

CHEMICAL COMPATIBILITY AND HIGH-TEMPERATURE LIMITS FOR STRUCTURAL MATERIALS

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COOLANT - STRUCTURAL MATERIAL SYSTEMS

COOLANT	STRUCTURAL MATERIAL
<ul style="list-style-type: none">• Liquid Lithium• Liquid Lithium-Lead• Molten Salts (FLiBe)• Helium	<ul style="list-style-type: none">• Vanadium Alloys• Silicon Carbide Composites• Ferritic Steels• Refractory Alloys (Ta, Nb, Mo, W)

LIQUID METAL CHEMICAL COMPATIBILITY (Basic Mechanisms)

► Dissolution in Liquid Metal

$$\frac{dS}{dt} = \beta (c_{sat} - c_{bulk})$$

$$\frac{dS}{dt} = Ce^{\frac{-\Delta H_{act}}{RT}}$$

β = mass transfer coefficient

c_{sat} = element saturation concentration in liquid metal

c_{bulk} = actual element concentration in bulk

ΔH_{act} = activation energy for dissolution

LIQUID METAL CHEMICAL COMPATIBILITY (Basic Mechanisms) cont.

► Exchange due to non-metallic Elements

For oxygen, carbon, and nitrogen, the distribution coefficient is:

$$K = \frac{a_s^o [s]}{a_s^o [l]} e^{\left\{ \frac{\Delta G^o(l) - \Delta G^o(s)}{RT} \right\}}$$

a_s^o are saturation activities for solid (s) and liquid (l).

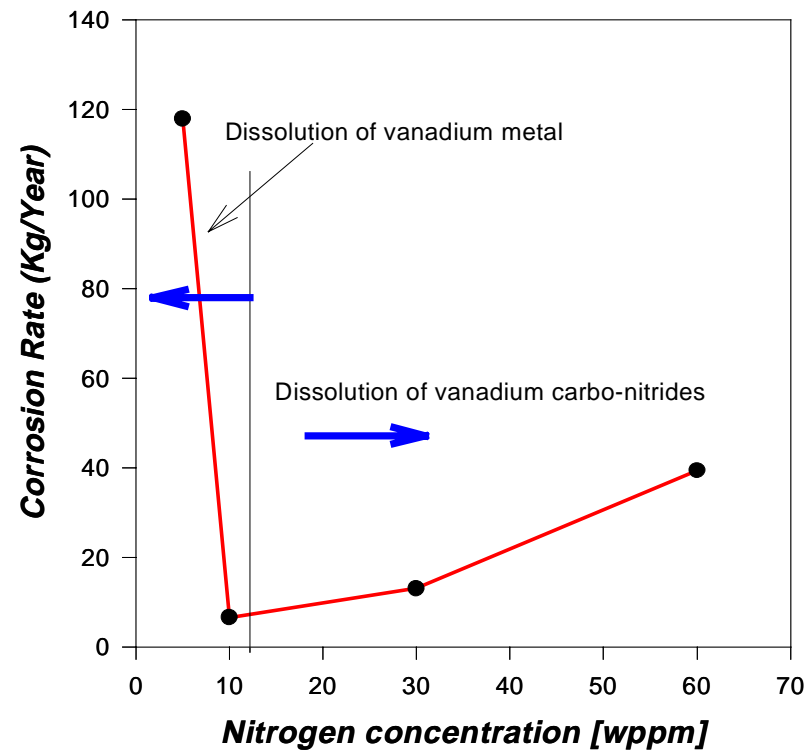
- For $K > 1$, we get pick-up.
- For $K < 1$, we get loss.

COMPATIBILITY OF VANADIUM ALLOYS WITH LIQUID LITHIUM

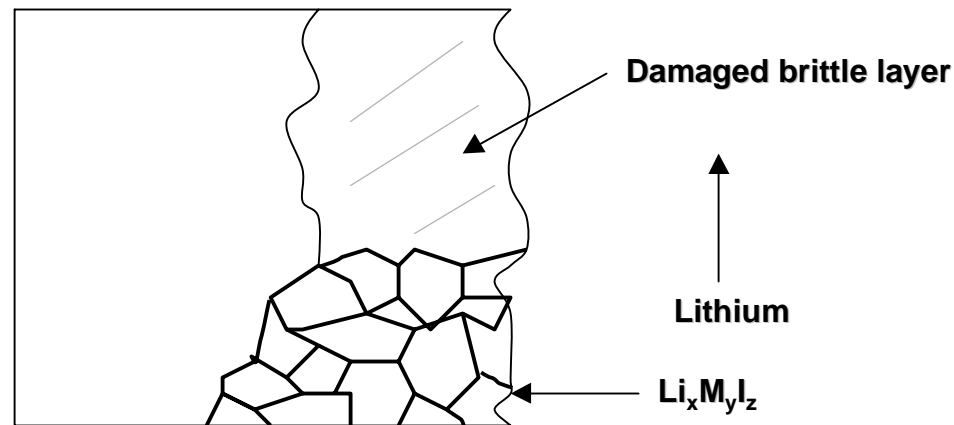
- **For V-3Ti-1Si and V-15Cr-5Ti at 550°C in flowing lithium (Borgstedt):**
 - **weight loss: 10^{-3} - 3×10^{-3} g/m²hr**
 - **weight loss is strongly influenced by nitrogen content of the liquid metal.**
 - **Reaction is parabolic with an activation energy of 180kJ/mol (\approx nitrogen diffusion energy in vanadium)**

