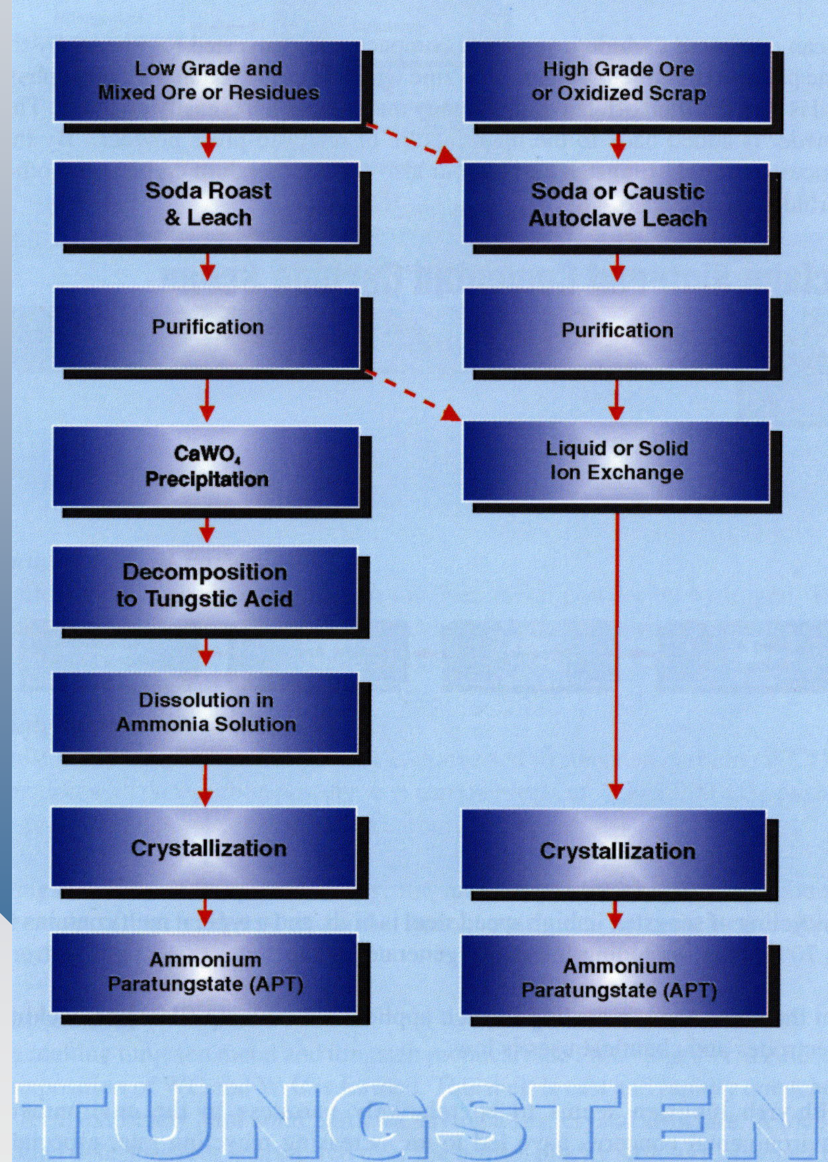
Tungsten

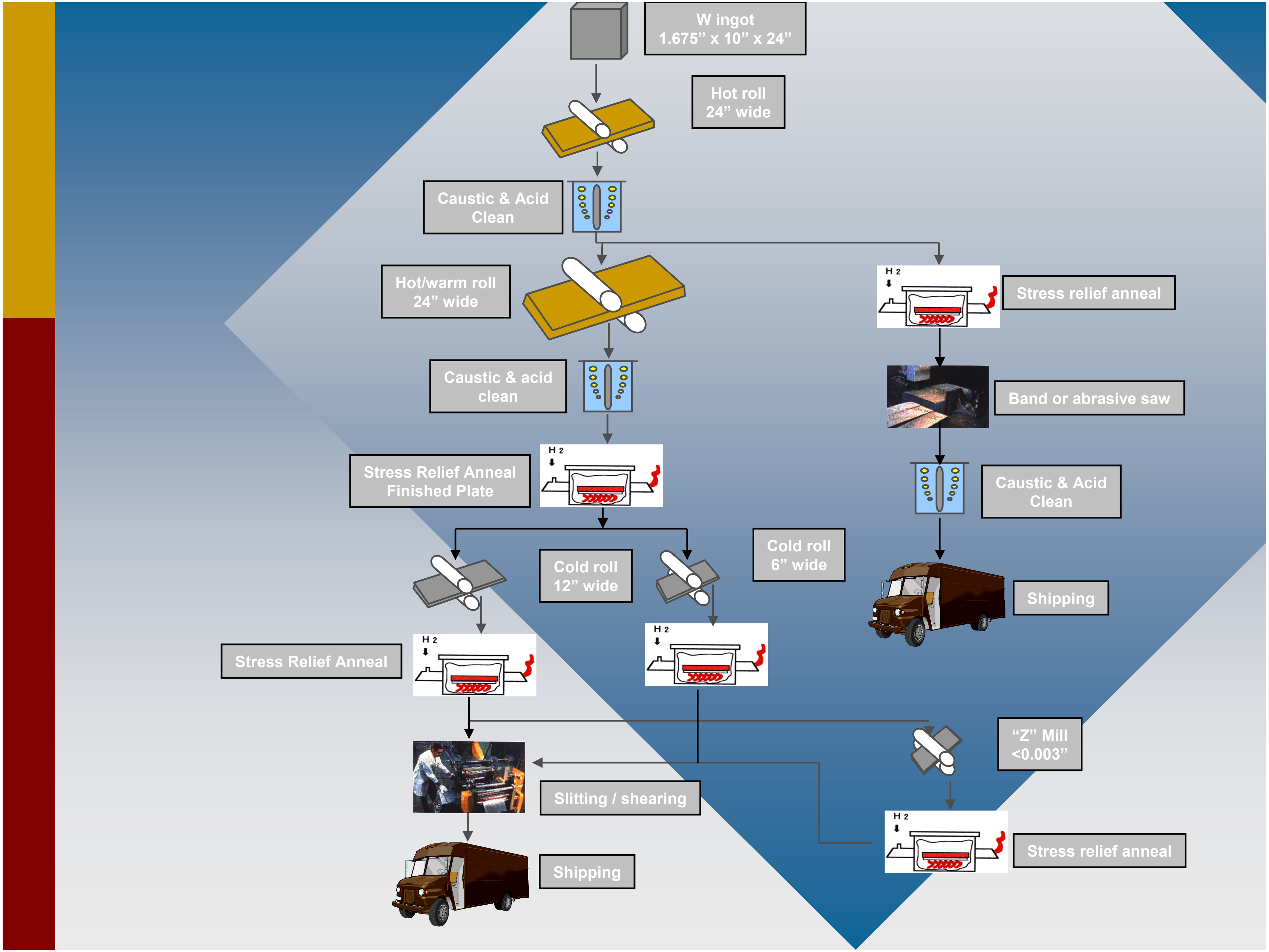
183.85

Typical Wolframite Upgrading Process



Concentrates Processing




W ingot
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
H 2
Cold roll
12” wide
Cold roll
6” wide
Stress Relief Anneal
Slitting / shearing
Shipping
Stress relief anneal
Band or abrasive saw
Caustic & Acid
Clean
Shipping
“Z” Mill
<0.003”
Stress relief anneal

