

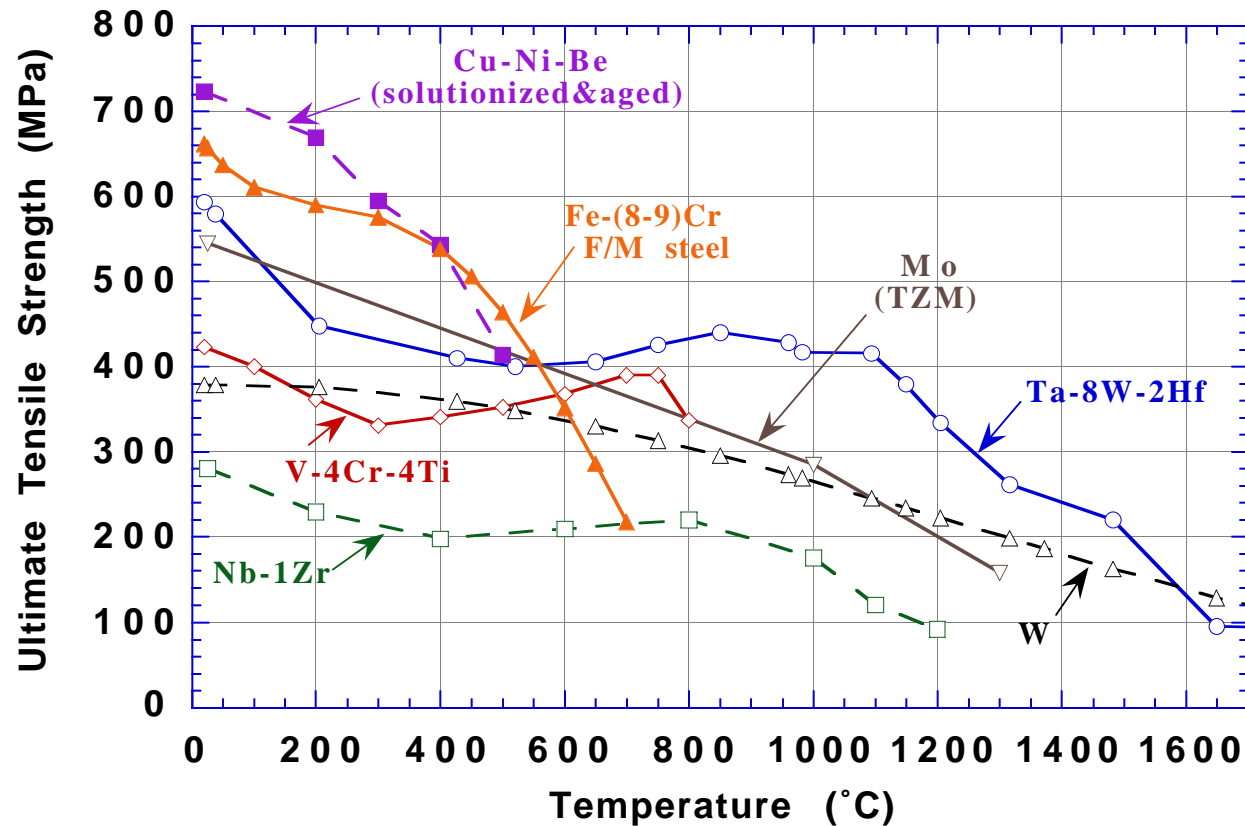
**Oxygen Pressure Limits for V, Nb and Ta Alloys  
and  
Overview of Experimental Database on Tin Corrosion**