CALCULATED WEIGHT LOSS IN 1000 m² SYSTEM

Weight Loss for 1000 m² at 550 °C
in Flowing Lithium



MAIN CORROSION MECHANISM FOR REFRACTORY METALS



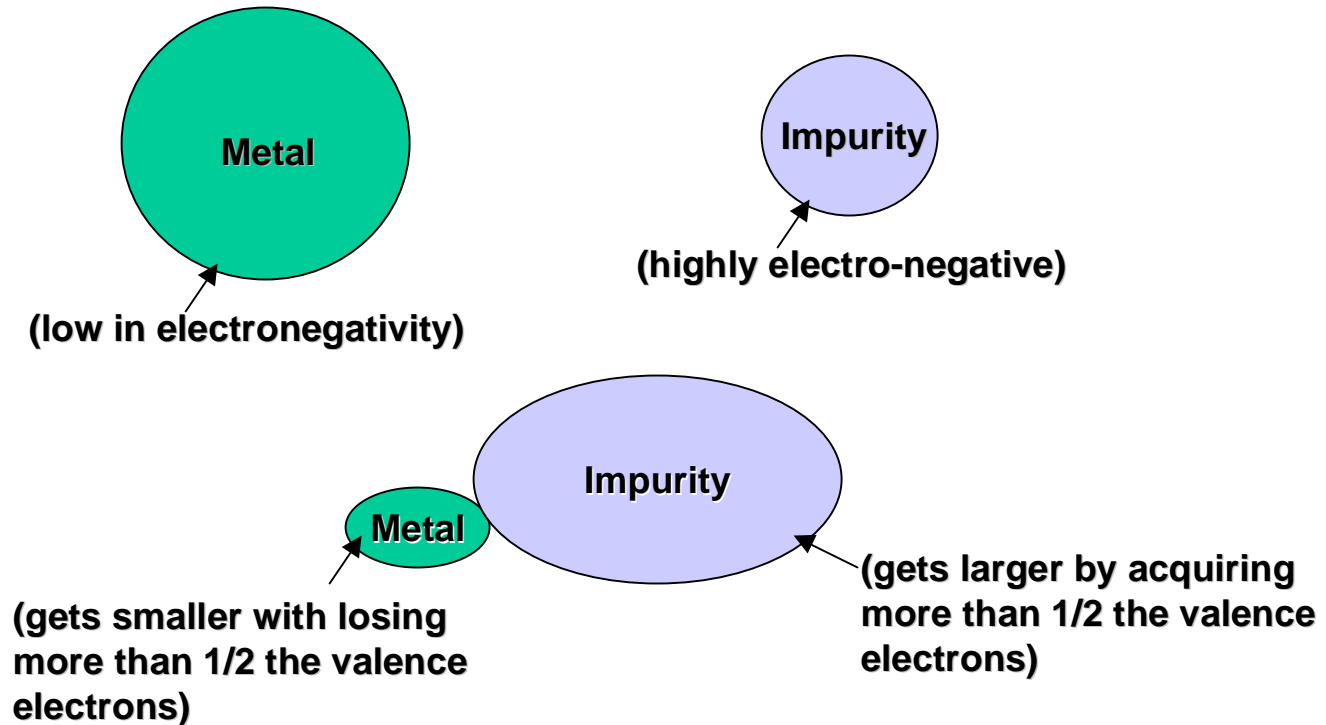
M = refractory metal I = interstitial impurity