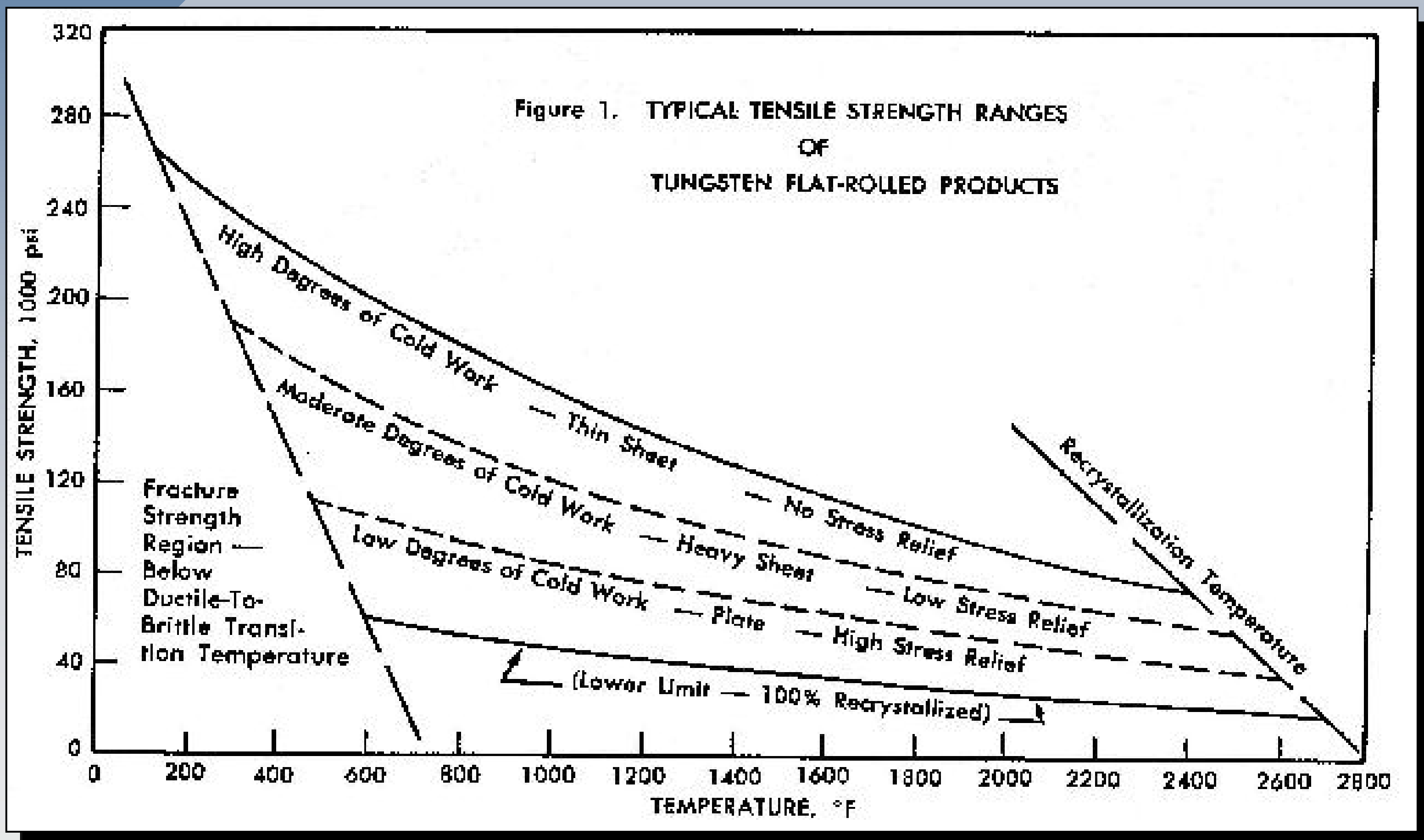
Tungsten Alloys

Alloy	Composition	Consolidation	Specification
W	99.95%	P/M	ASTM B760
W 3Re	3% Re	P/M	Manufacturer
W 5Re	5% Re	P/M	Manufacturer
W ThO_2	1%-3% ThO_2	P/M	Manufacturer
K/Si doped W	50-100 ppm K, 30-50 ppm Si	P/M	Manufacturer

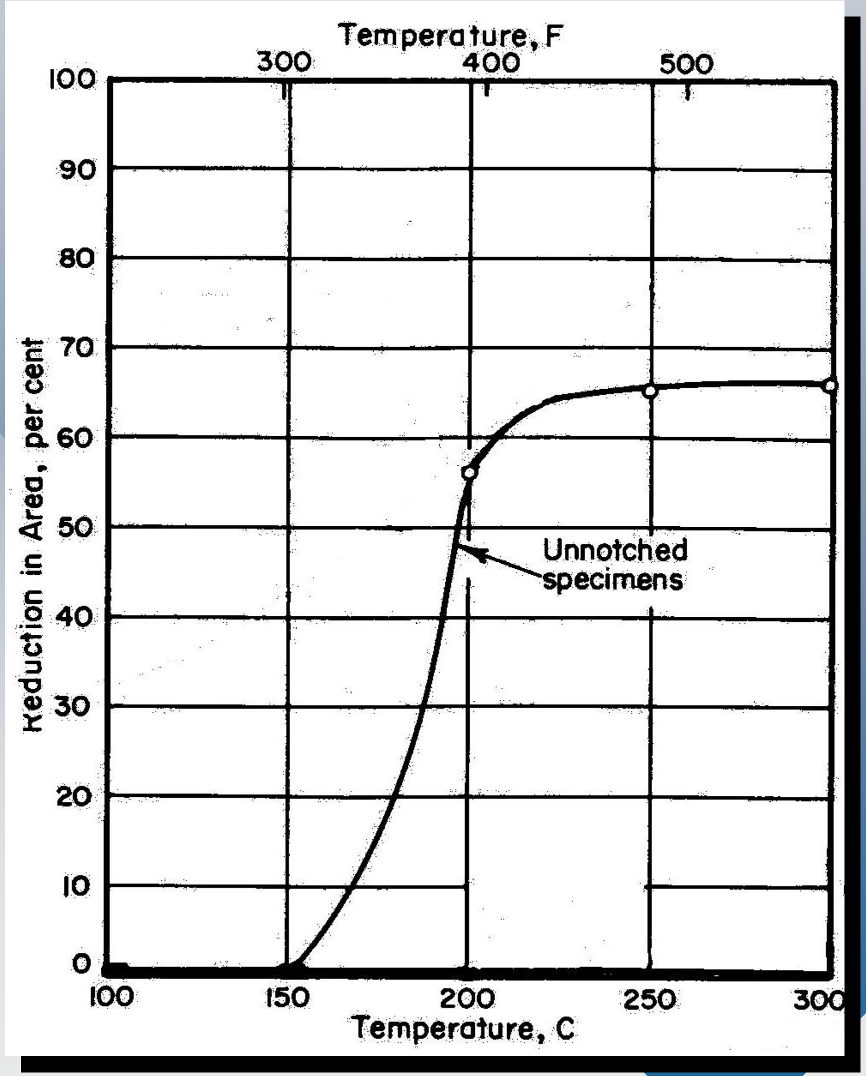
Tungsten Physical Properties

- 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



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)