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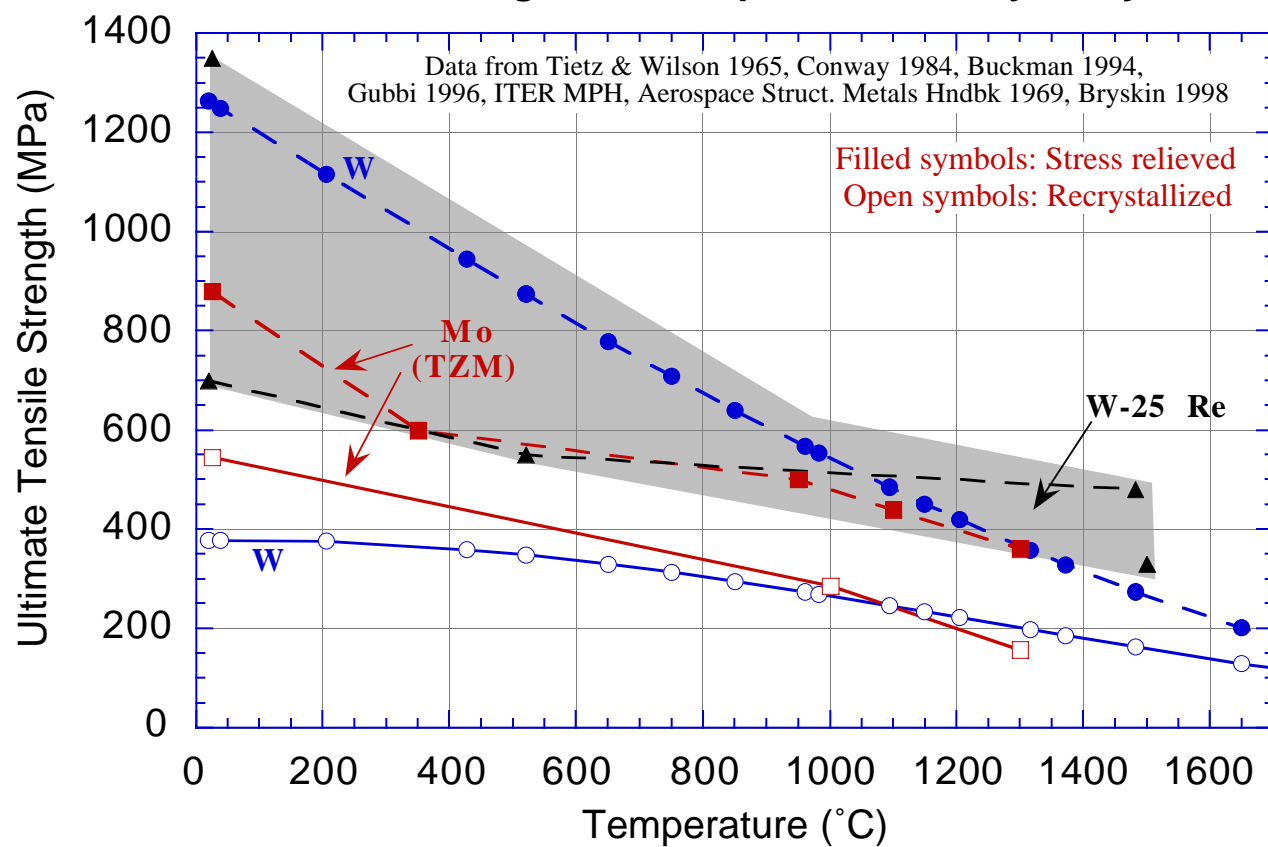
**presented at APEX Study Meeting  
UCLA, February 16-19, 1999**

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



## Ultimate Strength of Group VI Refractory Alloys



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

### **Ultimate Tensile Strength (unirradiated)**

$$\sigma_{\text{UTS}}(\text{MPa}) = 377.9 + 0.03207 * T - 1.955 \times 10^{-4} * T^2 + 5.129 \times 10^{-8} * T^3 \quad (T \text{ in } ^\circ\text{C}) \text{ --use pure W values}$$

### **Yield Strength (Unirradiated)**

$$\sigma_Y(\text{MPa}) = 94.2 - 0.0214 * T - 2.12 \times 10^{-6} * T^2 - 7.48 \times 10^{-10} * T^3 \quad (T \text{ in } ^\circ\text{C}) \text{ --use pure W values}$$

### **Elongation**

$$e_{\text{tot}}(\%) = 20.8 + 0.053 * T - 2.18 \times 10^{-5} * T^2 \quad (T > 500^\circ\text{C}) \quad \text{--use pure W values}$$

