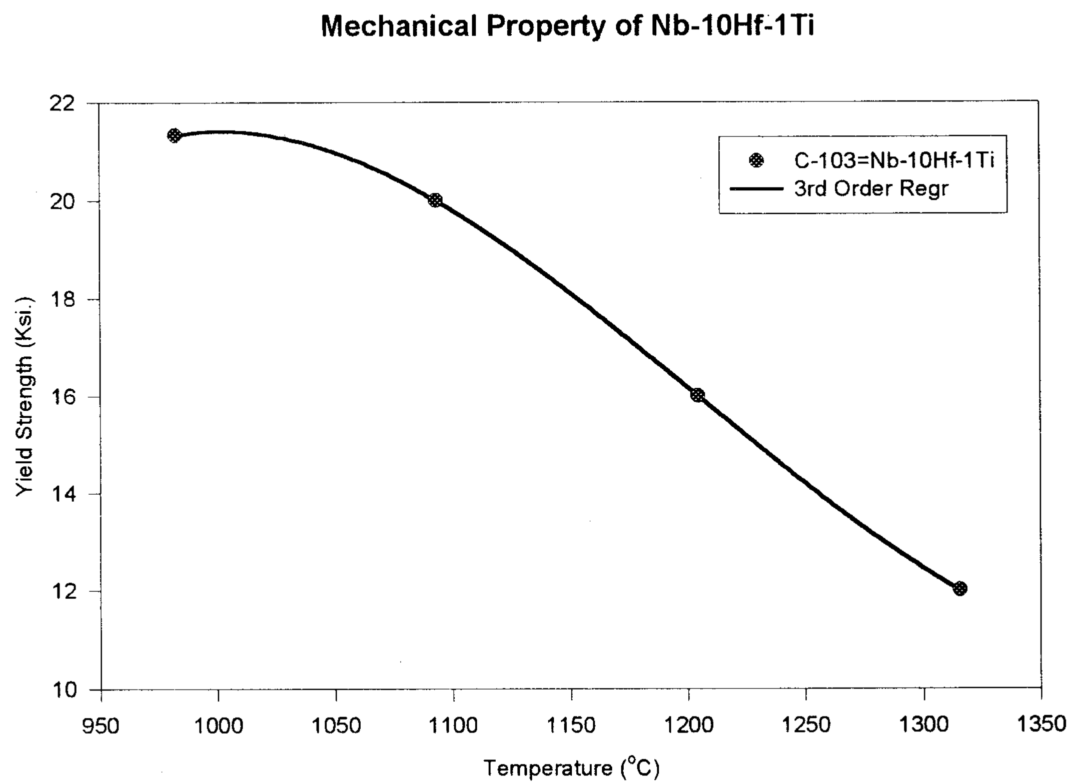
Assessment of High-Temperature Refractory Metals

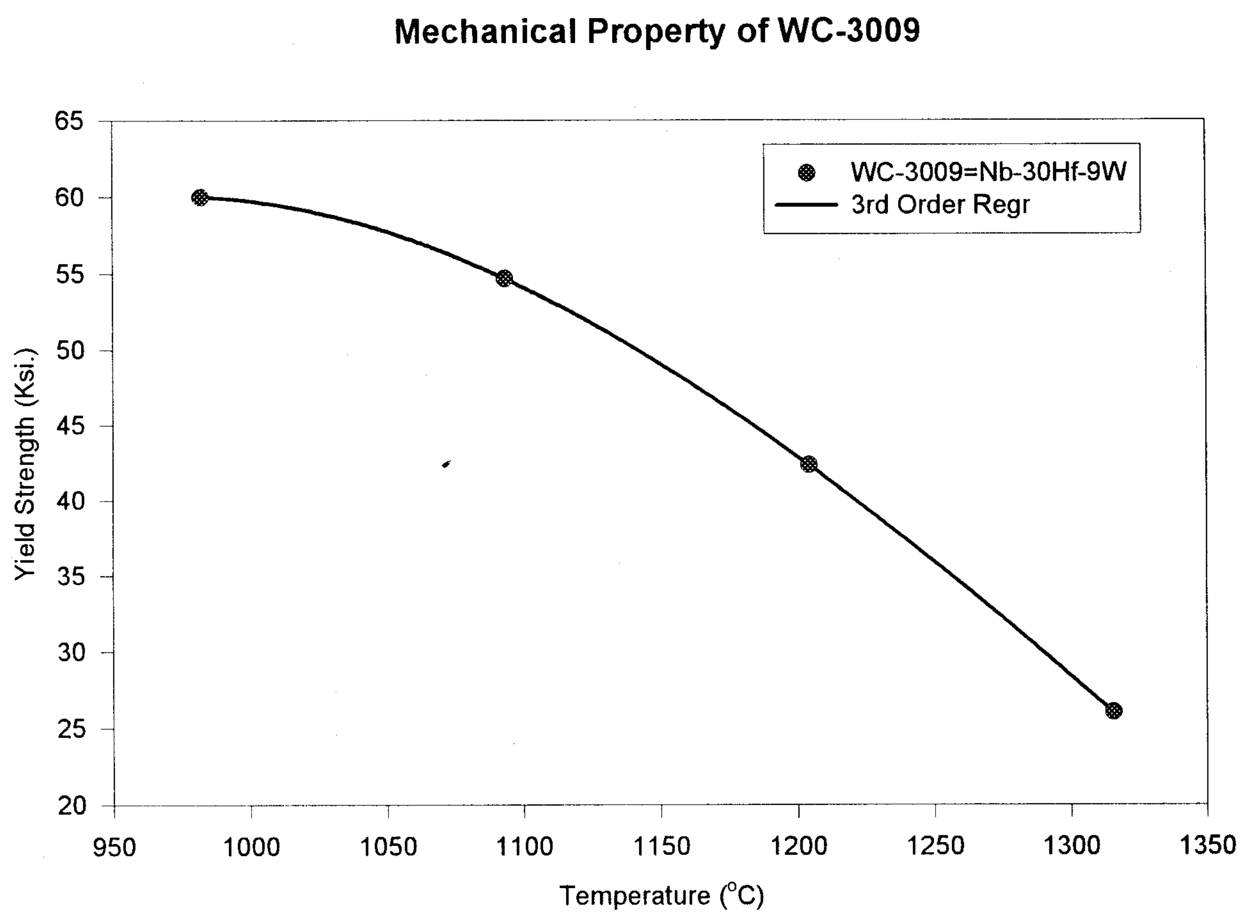
Nasr M. Ghoniem
Mechanical and Aerospace Engineering Department
University of California at Los Angeles (UCLA)