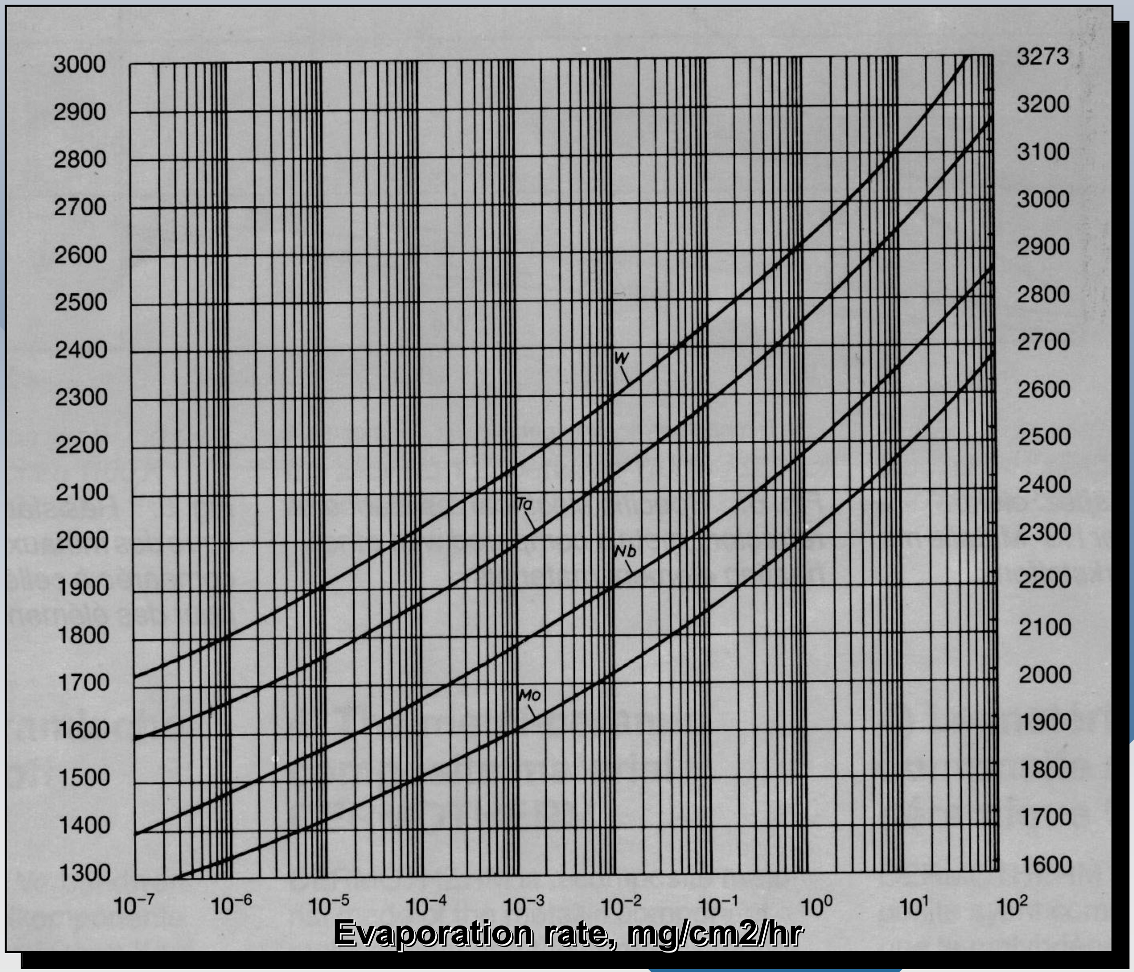
Issues for W in Implantation

- Purity
  - Contamination of ion beam
    - M/e problems do not affect performance
    - Surface contamination 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



Summary

Material	Material Cost	Manufacturing Costs	Performance Issues
Mo	Lowest	Lowest	Highest P_v, M/e problems, embrittlement with use
Ta	Highest	Intermediate	P_v << Mo, no M/e problems, remains ductile w/ use
W	Intermediate	Highest	P_v<<<Mo, no M/e problems, embrittlement with use