### **Elastic constants**

$$E_Y (\text{GPa}) = 398 - 0.00231 * T - 2.72 \times 10^{-5} T^2 \quad (T \text{ in } ^\circ\text{C}) \quad \text{--pure W values; W-25Re } E(20^\circ\text{C}) = 410 \text{ GPa}$$

$$\nu = 0.279 + 1.09 \times 10^{-5} T \quad (T \text{ in } ^\circ\text{C}) \quad \text{W-25Re } \nu(20^\circ\text{C}) = 0.30, G(20^\circ\text{C}) = 159 \text{ GPa}$$

### **Thermophysical properties**

$$\alpha_m (10^{-6}/^\circ\text{C}) = 3.9 + 5.8 \times 10^{-5} * T + 5.7 \times 10^{-11} * T^2 - 2.0 \times 10^{-14} * T^3 \quad (T \text{ in } ^\circ\text{C}) \quad \text{--use pure W values}$$

$$C_p (\text{J/kg-K}) = 128 + 0.033 * T - 3.4 \times 10^{-6} * T^2 \quad ??? \quad (T \text{ in } ^\circ\text{C}) \quad \text{--use pure W values}$$

$$K_{\text{th}} (\text{W/m-K}) \sim 85 \text{ W/m-K} \quad (1000-2400^\circ\text{C}) \quad \text{--conductivity decreases with increasing Re content}$$

### **Recommended operating temperature limits (structural applications)**

$T_{\text{min}} = 800^\circ\text{C}$  (due to rad.-induced increase in DBTT at low  $T_{\text{irr}}$ )

$T_{\text{max}} = 1400^\circ\text{C}$  (Li, Pb-Li corrosion/chemical compatibility and thermal creep)

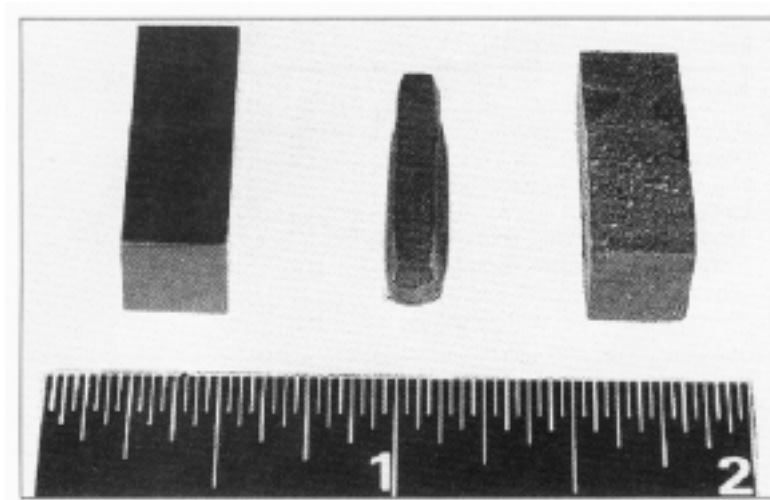


Fig. 5 — On the left is a block of Mo-TZM prior to oxidation. The center shows the same alloy after exposure to air for one hour at 1100°C (2000°F). The block on the right is a Mo-6Ti-2Al-2Si-1.1B alloy after exposure for two hours at 1370°C (2500°F).

