Oxygen Pressure Limits for V, Nb and Ta Alloys
and
Overview of Experimental Database on Tin Corrosion

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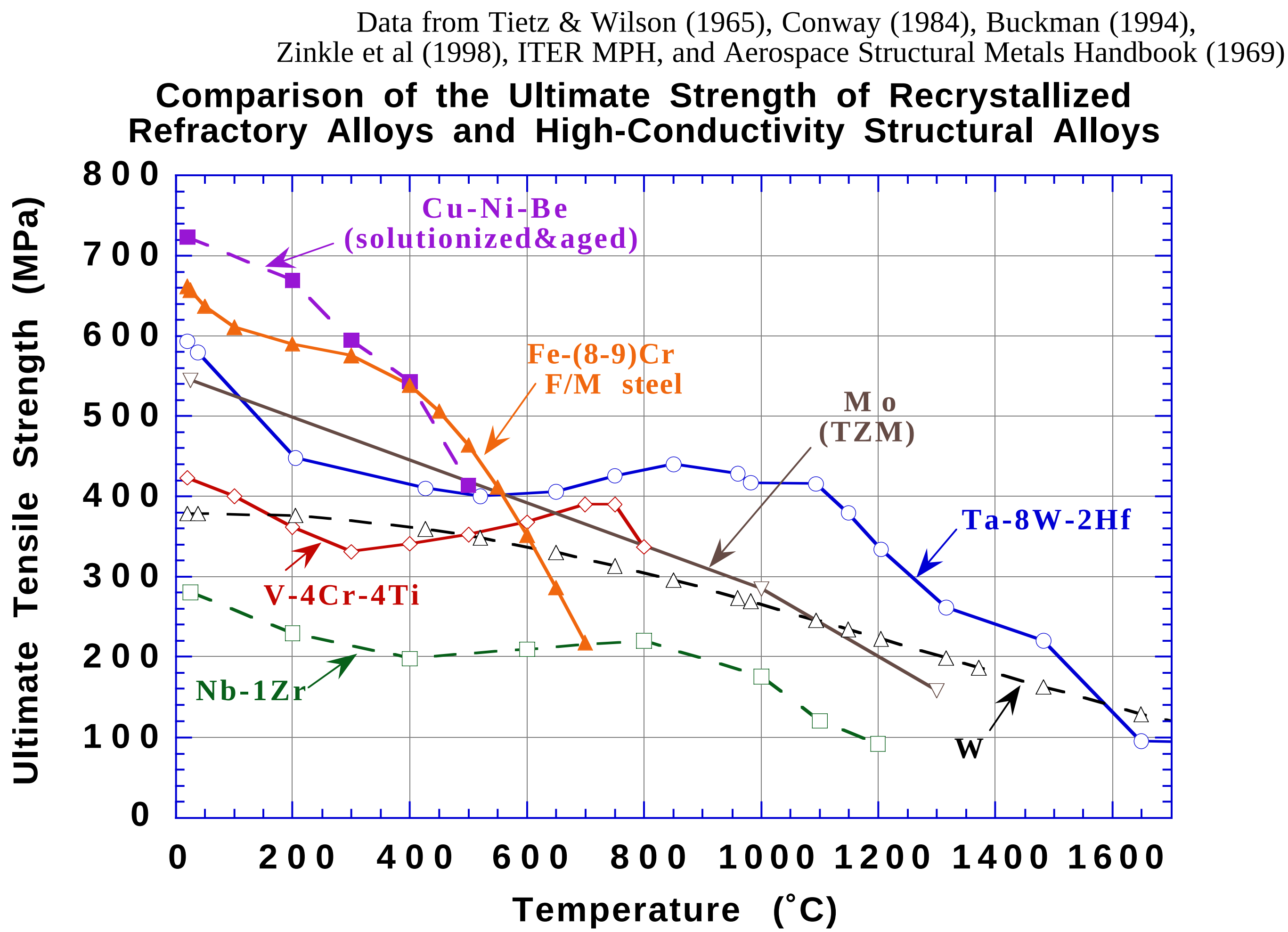
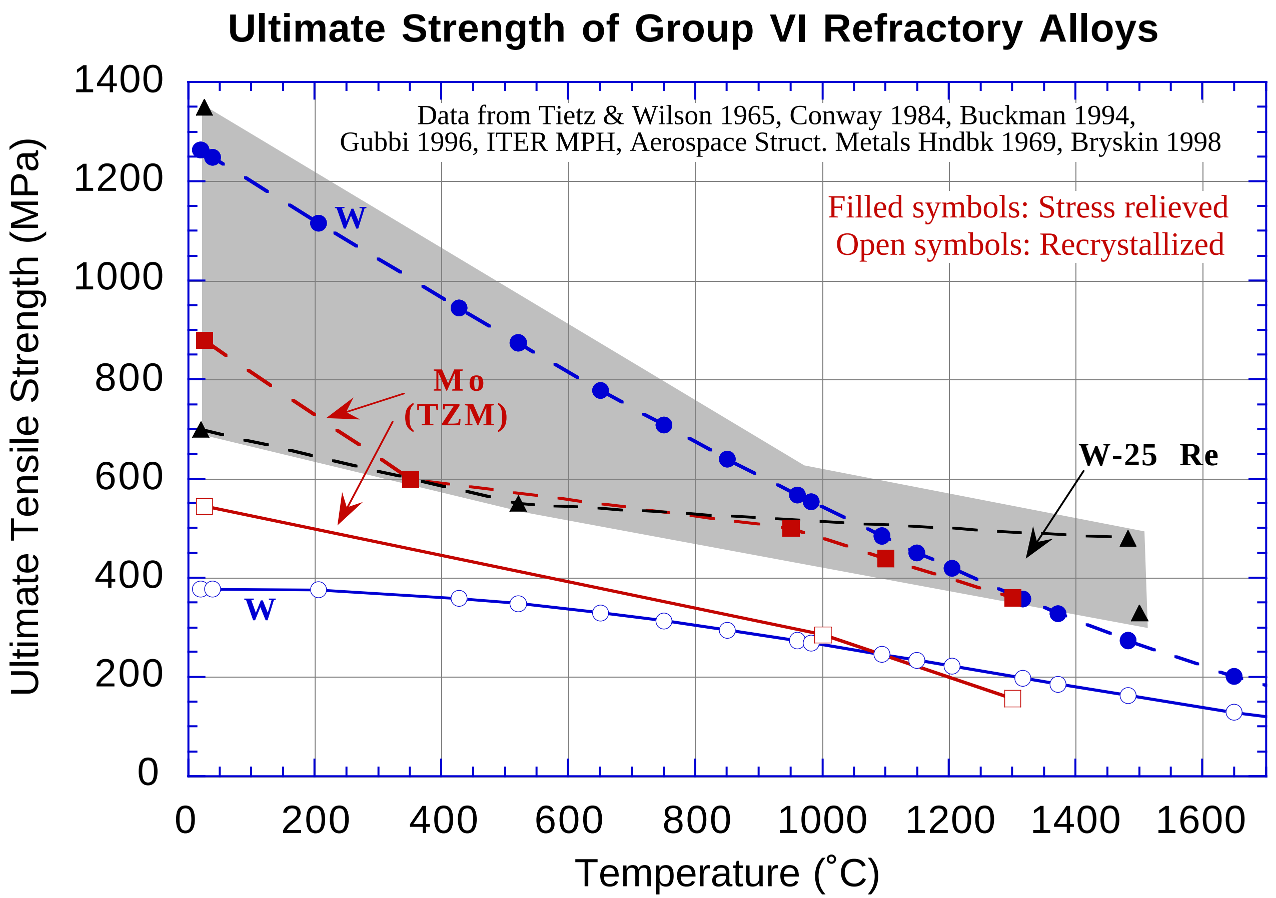
presented at APEX Study Meeting
UCLA, February 16-19, 1999