Electronegativity Chart

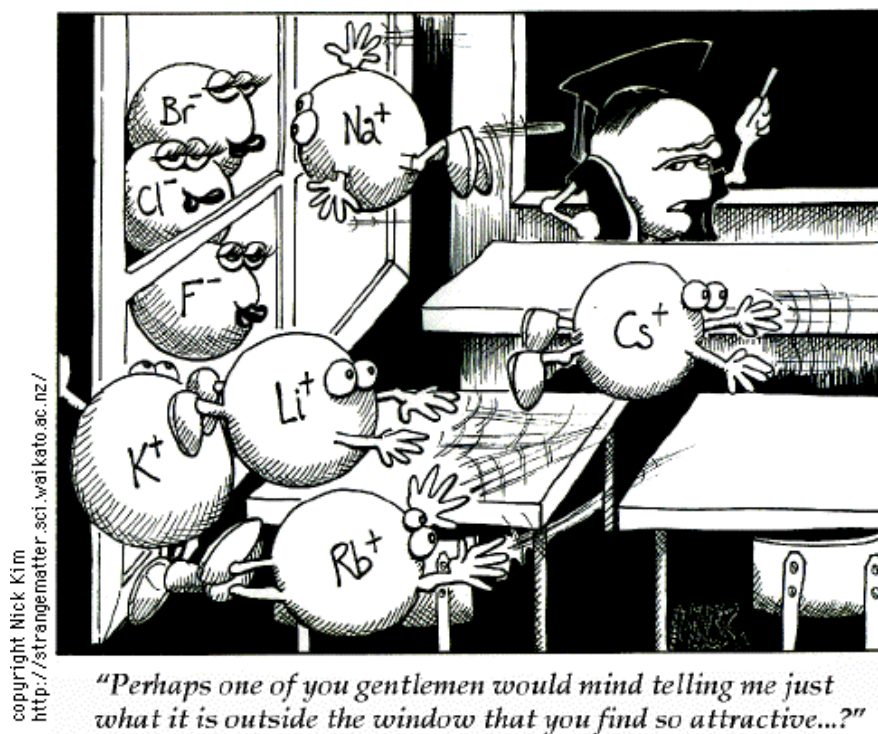
Metal				Impurity			Li
IV A	V A	VI A	VII A	IV B	V B	VI B	0.98
Ti	V	Cr		C	N	O	
1.54	1.63	1.66		2.55	3.04	3.44	
Zr	Nb	Mo					
1.33	1.6	2.16					
Hf	Ta	W	Re				
1.3	1.5	2.36	1.9				

EQUALIZATION OF ELECTRONEGATIVITY

Electronegativity \equiv the relative ability to acquire a negative charge.



CONCEPT OF ELECTRONEGATIVITY



COMPOUND STABILITY BASED ON ELECTRONEGATIVITY

		Carbides	Nitrides	Oxides	Comments
IV A	Ti	1.01	1.5	1.9	oxide formers (alloying elements)
	Zr	1.22	1.71	2.11	
	Hf	1.25	1.74	2.14	
V A	V	0.92	1.41	1.81	
	Nb	0.95	1.44	1.84	
	Ta	1.05	1.54	1.94	
VI A	Cr	0.89	1.38	1.78	most corrosion resistant
	Mo	0.39	0.88	1.28	
	W	0.19	0.68	1.08	
VII A	Re	0.65	1.14	1.54	

EXPERIMENTAL OBSERVATIONS OF LITHIUM COMPATIBILITY WITH REFRACTORY METALS

Up to lithium velocities of 6m/s, the temperature limit for acceptable corrosion for Nb alloys is ~1250°C, while that for Ta alloys is ~1350°C.*

Corrosion Rates for Nb-1Zr

T (°C)	ΔT (°C)	Time (hr)	Li velocity (m/s)	corrosion rate (μm/yr)
1100	200	10,000	3-6	negligible
1200	200	1,550	3-4	negligible
1297	179	3,000	.05	7.5
1073-1143	~10	500	48.5	120
1330	200	500	3-4	1000

*References:

1. A.J. OVERMAN, et al, LCRE Non Nuclear System Test, Final Report PWAC-402, Part IV, Pratt and Whitney Aircraft, Middletown, Connecticut (October 1965).
2. L.G. HAYES, Corrosion of Niobium-1Zr Alloy by Lithium at High Velocities, JPL Technical Report 32-1233 (December 1, 1967).
3. M.S. FREED, Corrosion of Columbian Base and Other Structural Alloys in High Temperature Li, PWCA-3555 (June 30, 1961).

EXPERIMENTAL OBSERVATIONS OF LITHIUM COMPATIBILITY W/ REFRACTORY METALS (cont.)

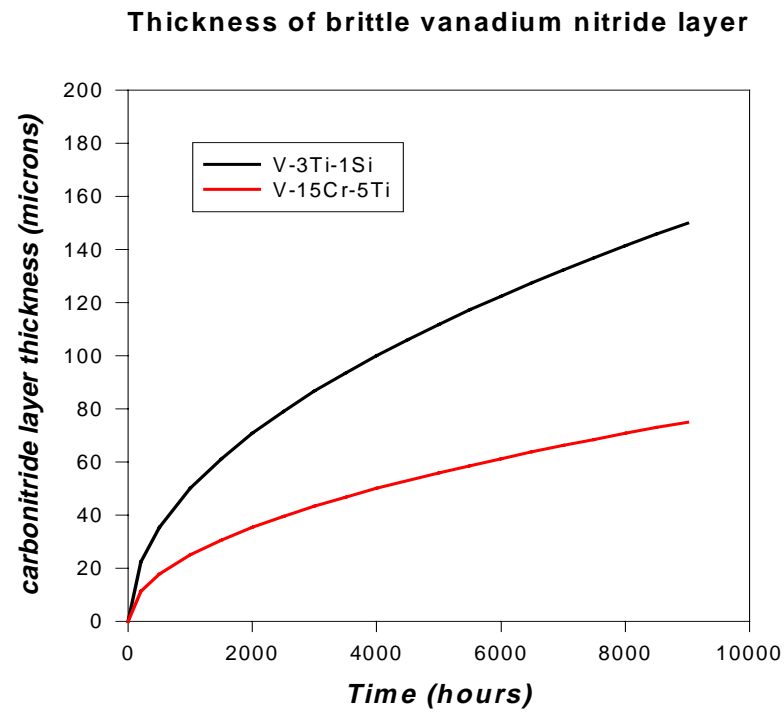
Corrosion Rates of Tantalum Alloys in Flowing Lithium