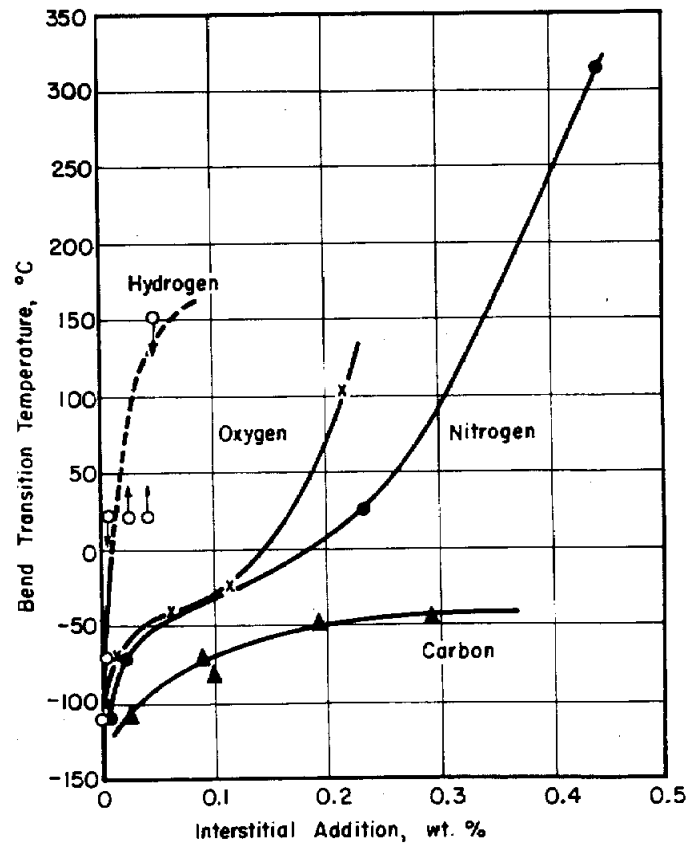
**J.A. Shields, Jr. and E.L. Baker,  
Adv. Mater. & Processes (Jan. 1999) 61.**

**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)	<i>As-fabricated</i>	<i>350</i>	<i>200</i>	<i>220</i>
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)	<i>As-fabricated</i>	<i>230</i>	<i>100</i>	<i>31</i>
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  $T > 400^\circ\text{C}$  requires  $\sim 1$  Langmuir exposure ( $10^{-6}$  torr-s)
- The oxygen impingement flux is  $J_{\text{O}} = P_{\text{O}}(2\pi m_{\text{O}}RT)^{1/2}$ , assuming an equilibration constant of unity
- § A protective oxide surface film initially forms, except at very low oxygen partial pressures ( $\ll 10^{-6}$  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.)



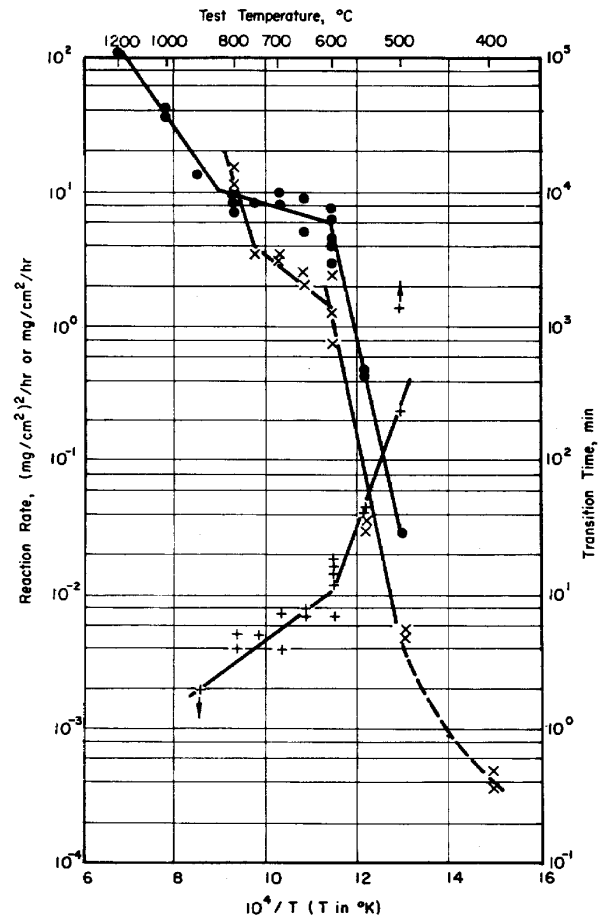


FIG. 7.39. Rate constants and transition times for the tantalum-air reaction from 400 to 1200 °C.  $\times$  Parabolic rate ( $\text{mg}/\text{cm}^2)^2/\text{hr}$ ;  $\bullet$  Linear rate ( $\text{mg}/\text{cm}^2/\text{hr}$ );  $+$  Time for transition from parabolic to linear rate.