Data from Tietz & Wilson (1965), Conway (1984), Buckman (1994),
Zinkle et al (1998), ITER MPH, and Aerospace Structural Metals Handbook (1969)
Comparison of the Ultimate Strength of Recrystallized
Refractory Alloys and High-Conductivity Structural Alloys
Cu-Ni-Be
(solutionized&aged)
Fe-(8-9)Cr
F/M steel
Mo
(TZM)
Ta-8W-2Hf
V-4Cr-4Ti
Nb-1Zr
W
Ultimate Tensile Strength (MPa)
Temperature (˚C)
0
100
200
300
400
500
600
700
800
0
200
400
600
800
1000
1200
1400
1600



Ultimate Strength of Group VI Refractory Alloys
Data from Tietz & Wilson 1965, Conway 1984, Buckman 1994,
Gubbi 1996, ITER MPH, Aerospace Struct. Metals Hndbk 1969, Bryskin 1998
Filled symbols: Stress relieved
Open symbols: Recrystallized
W
Mo
(TZM)
W-25 Re
W
Ultimate Tensile Strength (MPa)
Temperature (°C)
0
200
400
600
800
1000
1200
1400
1600

Summary of Recrystallized W-(5-10%) Re Properties (typo in earlier VG)

Ultimate Tensile Strength (unirradiated)

σ_{UTS}(MPa)=377.9 + 0.03207*T - 1.955x10^{-4}*T^{2} + 5.129x10^{-8}*T^{3} (T in ˚C) –use pure W values

Yield Strength (Unirradiated)

σ_{Y}(MPa)= 94.2 - 0.0214*T -2.12x10^{-6}*T^{2} -7.48x10^{-10}*T^{3} (T in ˚C) –use pure W values

Elongation

e_{tot}(%)=20.8 + 0.053*T-2.18x10^{-5}*T^{2} (T>500˚C) --use pure W values

Elastic constants

E_{Y} (GPa) =398 - 0.00231*T - 2.72x10^{-5} T^{2} (T in ˚C) --pure W values; W-25Re E(20˚C)=410 GPa

ν=0.279 + 1.09x10^{-5} T (T in ˚C) W-25Re ν(20˚C)=0.30, G(20˚C)=159 GPa

Thermophysical properties

α_{m} (10^{-6}/˚C)= 3.9 + 5.8x10^{-5}*T + 5.7x10^{-11}*T^{2} - 2.0x10^{-14}*T^{3} (T in ˚C) --use pure W values

C_{P} (J/kg-K) = 128+ 0.033*T - 3.4x10^{-6}*T^{2} ??? (T in ˚C) --use pure W values

K_{th} (W/m-K)~85 W/m-K (1000-2400˚C) --conductivity decreases with increasing Re content

Recommended operating temperature limits (structural applications)

Tmin = 800˚C (due to rad.-induced increase in DBTT at low T_{irr})
Tmax = 1400˚C (Li, Pb-Li corrosion/chemical compatibility and thermal creep)

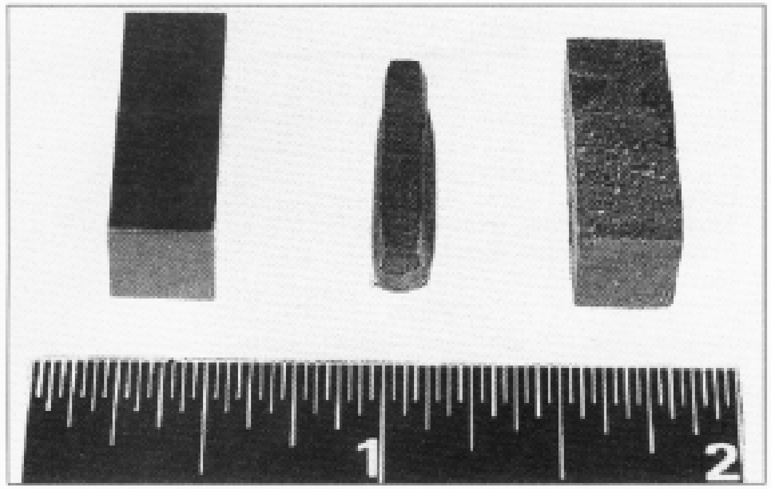


Fig. 5 — On the left is a block of Mo-TZM prior to oxidation. The center shows the same alloy after exposure to air for one hour at 1100°C (2000°F). The block on the right is a Mo-6Ti-2d.2Si-1.1B alloy after exposure for two hours at 1370°C (2500°F).