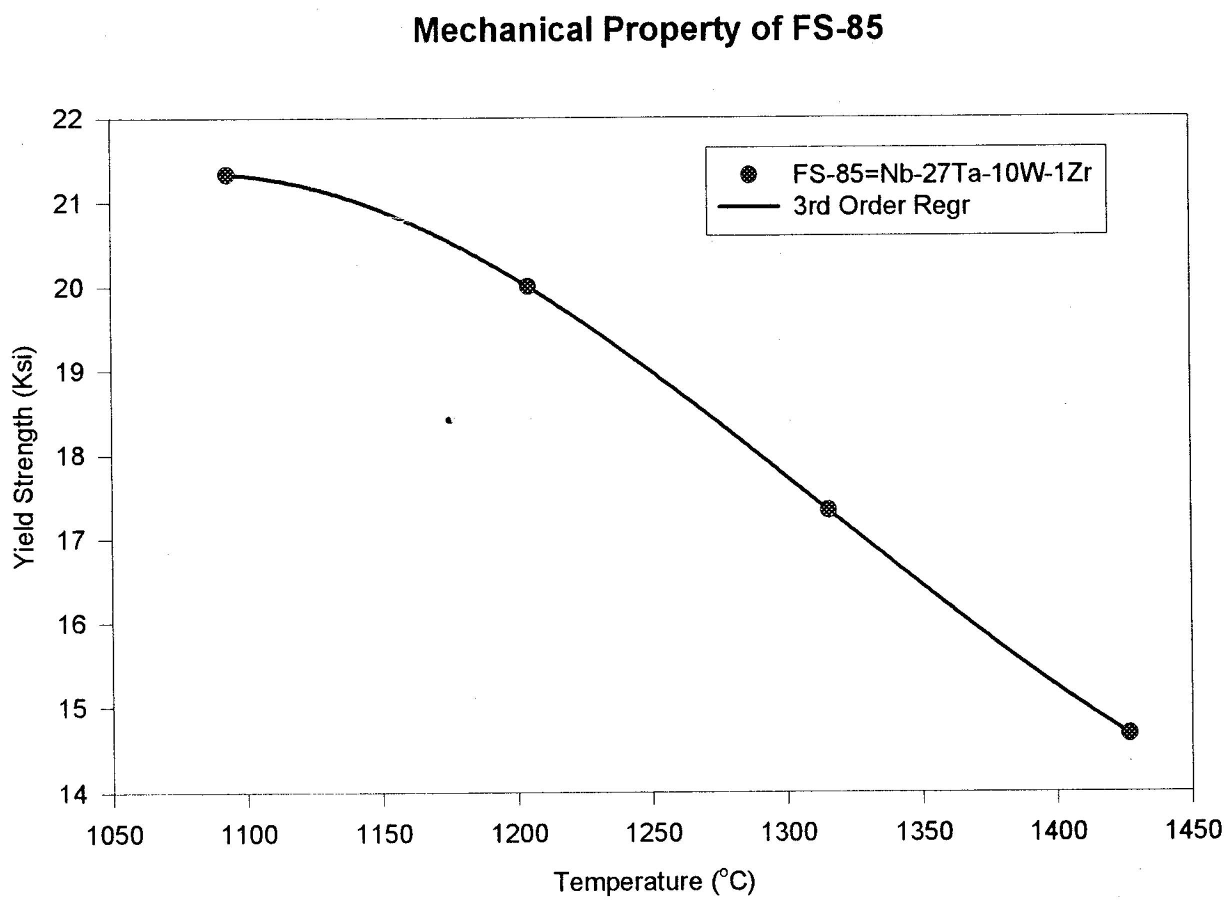
OUTLINE

1. High Temperature Refractory Materials
2. Properties of Niobium and its Alloys (Z=41, $[Kr]5s^1 4d^4$)
3. Properties of Molybdenum and its Alloys (Z=42, $[Kr]5s^1 4d^5$)
4. Properties of Tantalum and its Alloys (Z=73, $[Xe]6s^2 4f^{14} 5d^3$)
5. Properties of Tungsten and its Alloys (Z=74, $[Xe]6s^2 4f^{14} 5d^4$)
6. Properties of Rhenium and its Alloys (Z=75, $[Xe]6s^2 4f^{14} 5d^5$)
7. Comparisons with conventional Alloys, including Cost.
8. Nickel-Bearing Alloys
9. Compatibility with Lithium and Interstitial Elements.
10. Conclusions.

2.2. Selected Niobium Alloys

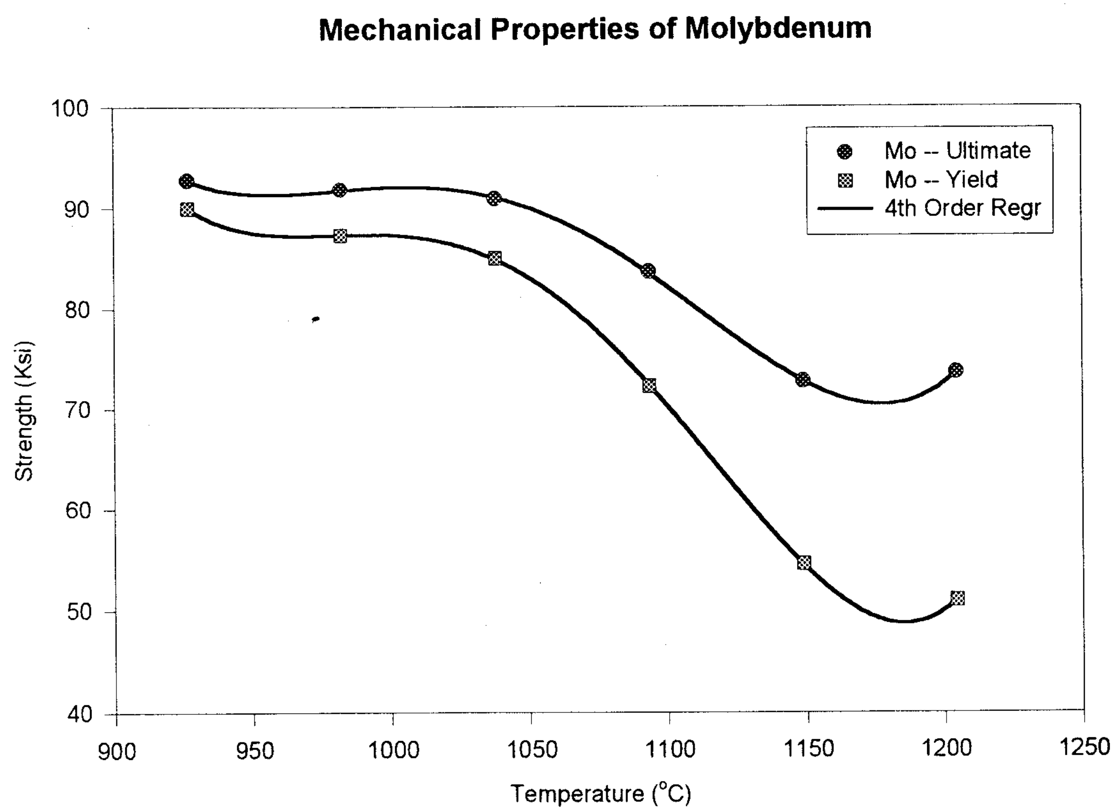



Mechanical Property of WC-3009
WC-3009=Nb-30Hf-9W
3rd Order Regr
Yield Strength (Ksi.)
65
60
55
50
45
40
35
30
25
20
950
1000
1050
1100
1150
1200
1250
1300
1350
Temperature (°C)


Mechanical Property of FS-85
Yield Strength (Ksi)
Temperature (°C)
FS-85=Nb-27Ta-10W-1Zr
3rd Order Regr
22
21
20
19
18
17
16
15
14
1050
1100
1150
1200
1250
1300
1350
1400
1450