Alloy	T (°C)	ΔT (°C)	Time (hr)	Li velocity (m/s)	corrosion rate ($\mu\text{m/yr}$)
T-111	1370	170	3,000	6	< 1.3
T-111	1330	200	5,000	< .05	< 1.3
ASTAR-811	1360	200	5,000	< .05	< 0.3
T-111, ASTAR-811	1150	95	5,000	3	No metal loss or Li attack
T-111	1230	95	10,000	6-6	No metal loss or Li attack

*References cont.:

4. J.E. DEVAN and C.E. SESSIONS, Nucl. App. Tech 3, 102-109 (February 1967).
5. J.E. DEVAN and C.E. SESSIONS, Nucl. App. Tech 9, 250-259 (August 1967).
6. G.W. AUSTON, Lithium Corrosion Investigation of Columbian-Zirconium Alloy System PWAC-343 (June 27, 1961).

CALCULATED EVOLUTION OF CARBONITRIDE LAYER ON VANADIUM

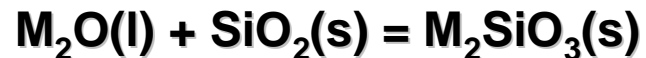
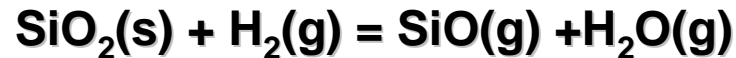
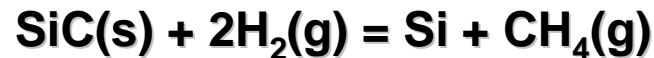


INTERSTITIAL TRANSPORT IN REFRACTORY METAL-LITHIUM SYSTEM

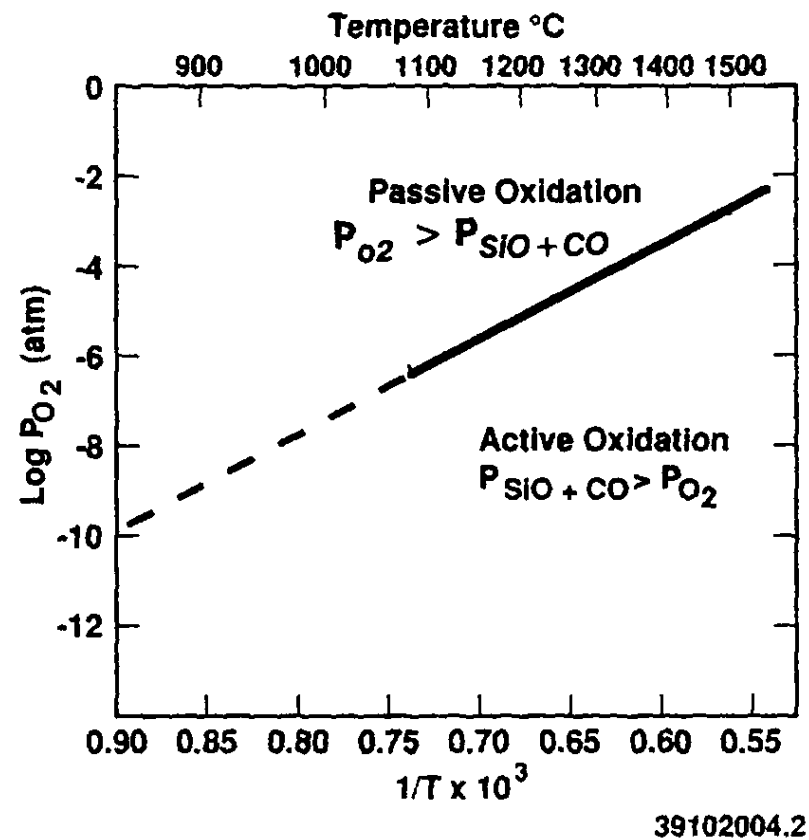
- **Oxygen**: Will be transported from all refractories to lithium (except for yttrium, hafnium, and zirconium)
- **Carbon**: All metals (except for Mo and W) will be a sink for carbon.
- **Nitrogen**: All metals (except for Mo and W) will getter nitrogen.

COMPATIBILITY OF SiC/SiC COMPOSITES WITH COOLANTS

Corrosion Reactions:



COMPATIBILITY OF SiC/SiC COMPOSITES WITH COOLANTS (cont.)



COMPATIBILITY OF SiC/SiC COMPOSITES WITH COOLANTS (cont.)

Experimental Observations

- For α -SiC exposed to a thin layer of Li (30-60min, $T < 500^\circ\text{C}$), RT fracture strength decreased from 350MPa to 150MPa, and fracture toughness from $4\text{MPa}\cdot\text{m}^{1/2}$ to $2\text{MPa}\cdot\text{m}^{1/2}$.
- Intergranular penetration and crack growth is a result of reduction of the protective SiO_2 glassy phase.
- Flowing Lithium will accelerate corrosion.
- SiC/SiC may not be compatible with lithium.