J.A. Shields, Jr. and E.L. Baker,
Adv. Mater. & Processes (Jan. 1999) 61.

Volatile oxidation of Mo-based alloys
(see accompanying APEX presentation by S. Sharafat and N.M. Ghoniem)

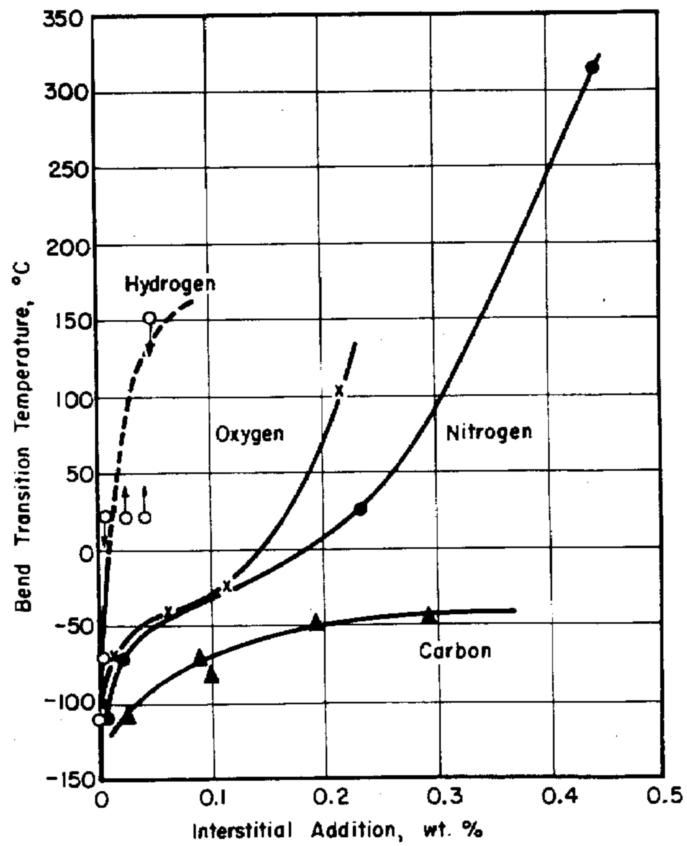
Oxygen Pressure Limits for V, Nb and Ta Alloys

- Oxygen pickup in the Group V metals causes matrix hardening, which in turn produces an increase in the ductile-to-brittle transition temperature (DBTT)
  - **oxygen concentration must be below ~1000 ppm to keep Charpy DBTT below room temperature in vanadium (Loomis & Carlson, 1959)**
  - **the oxygen solubility limit in vanadium is ~1-3 wt.% at T=20-900˚C**

- All of the Group V metals have high affinity for oxygen; based on thermodynamics alone, extremely low oxygen partial pressures are required to prevent oxygen pickup
  - the vanadium/vanadium oxide solvus occurs at 10^{-47} atm for T=525˚C and at 10^{-36} atm at T=725˚C (Worrell & Chipman, 1965)

- The oxygen pressure limits will be determined by kinetic considerations (oxygen diffusion through oxide scale, flux of impinging oxygen atoms)
  - significant oxygen pickup has been observed in V-Cr-Ti alloys during creep testing in an "ion-pumped" vacuum system at 600˚C (Chung et al., 1994)