Tietz & Wilson (1965)

Tantalum oxidation shifts from parabolic to linear growth above  $\sim 600^\circ\text{C}$

§ 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  $p_{\text{O}}$  levels)
  - Additional assumptions were planar geometry, 3 mm slab thickness, oxygen ingress from one side only

Oxygen partial pressure	Exposure time to achieve listed oxygen content	
	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**

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

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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	<b>450°C</b>	<b>~400°C</b>	700°C ? 304/316 st. steel	–
V alloy	600-700°C	~650°C	?	?	<b>~600°C?§</b>
Nb alloy	>1300°C	>600°C (>1000°C in Pb)	800-850°C	>800°C	<b>~600°C?§</b>
Ta alloy	>1370°C	>600°C (>1000°C in Pb)	>600°C (>900°C/Sze)	?	<b>~600°C?§</b>
Mo	>1370°C	>600°C	>700°C (1000°C/Sze)	>1100°C?	<b>~1100°C **</b>
W	>1370°C	>600°C	~1000°C	>900°C?	<b>~1100°C **</b>
SiC	<b>~550°C ?</b>	>800°C ?	(>760°C)	?	–

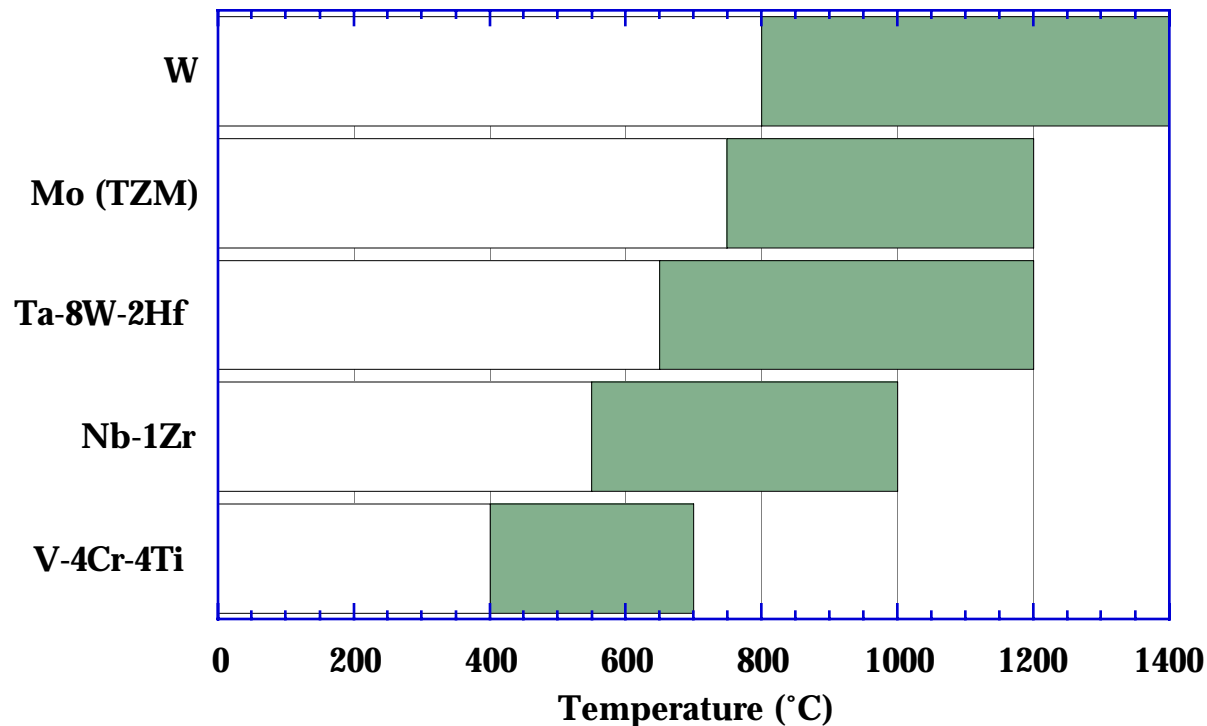
\* assumes 1 appm O in 50 MPa He gas

\*\* 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 ( $K_{IC} < 30 \text{ MPa}\cdot\text{m}^{1/2}$ )
- 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.