COMPATIBILITY OF SiC/SiC COMPOSITES WITH COOLANTS (cont.)

Molten Salt Effects on SiC/SiC


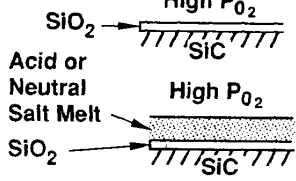
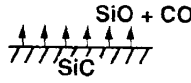
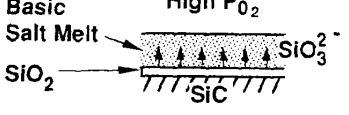
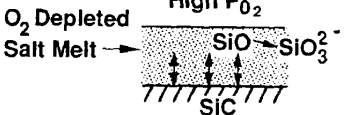
Environment	Reaction Mode	Effect
H_2 	No Reaction	No Material Loss Inert
High P_{O_2} SiO_2 → Acid or Neutral Salt Melt → High P_{O_2} SiO_2 → 	Passivation	Forms Protective SiO_2 Scale, Almost Inert to Salt Melt
Low P_{O_2} 	"Active" Oxidation	Evolution of $SiO(g)$ and $CO(g)$ at SiC Surface
Basic Salt Melt → High P_{O_2} SiO_2 → 	Accelerated Corrosion	Formation of Soluble Ionic Species
O_2 Depleted Salt Melt → High P_{O_2} 	Gasification and Active Corrosion	Formation of SiO , SiO_2 Scale Absent or Ruptured, Silicate Formation in Melt

Figure 4. Possible modes of behavior of SiC in gas-molten-salt environments.

COMPATIBILITY OF SiC/SiC COMPOSITES WITH COOLANTS (cont.)

Molten Salt Effects on SiC/SiC (cont.)

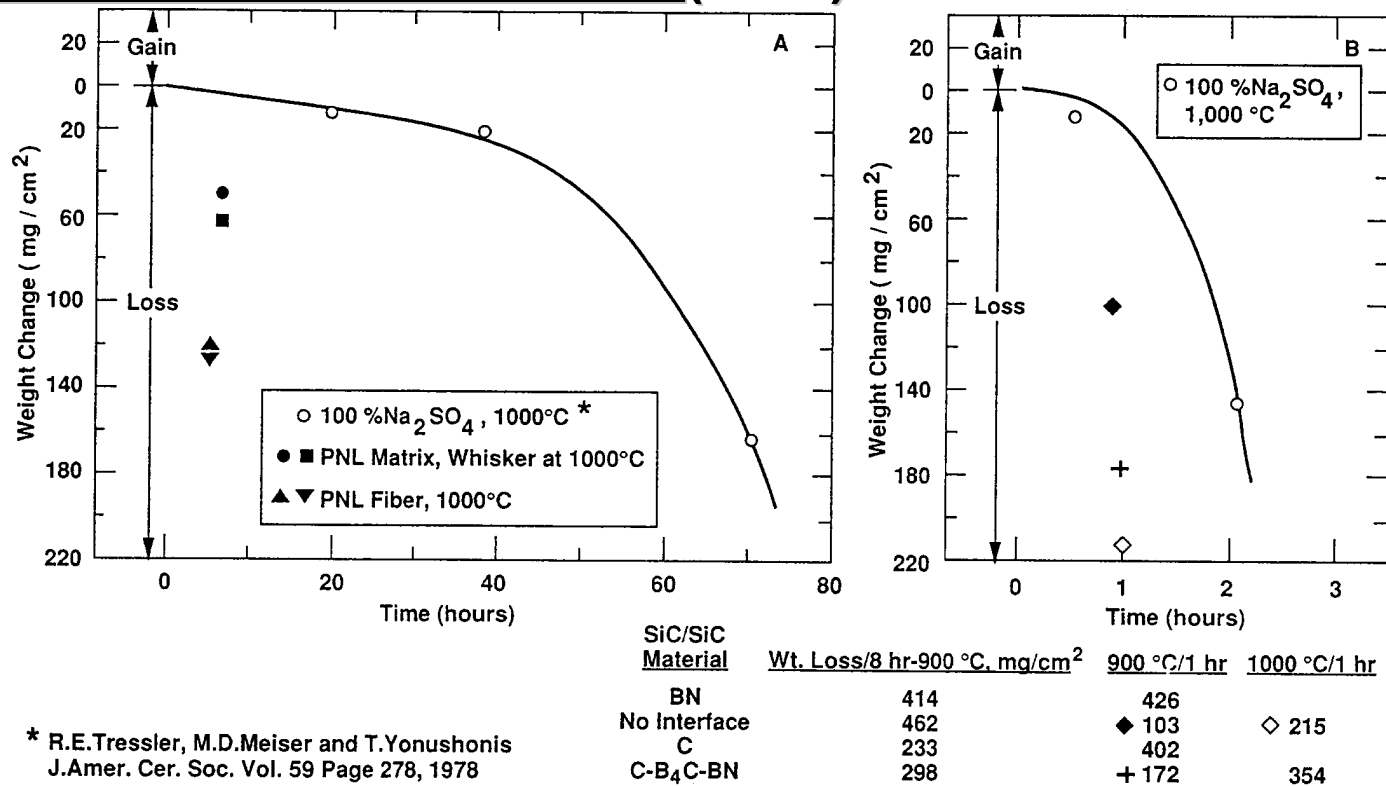
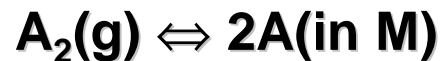