Material	Exposure time	Oxygen (wt. ppm)	Carbon (wt. ppm)	Nitrogen (wt. ppm)
V-4Cr-4Ti (BL-47)	*As-fabricated*	*350*	*200*	*220*
V-4Cr-4Ti (BL-47)	1 h (Ta wrap)	520	260	200
V-4Cr-4Ti (BL-47)	213 h (Ta wrap)	520	270	190
V-4Cr-4Ti (BL-47)	541 h (Ta wrap)	770	—	200
V-10Cr-5Ti (BL-43)	*As-fabricated*	*230*	*100*	*31*
V-4Cr-4Ti (BL-47)	162 h (Ti wrap)	370	—	99
V-4Cr-4Ti (BL-47)	243 h (no wrap)	600	—	120



Effect of interstitial solute additions on the (un-notched) bend transition temperature of vanadium.

Tietz and Wilson (1965), based on data from Loomis and Carlson (1959)

Similar embrittlement behavior also observed for V-4Cr-4Ti alloys (e.g., B.A. Pint et al., 1998)

Oxygen Pressure Limits for V, Nb and Ta Alloys, cont'd

- The observed oxygen contents can be significantly lower than thermal equilibrium values
  - **Protective surface oxide film at low temperatures (logarithmic oxide film growth at very low temperatures; parabolic growth at moderate temperatures, >400˚C in vanadium); however, linear (rapid) growth occurs at high temperature**
  - **The oxygen impingement flux is strongly reduced at low oxygen partial pressures**

- Creation of a monolayer of chemisorbed oxygen on Group V metals at T>400˚C requires~1 Langmuir exposure (10^{-6} torr-s)

- The oxygen impingement flux is $J_O=P_O(2\pi m_O RT)^{1/2}$, assuming an equilibration constant of unity

§ A protective oxide surface film initially forms, except at very low oxygen partial pressures (<<10^{-6} torr) and/or high temperatures

§ A high oxygen content (sufficient for embrittlement) exists at depths beyond the oxide scale layer (Natesan et al. 1998, etc.)

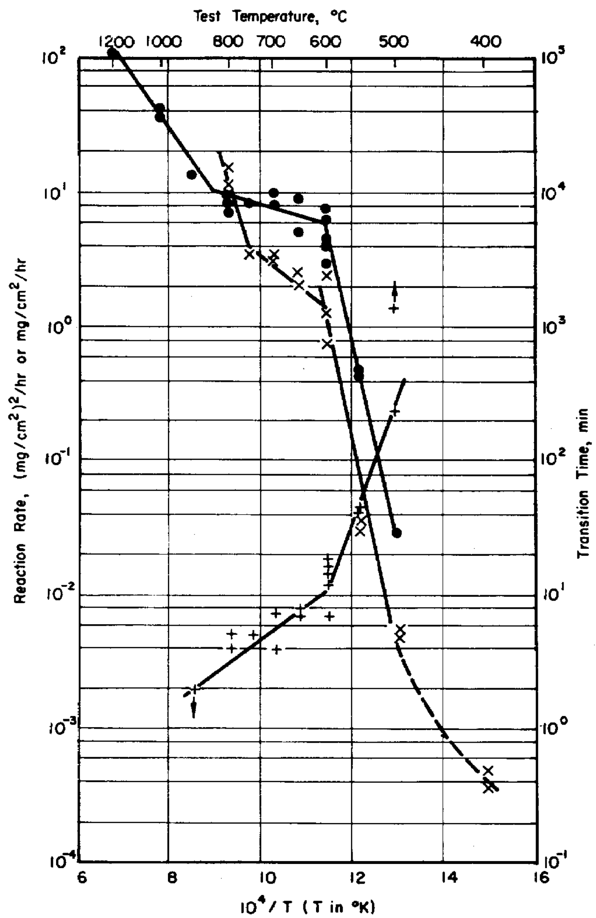


FIG. 7.39. Rate constants and transition times for the tantalum-air reaction from 400 to 1200 °C.[4] × Parabolic rate $(mg/cm^2)^2/hr$; ● Linear rate $(mg/cm^2/hr)$; + Time for transition from parabolic to linear rate.