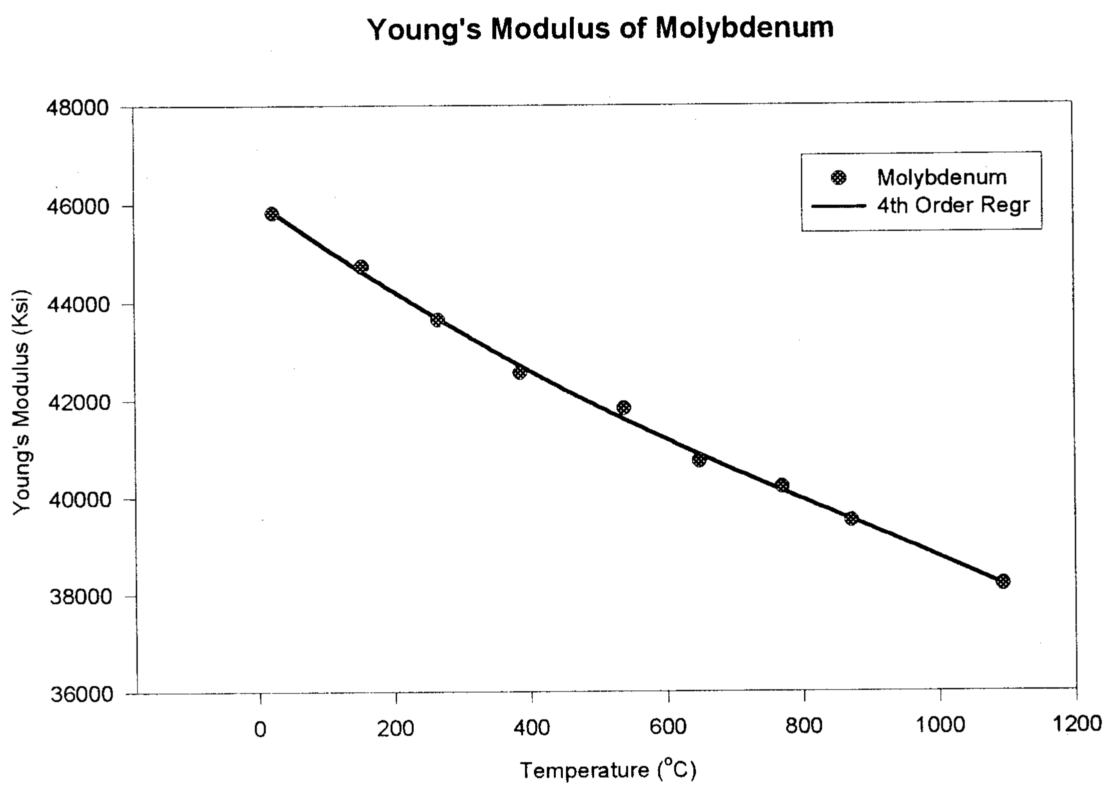
3. Properties of Molybdenum and its Alloys (Z=42, [Kr]$5s^1 4d^5$)