Figure 6. Molten salt corrosion data for a) monolithic Si₃N₄ (PNL data) and b) monolithic SiC (Tressler et al.) and SiC/SiC composites (PNL data).

COMPATIBILITY OF REFRACTORY METALS WITH NON-METALLIC IMPURITIES

1. Hydrogen and Nitrogen Reactions



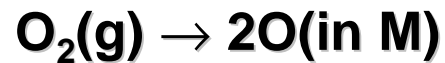
$$\text{Equilibrium} \Rightarrow K_p = \frac{a}{\sqrt{P_{A_2}}} = e^{\left[\frac{\Delta G_s^o}{RT} \right]}$$

**K_p = equilibrium constant, a = activity.
For dilute solutions \Rightarrow Sievert's Law:**

$$X_A = K_p \sqrt{P_{A_2}} = \sqrt{P_{A_2}} e^{\left(\frac{\Delta S_s^o}{R} \right)} e^{\left(-\frac{\Delta H_s^o}{RT} \right)}$$

COMPATIBILITY OF REFRACTORY METALS WITH NON-METALLIC IMPURITIES (cont.)

2. Oxygen



[absorption]



[desorption]

$$X_o = (KP_{\text{O}_2})^{\frac{1}{n}} = \left[K_o P_{\text{O}_2} e^{\left(-\frac{\Delta Q}{RT} \right)} \right]^{\frac{1}{n}}$$

$$K_o = \frac{K_{abs}}{K_{des}},$$

$$\Delta Q = Q_{abs} - Q_{des}$$

COMPATIBILITY OF REFRACTORY METALS WITH NON-METALLIC IMPURITIES (cont.)

3. Compound Formation

Gas/metal: $1/2A_2(g) + (m/n)*M(s) \Leftrightarrow (1/n)*M_mA_n(s)$

Saturated solution: $A(\text{in } M) + (m/n)*M(s) \Leftrightarrow (1/n)*M_mA_n(s)$

$$K = \frac{1}{X_{A,\max}} = e^{\left(\frac{\Delta G_f^o}{RT} \right)}$$

$X_{A,\max}$ = maximum solid solubility

$\Delta G_f^o = \Delta H_f^o - T\Delta S_f^o$ = Formation energy

COMPATIBILITY OF REFRACTORY METALS WITH NON-METALLIC IMPURITIES (cont.)

ΔH_s° and ΔH_f° Values in kJ/(g·atom) for Solution of H, N, and O in Solid Refractory Metals or Formation of the Corresponding Metal-Rich Compounds with H, N, O and C.*

Metal	<u>Hydrogen</u>		<u>Nitrogen</u>		<u>Oxygen</u>		<u>Carbon</u>
	ΔH_s°	ΔH_f°	ΔH_s°	ΔH_f°	ΔH_s°	ΔH_f°	ΔH_f°
α -Zr	-59.5	-95.3		-364	-619	-541	-185
α -Hf	-37.6	-65.5		-369	-552	-553	
V	-32.4	-41.5		-282	-422	-432	-147
Nb	-39.6		-178	-272	-386	-418	-159
Ta	-36.4		-182	-204	-383	-402	-126
Mo	52.2		95	-57		-288	-49
W	100.4		195				-27

*References:

7. E. Fromm and E. Gebhardt, eds., *Gase und Kohlenstoff in Metallen*, (Berlin, Springer, 1976)

8. H. Jehn, H. Speck, E. Fromm, W. Hehn and G. Hörz, "Gases and Carbon in Metals (Thermodynamics, Kinetics and Properties)," *Physics Data, Series 5*, Fachinformationszentrum Energie, Physik, Mathematik, Karlsruhe; "Pt. V, GroupIVa Metals (1), Titanium" [no.5-5 (1979), 78 pp.]; "Pt. VI, Group Iva Metals(2), Zirconium, Hafnium" [no5-6 (1979), 74pp.]; "Pt. VII, Group Va Metals(1), Vanadium" [no.5-7 (1981), 64pp.]; "Pt. VIII, Group Va Metals(2), Niobium" [no. 5-8 (1981), 117pp.]; "Pt. IX, Group Va Metals(3), Tantalum" [no. 5-9 (1981), 74pp.]; "Pt. X, Group Via Metals(1), Chromium, Tungsten" [no. 5-10(1980), 60pp.]; "Pt. XI, Group Via Metals(2) Molybdenum" [no. 5-11(1980) 51pp.]; and "Pt. XII, Group VIIa Metals, Manganese, Technetium, Rhenium" [no. 5-12(1981), 27pp.].