Tietz & Wilson (1965)

Tantalum oxidation shifts from parabolic to linear growth above ~600˚C

- The kinetics for oxygen pickup in vanadium alloys is controlled by the protective oxide growth rate
  - the V-4Cr-4Ti activation energy for oxygen diffusion is ~130 kJ/mol (Nakajima et al. 1993, etc.), whereas V-4Cr-4Ti oxide growth has an activation energy of ~180-200 kJ/mol (Uz et al. 1997, etc.)

Temperature	Oxygen diffusion depth (10^4 h)	Oxide thickness (assum. parabolic growth)
500˚C	0.5 mm	~0.01 mm
600˚C	1.6 mm	~0.07 mm
700˚C	3.8 mm	~0.4 mm

- The following oxygen pressure limits for Group V metals are obtained using the assumptions that subsurface incorporation of the chemisorbed oxygen and matrix oxygen diffusion are not rate-limiting steps (valid for high temperatures and low p_O levels)
  - Additional assumptions were planar geometry, 3 mm slab thickness, oxygen ingress from one side only

	Exposure time to achieve listed oxygen content	
Oxygen partial pressure	100 wt.ppm O	1000 wt.ppm O
10^{-8} torr	94 h	940 h
10^{-10} torr	9400 h	94,000 h (11 yr)

- In conclusion, oxygen partial pressures below 10^{-11} torr would be sufficient to keep oxygen pickup to acceptably low levels in Group V metals for expected structural material lifetimes (10 to 50 years)

Maximum temperatures of structural alloys (bare walls) in contact with high-purity liquid coolants, based on a 5 μm/yr corrosion limit

	Li	Pb-17 Li	Flibe
F/M steel	550-600°C [1,2,3]	450°C [1,2,9]	700°C ? 304/316 st. steel [14]
V alloy	600-700°C [1,4,5]	~650°C [1,10]	?
Nb alloy	>1300°C [6,7]	>600°C [10] (>1000°C in Pb) [11]	>800°C [15]
Ta alloy	>1370°C [6,7]	>600°C [10] (>1000°C in Pb) [11]	?
Mo	>1370°C [6,7]	>600°C [10]	>1100°C? [16,17]
W	>1370°C [6,7]	>600°C [10]	>900°C? [16]
SiC	~550°C ? [8]	>800°C ? [12,13]	?

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Chemical Compatibility of Structural Materials with Molten Tin (static tests)

Nb: no corrosion observed at ~600˚C
chemical attack occurred at 800˚C [1] and 1000˚C [2,3]

Ta: chemical attack observed at both 600-630 [1,4] and 800˚C [1]
intergranular penetration observed at 1000˚C [2,3,5]

Mo: minimal corrosion observed below ~600˚C [4]
chemical attack observed at both 630 and 800˚C [1]
significant corrosion (predominantly intergranular) observed at 1000˚C [2,3-5,6]
-1.7% weight loss after 340 h at 1000˚C [4,6]

W: good chemical resistance at 630˚C; moderate attack at 800˚C [1]
Very little corrosion (10 ppm weight loss) observed after 40 h at 1000˚C [6]
moderate corrosion (<5 μm) observed after 100 h at 1000˚C [3]

Austenitic, Ferritic stainless steels: rapid attack at temperatures above 400-500˚C [7]

SiC: "no interactions detected" for SiC exposed to Sn-Pb-Bi mixture at 760˚C [8]

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Summary of maximum temperatures of structural alloys (bare walls) in contact with high-purity liquid or gaseous coolants, based on a 5 μm/yr corrosion limit