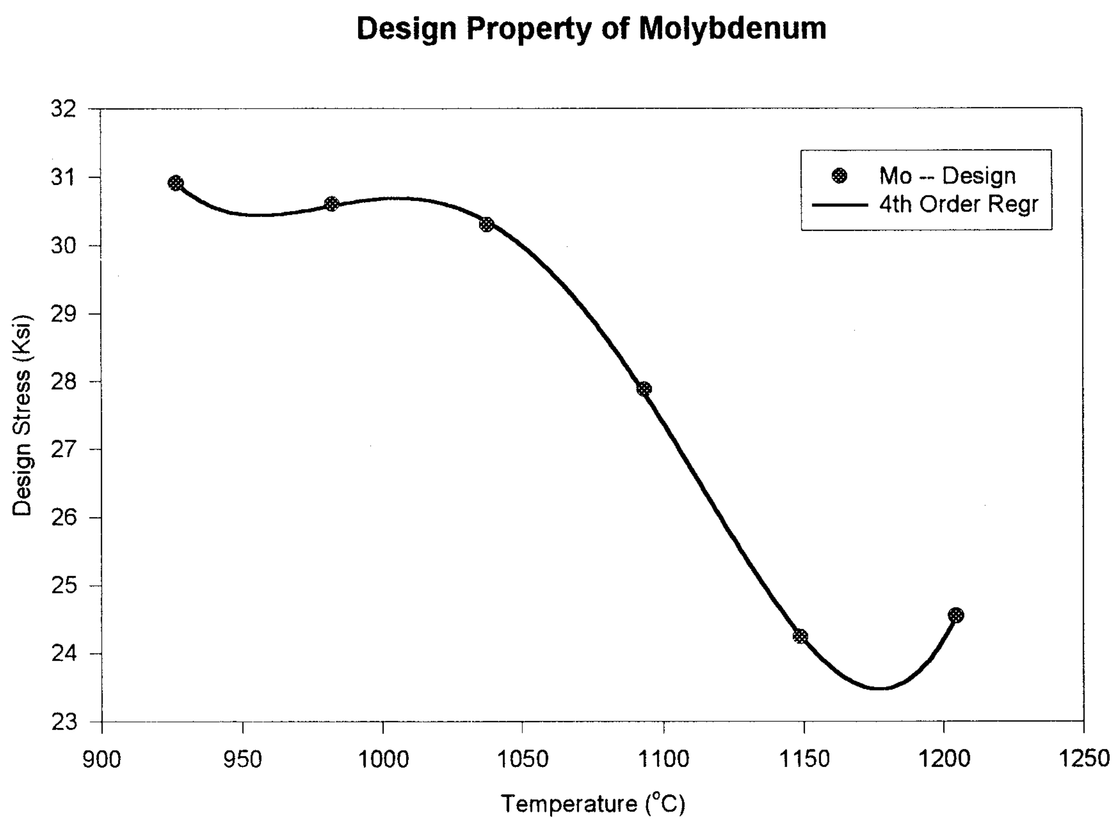
3.1. Pure Molybdenum



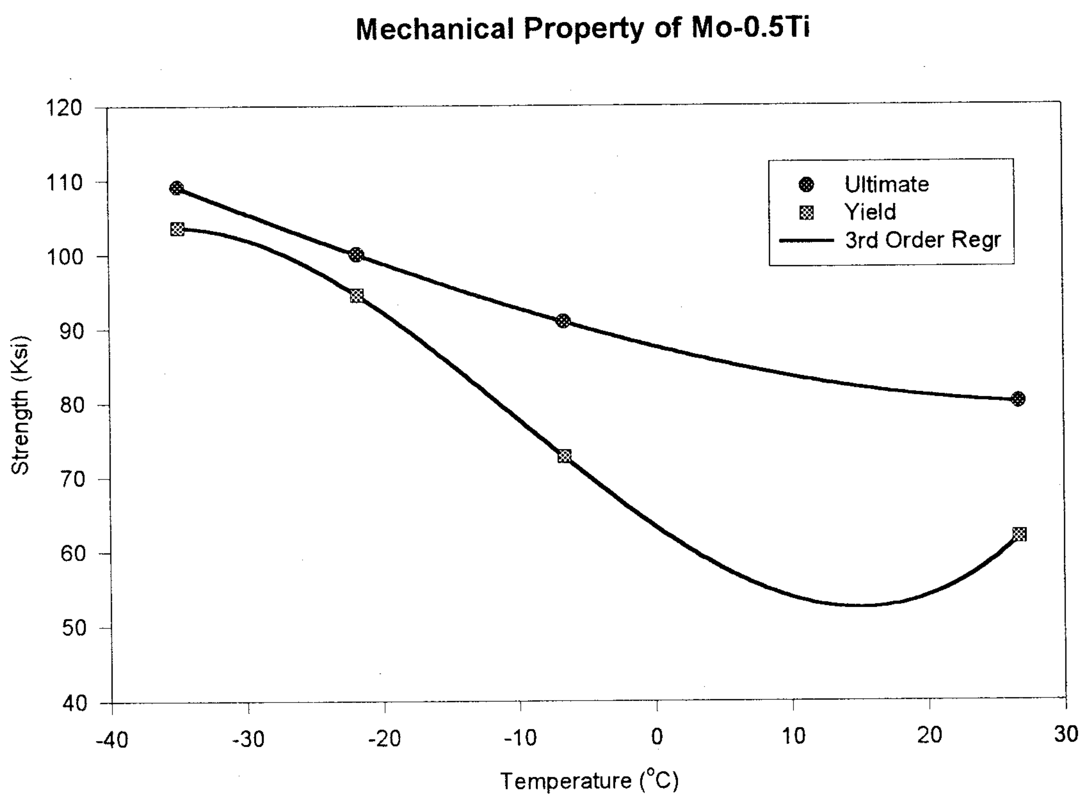
PHYSICAL PROPERTIES OF MOLYBDENUM

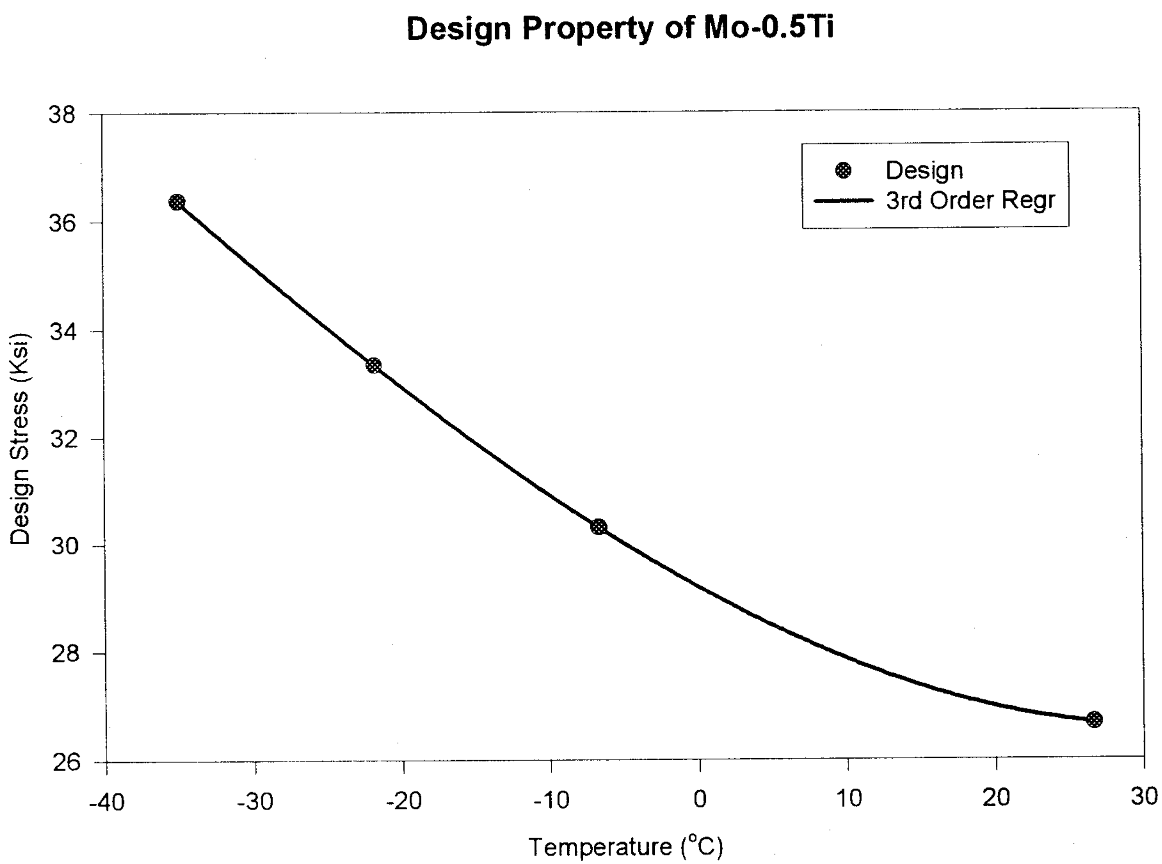
	Mo
Density (g/cm^3)	10.2
Melting Point (^oC)	2617
CTE ($ppm/^oC$)	4.8
Crystal structure	BCC
Thermal conductivity ($W/cm\ ^oC$)	1.4
Specific heat ($J/g\ ^oC$)	0.25


Young's Modulus of Molybdenum
Young's Modulus (Ksi)
48000
46000
44000
42000
40000
38000
36000
0
200
400
600
800
1000
1200
Temperature (°C)
Molybdenum
4th Order Regr


Design Property of Molybdenum
Mo -- Design
4th Order Regr
Design Stress (Ksi)
32
31
30
29
28
27
26
25
24
23
900
950
1000
1050
1100
1150
1200
1250
Temperature (°C)

3.2. Selected Molybdenum Alloys





Design Property of Mo-0.5Ti
Design
3rd Order Regr
Design Stress (Ksi)
38
36
34
32
30
28
26
-40
-30
-20
-10
0
10
20
30
Temperature (°C)

Mo-0.5Ti COMPOSITION

Nominal Composition (wt.%)

Source	Nominal
Tungsten	
Titanium	0.5
Molybdenum	Balance
Nickel	
Iron	0.05
Oxygen	0.005
Carbon	0.04
Nitrogen	
Hydrogen	
Silicon	0.005
Cobalt	
Hafnium	
Vanadium	
Tantalum	