9. E. Fromm and G. Hörz, "Hydrogen, Nitrogen, Oxygen, and Carbon in Metals," *Intern. Met. Rev.*, Nos. 5 and 6, (1980), pp.269-311.

COMPATIBILITY OF REFRACTORY METALS WITH NON-METALLIC IMPURITIES (cont.)

Rate laws and Activation Energies of Nitrogen Absorption and Desorption for Nb, Ta, Mo and W.*

Metal	Rate Law	Q_{ab} (kJ/mol)	Q_{des} (kJ/mol)	Temperature (°C)
Nb	$v = kp_{N_2} - k'c_n^2$	67	519	1650-2100
Ta		68	562	1480-2730
Mo	$v = k(p_{N_2})^{1/2} - k'c_N$	189	95	1300-2400
W		287	92	>1400

*References:

10. G. Hörz, "Niob," in Ref. 7, pp.460-494.
11. G. Hörz, "Tantal," in Ref. 7, pp. 494-520.
12. H. Jehn, "Molybdän," in Ref. 7, pp. 534-551.
13. H. Jehn, "Wolfram," in Ref. 7, pp. 552-563.

COMPATIBILITY OF REFRACTORY METALS WITH NON-METALLIC IMPURITIES (cont.)

Rate laws and Activation Energies of Nitrogen Absorption or Desorption of Oxygen.*

Metal	Rate Law	Q_{ab} (kJ/mol)	Q_{des} (kJ/mol)	Temperature (°C)
V	$v_{ab} = (kp_{O_2})/(1+k'\exp(Q_{ab}/RT))$	73.1		1030-1430
V	$v_{des} = k'c_o$		572	>1500
Nb	$v_{des} = k'c_o + k''c_o^2$		543	>1700
Ta	$v_{des} = k'c_o + k''c_o^2$		553	>1700
Ta	$v_{ab} = kp_{O_2}(1-\theta)^2$ $v_{ab} = (1/(1+kc_o))^2$	~0		1000-1700

*References:

14. G. Hörz, "Vanadium," in Ref. 7, pp.441-460.

15. G. Hörz, H. Kanbach, R. Klaiss and H. Vetter, "Influence of the Surface State on the Reactions of Transition Metals with Nitrogen, Oxygen and Hydrocarbons," *Proc. 7th Intern. Vac. Congress and 3rd Intern. Conf. On Solid Surf.*, Vienna, (1977), pp. 999-1002.

COMPATIBILITY OF REFRACTORY METALS WITH NON-METALLIC IMPURITIES (cont.)

Values of ΔQ and K_o Determining the Steady-State Relations for the Reaction Systems of Nb and Ta with O_2 and H_2O .*

<u>System</u>	<u>Nb-O</u>	<u>Nb-H₂O</u>	<u>Ta-O</u>	<u>Ta-H₂O</u>
ΔQ (kJ/mol)	502	480	560	530
K_o (at. %•Pa)	9.1×10^{-10}	1.5×10^{-10}	1.35×10^{-10}	6.4×10^{-10}

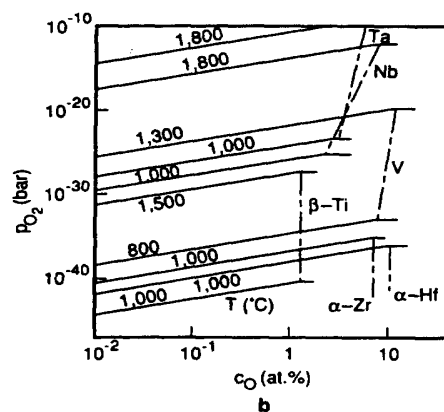
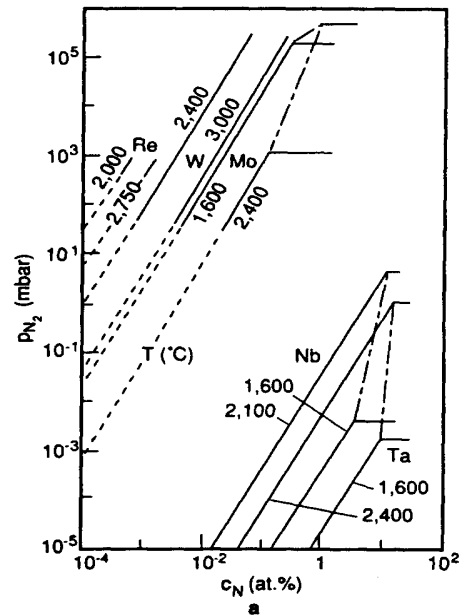
*References:

16. G. Hörz, "Kinetik und Mechanismen," in Ref. 7, pp.1-83.

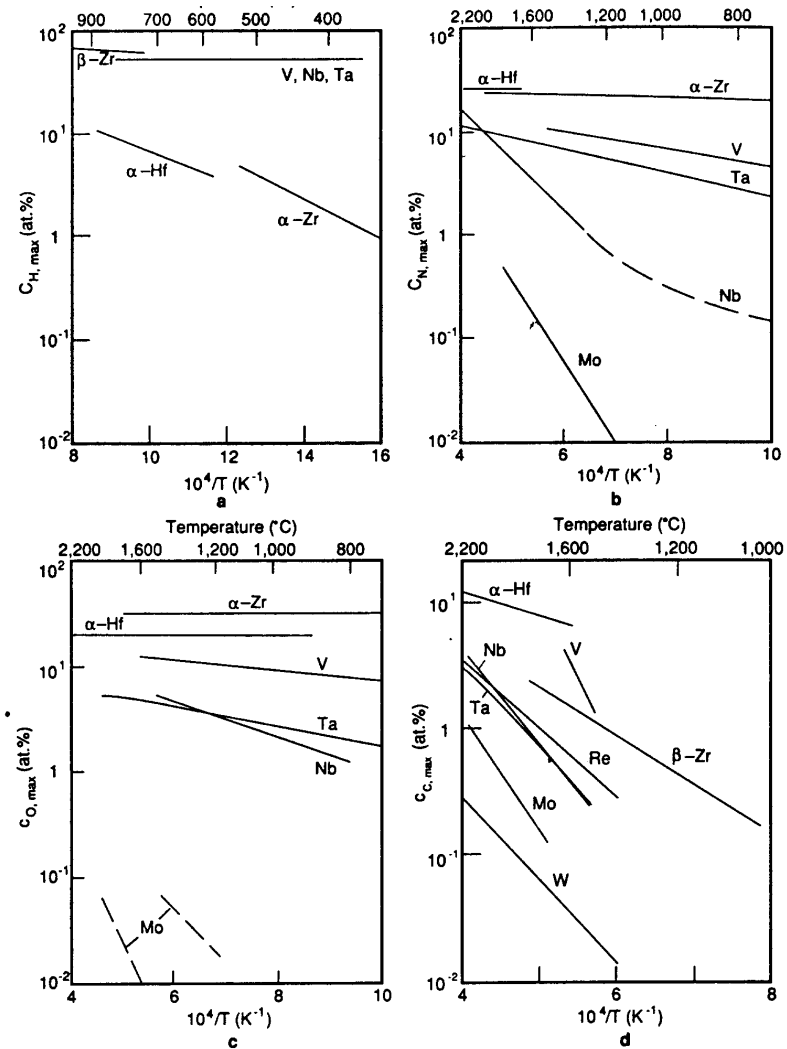
17. H. Jehn, "Vorgänge beim Glühen der Via- und Va- Metalle in Sauerstoff, Luft und Wasserdampf bei niedrigen Drücken," *Metall*, 28 (1974), pp. 699-705.

18. K. Schulze and H. Jehn, "Behaviour of Niobium and Tantalum at High Temperatures in Low-Pressure Oxygen-Containing Atmospheres," Proc. 8th Intern. Vacuum Congress, Cannes, France (1980), Vol. II, pp. 554-557.

COMPATIBILITY OF REFRACTORY METALS WITH NON-METALLIC IMPURITIES (cont.)



COMPATIBILITY OF REFRACTORY METALS WITH NON-METALLIC IMPURITIES (cont.)



COMPATIBILITY OF REFRACTORY METALS WITH NON-METALLIC IMPURITIES (cont.)

Experimental Observations and Conclusions

- Nb and Ta show high nitrogen solubilities (between 0.1 and 10 at %) at low pressures (10^{-4} - 10^{-3} bar).
- Nitrogen solution is exothermic (concentration decreases with temperature) for Nb, Ta, and V. It is endothermic for W and Mo, with very low solubilities.
- At extremely low oxygen pressures (10^{-40} - 10^{-10} bars), the solubility limit of (3-10 at %) is reached in Ta, Nb, and V.
- General Trend \Rightarrow Interstitial solubilities decrease in the order: IV A > V A > VI A.
- Because of the embrittlement effects of the interstitial impurities at low concentrations (10's ppm), severe restrictions are expected for helium-cooled systems.

COMPATIBILITY OF REFRACTORY METALS WITH NON-METALLIC IMPURITIES (cont.)

Recommended Maximum Interstitial Impurity Limits for Helium-Cooled Refractory Piping

Metal Group		C		N		O	
		Solubility Limit ($T_m/2$)	Maximum for 50 °C shift	Solubility Limit ($T_m/2$)	Maximum for 50 °C shift	Solubility Limit ($T_m/2$)	Maximum for 50 °C shift
V A	V, Nb, Ta	~10,000 wppm	~10,000 wppm	~8%	~4,000 wppm	10%	~2,000wppm
VI A	Cr, Mo, W	~10,000 wppm	~200 wpp,	0.10%	~150 wppm	0.10%	~100wppm

⇒ **Note that the most stringent control has to be on oxygen impurities at a level of less than 100wppm.**

ESTIMATED UPPER TEMPERATURE LIMITS ON THE BASIS OF COMPATIBILITY