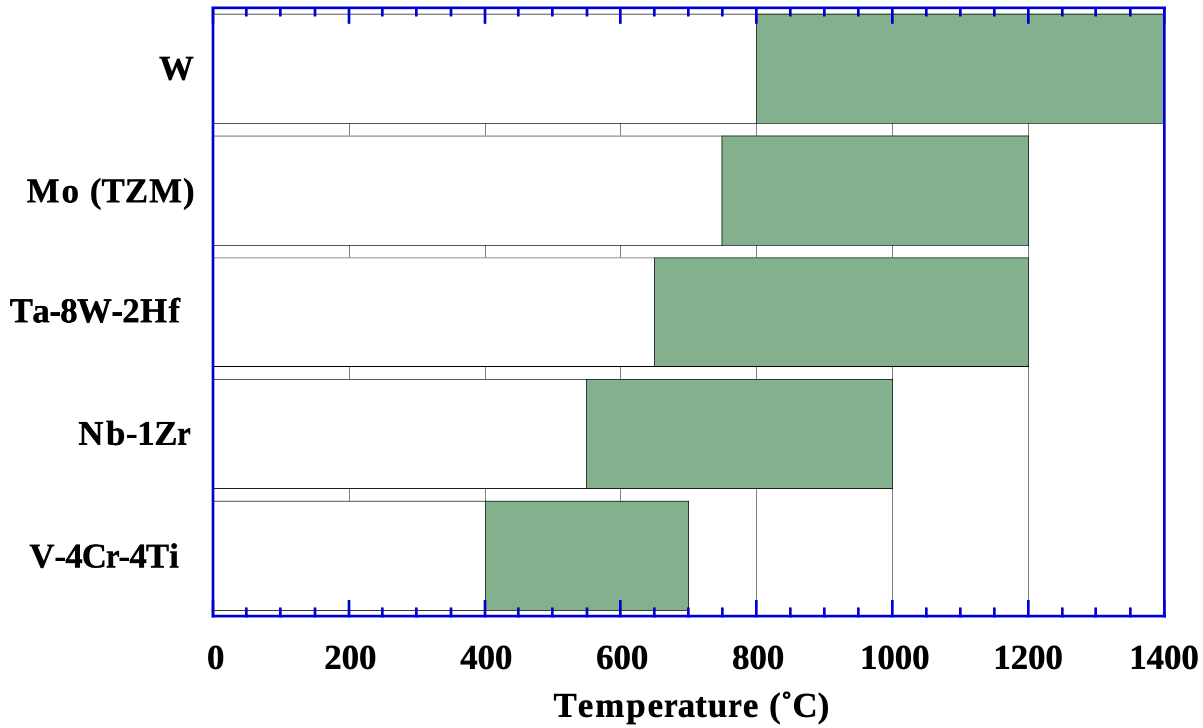
	Li	Pb-17 Li	Sn-20 Li (pure Sn)	Flibe	He*
F/M steel	550-600°C	450°C	~400°C	700°C ? 304/316 st. steel	–
V alloy	600-700°C	~650°C	?	?	~600˚C?§
Nb alloy	>1300°C	>600°C (>1000°C in Pb)	800-850°C	>800°C	~600˚C?§
Ta alloy	>1370°C	>600°C (>1000°C in Pb)	>600°C (>900°C/Sze)	?	~600˚C?§
Mo	>1370°C	>600°C	>700°C (1000°C/Sze)	>1100°C?	~1100°C **
W	>1370°C	>600°C	~1000°C	>900°C?	~1100°C **
SiC	~550°C ?	>800°C ?	(>760˚C)	?	–

* assumes 1 appm O in 50 MPa He gas
** see accompanying APEX presentation by S. Sharafat and N.M. Ghoniem

§ the temperature limit for vanadium and other Group V metals in helium will be determined by oxide dissolution and oxygen absorption kinetics; recent work (e.g., B.A. Pint et al. 1998) suggests that the temperature limit for V-4Cr-4Ti may be ~600˚C due to interstitial oxygen hardening/embrittlement effects

dashed line (--) indicates that the corrosion-based temperature limit is higher than the structural temperature (thermal creep) limit

Estimated Operating Temperature Limits for Refractory Alloys in Fusion Reactors



§ Lower temperature limit based on radiation hardening/ fracture toughness embrittlement (K_{1C}<30 MPa-$m^{1/2}$)

- Upper temperature limit based on 100 MPa creep strength (2% in 1000 h); chemical compatibility considerations may cause further decreases in the max operating temp.