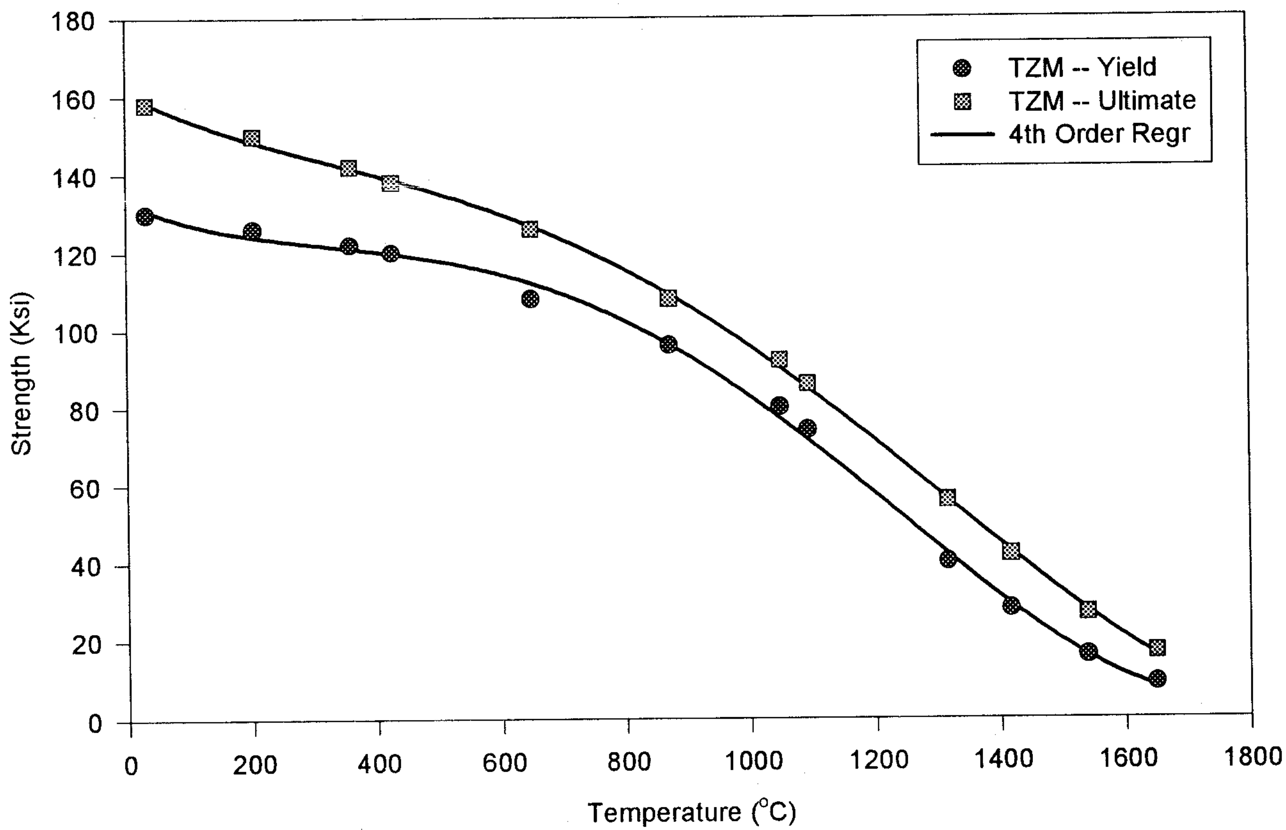
Commercial Designation: Mo-0.5Ti

1. Basic Properties of High-Temperature Materials

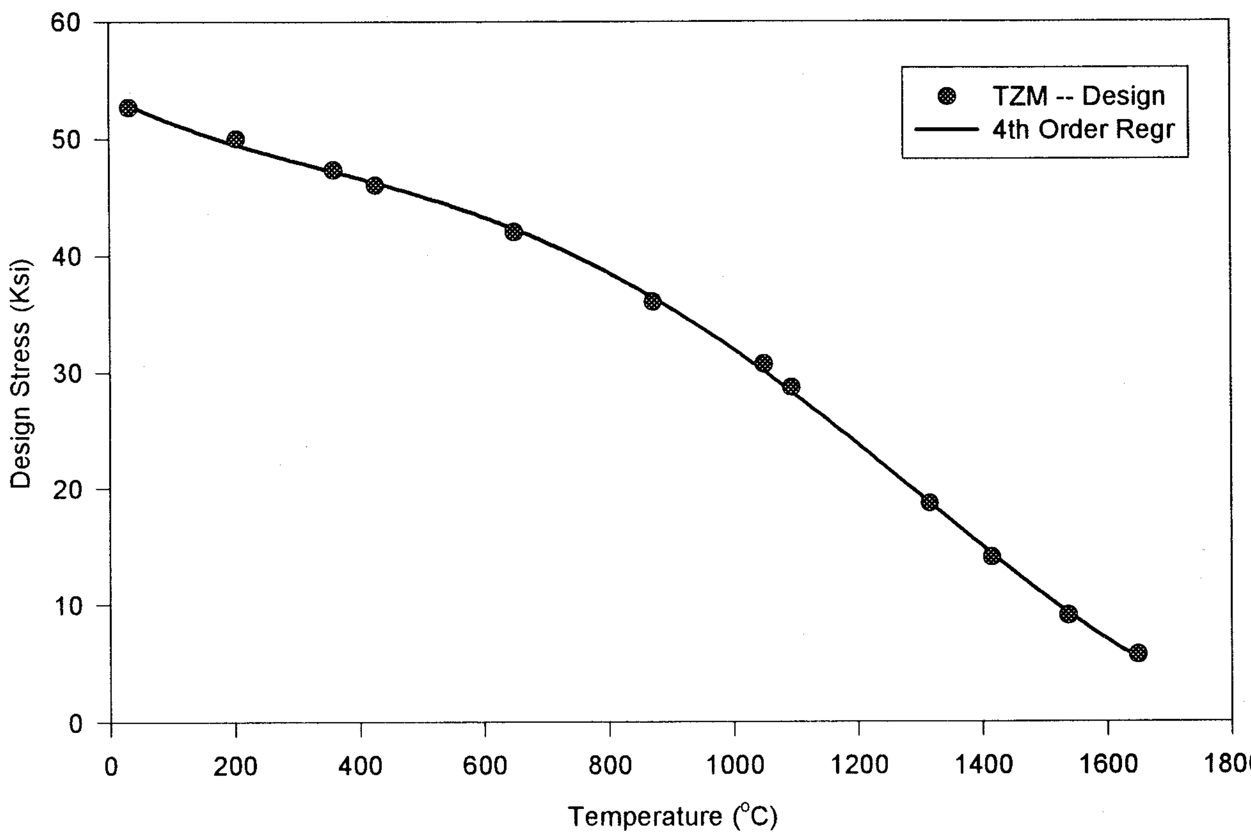
2.

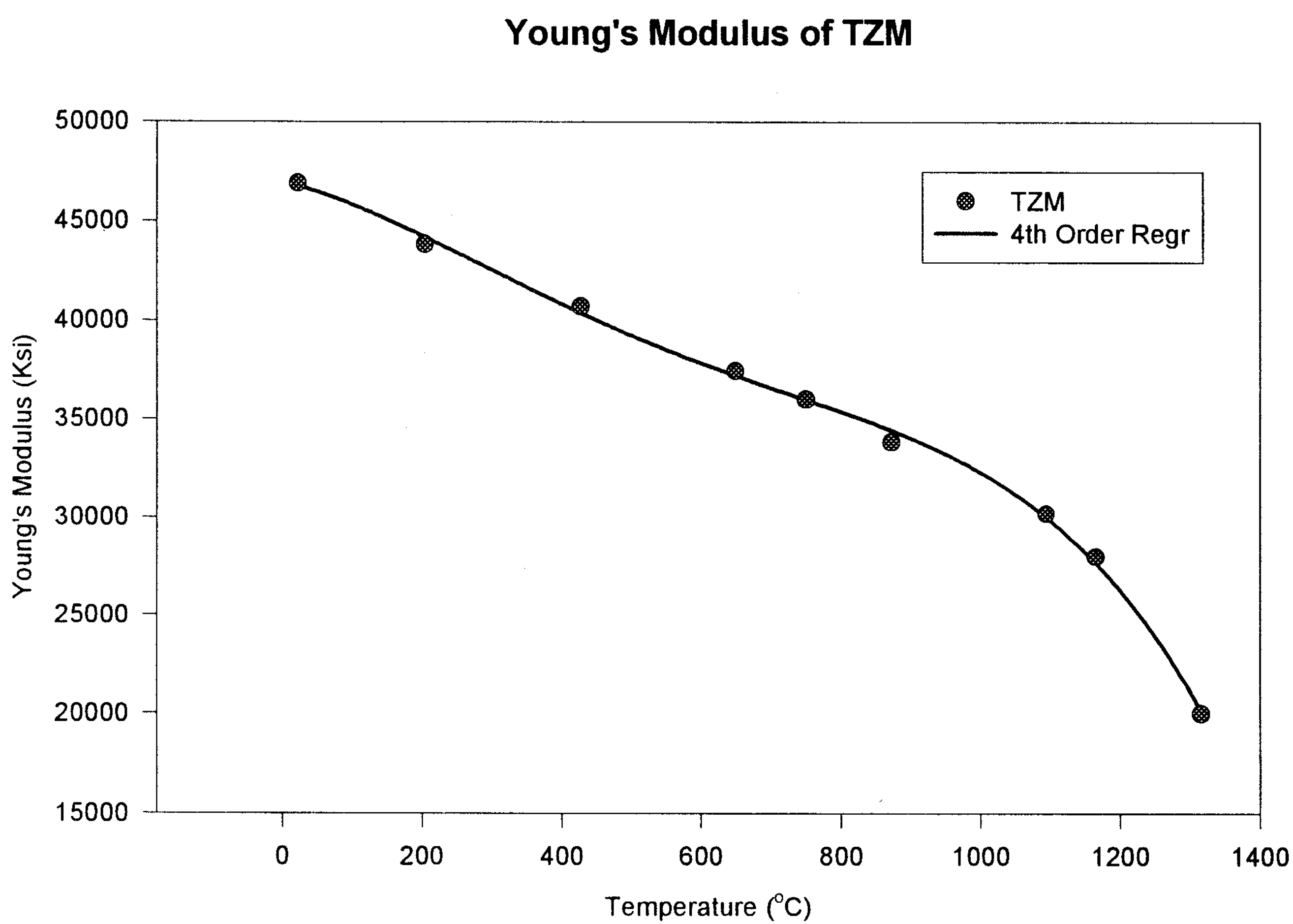
		Cr	Hf	Ir	Mo	Nb	Os	Pt	Re	Rh	Ru	Ta	V	W	Zr
Density (g/cm3)		7.2	13.1	22.4	10.2	8.55	22.4	21.4	21	12.4	12.2	16.6	6.1	19.3	6.5
Melting Point (oC)		1857	2227	2410	2617	2468	**3045**	1772	**3180**	1965	2310	**2996**	1890	**3410**	1852
CTE (ppm/°C)		4.9	5.9	6.4	4.8	7.3	5.1	8.8	6.2	8.2	6.4	6.3	8.4	4.5	5.7
Crystal Structure		BCC	HCP	FCC	BCC	BCC	HCP	FCC	HCP	FCC	HCP	BCC	BCC	BCC	HCP
Thermal Conductivity	(W/cm °C)	0.94	0.23	1.5	1.4	0.54	0.88	0.72	0.48	1.5	1.2	0.52	0.31	1.7	0.23
Specific Heat (J/g oC)		0.45	0.14	0.13	0.25	0.26	0.13	0.13	0.14	0.24	0.24	0.14	0.49	0.13	0.28
Electrical Resistivity (mW cm)		12.9	32	5.1	5.4	14.4	9.2	10.4	18.5	4.7	7.3	13.1	20	5.3	42
Spectral Emissivity	@ 0.65 mm		0.45	0.3	0.3	0.37		0.3	0.37	0.24		0.39		0.415	0.43
	and °C		[1727]	[20]	[2527]	[1730]		[20]	[2800]	[20]		[2500]		[2727]	[20]
	@ 20 oC		0.5	1.2	0.7 - 1.4	0.4 - 0.7		0.15	1.0 - 2.0	0.9		0.2 - 0.5		0.7 - 3.5	0.4 - 0.5

Mechanical Properties of TZM



Design Property of TZM




Young's Modulus of TZM
TZM
4th Order Regr
Young's Modulus (Ksi)
50000
45000
40000
35000
30000
25000
20000
15000
0
200
400
600
800
1000
1200
1400
Temperature (°C)

TZM COMPOSITION

Nominal Composition (wt.%)

Source	Nominal
Nickel	
Iron	
Oxygen	
Carbon	0.01
Nitrogen	
Hydrogen	
Silicon	
Titanium	0.4
Zirconium	0.06
Molybdenu	Balance

Commercial Designation: TZM = Mo-0.5Ti-0.08Zr

PHYSICAL PROPERTIES OF TZM

	TZM
Density (g/cm^3)	10.22
Melting Point (^{o}C)	2625
CTE (ppm/^{o}C)	3.6
Crystal structure	BCC
Thermal conductivity (W/cm ^{o}C)	1.4
Specific heat (J/g ^{o}C)	0.25

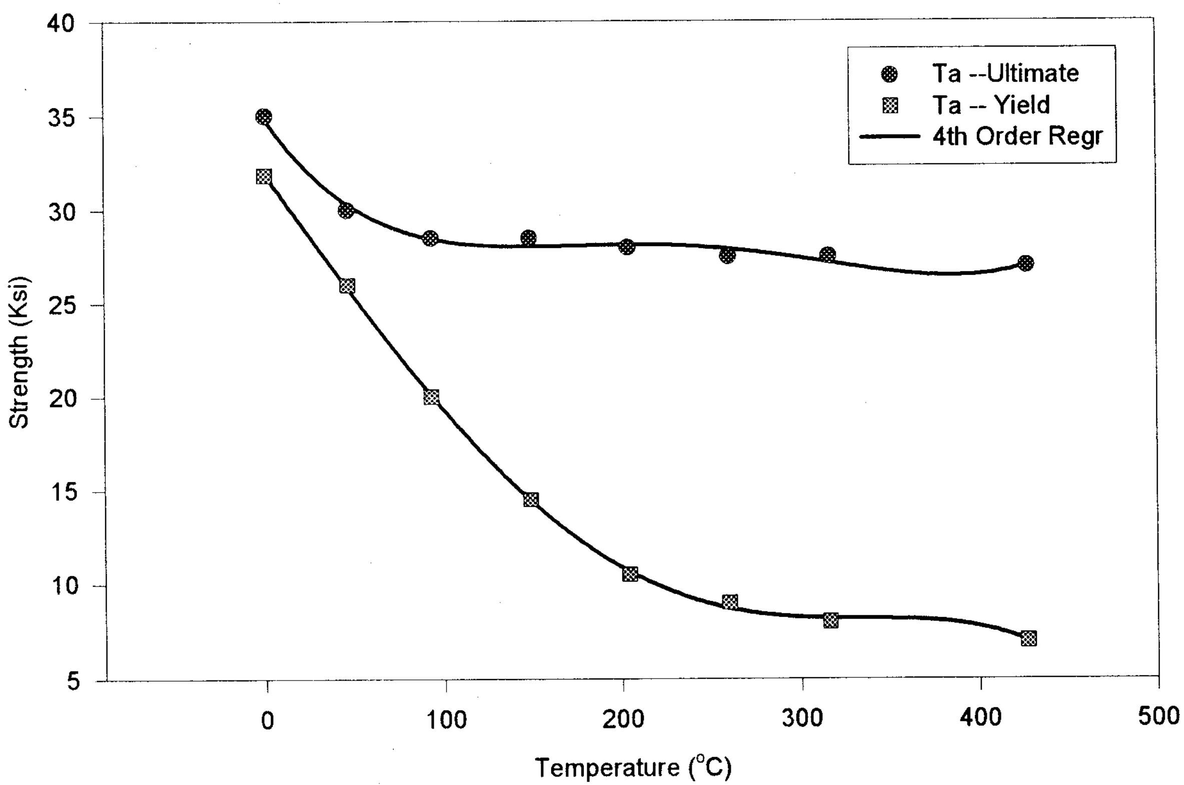
4. Properties of Tantalum and its Alloys (Z=73, [Xe]$6s^2 4f^{14} 5d^3$)

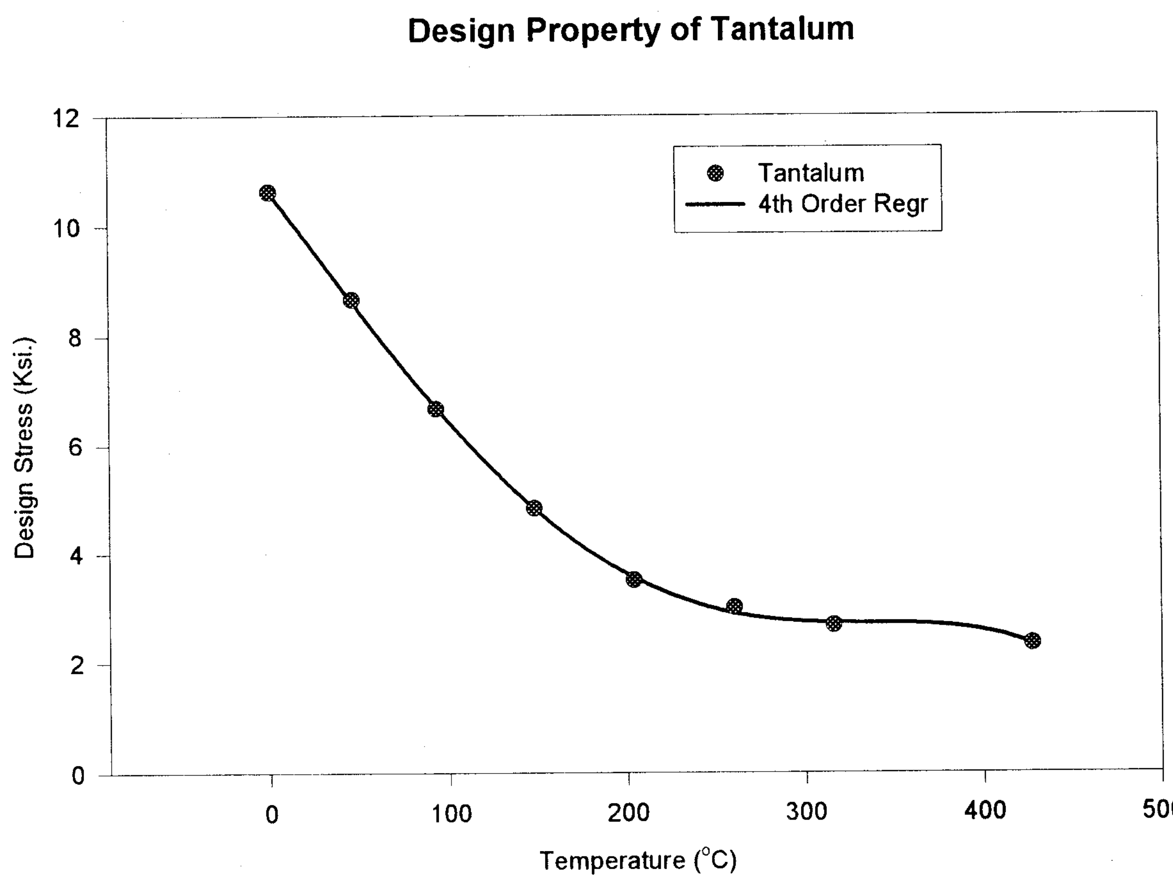
4.1. Pure Tantalum

PHYSICAL PROPERTIES OF TANTALU
M

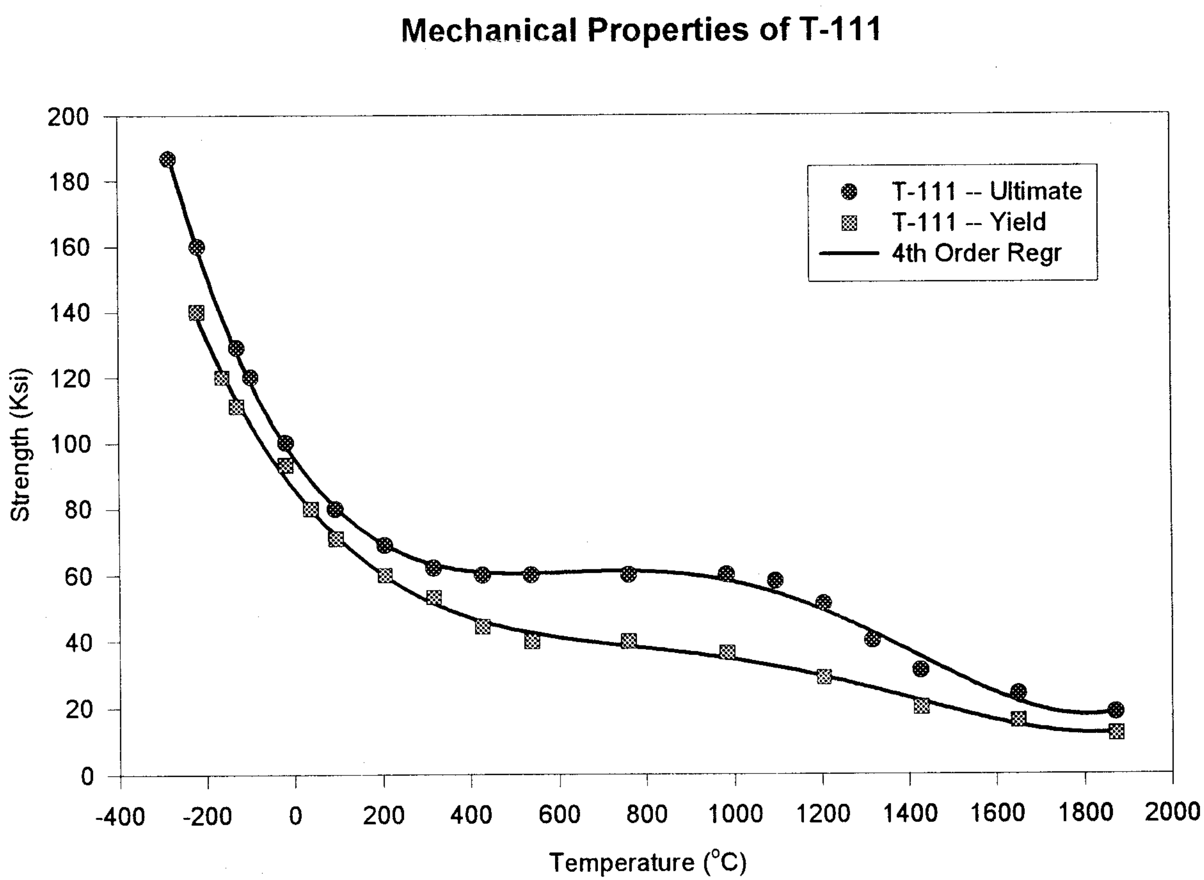
	Ta
Density (g/cm^3)	16.6
Melting Point (°C)	2996
CTE (ppm/°C)	6.3
Crystal structure	BCC
Thermal conductivity (W/cm °C)	0.52
Specific heat (J/g °C)	0.14

Mechanical Properties of Tantalum

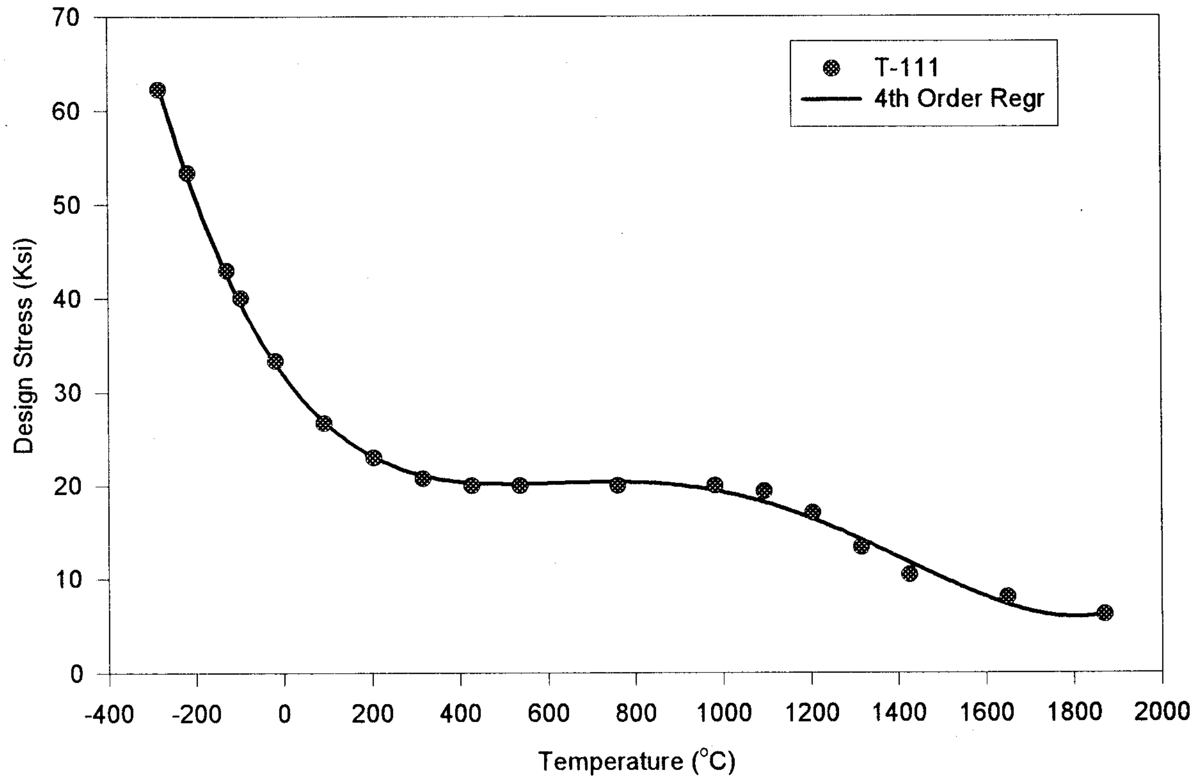



Design Property of Tantalum
Tantalum
4th Order Regr
Design Stress (Ksi.)
12
10
8
6
4
2
0
0
100
200
300
400
500
Temperature (°C)

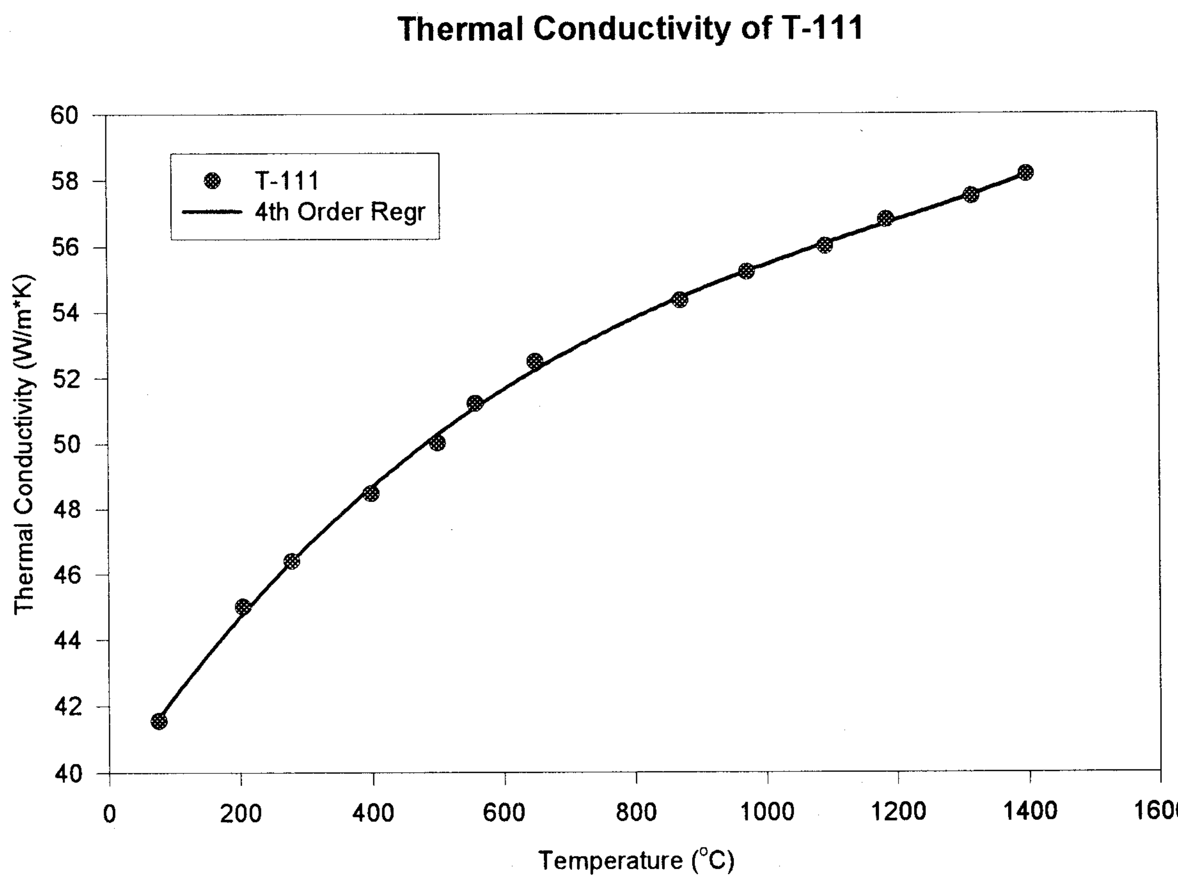
4.2. Selected Tantalum Alloys



Design Property of T-111



Tensile Strength (Gpa)			65	180	100 - 200	60 - 100		21	150 - 300	125		35 - 70		100 - 500	60 - 70
	@ 500 oC				0.2 - 0.5	0.3 - 0.5						0.2 - 0.3		0.5 - 1.4	
(Ksi)					35 - 65	40 - 75						25 - 45		75 - 200	
	@ 1000 oC				0.1 - 0.2	0.04 - 0.1			0.7			0.1		0.3 - 0.5	
					20 - 30	05 - 15			100			13 - 17		50 - 75	
	@ 20 oC	259	139	533	330	130	550	175	470	330	430	185	129	410	94
Young's Modulus (Gpa) (Msi)		38	20	77	48	19	80	25	68	48	62	27	19	60	14
	@ 500 oC				320	125			415			180		390	
					46	18			60			26		57	
	@ 1000 oC				280	110			360			170		365	
					41	16			52			25		53	
Recrystallization Temperature (oC)					900 - 1000	900 - 1250			1300 - 1500			1000 - 1200		1200 - 1400	
Stress Relief Temperature (oC)					800				1200			850		1100	

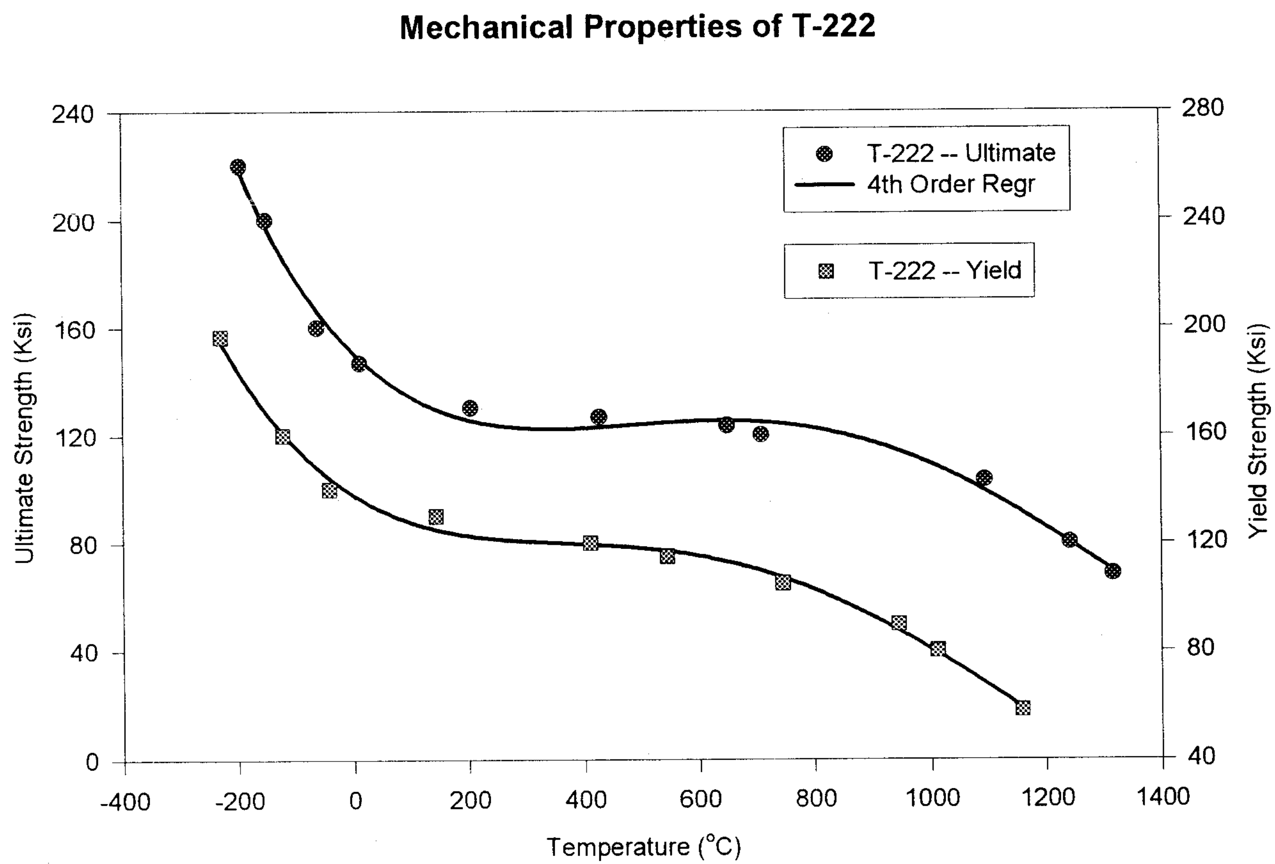

Thermal Conductivity of T-111
T-111
4th Order Regr
Thermal Conductivity (W/m*K)
Temperature (°C)
60
58
56
54
52
50
48
46
44
42
40
0
200
400
600
800
1000
1200
1400
1600

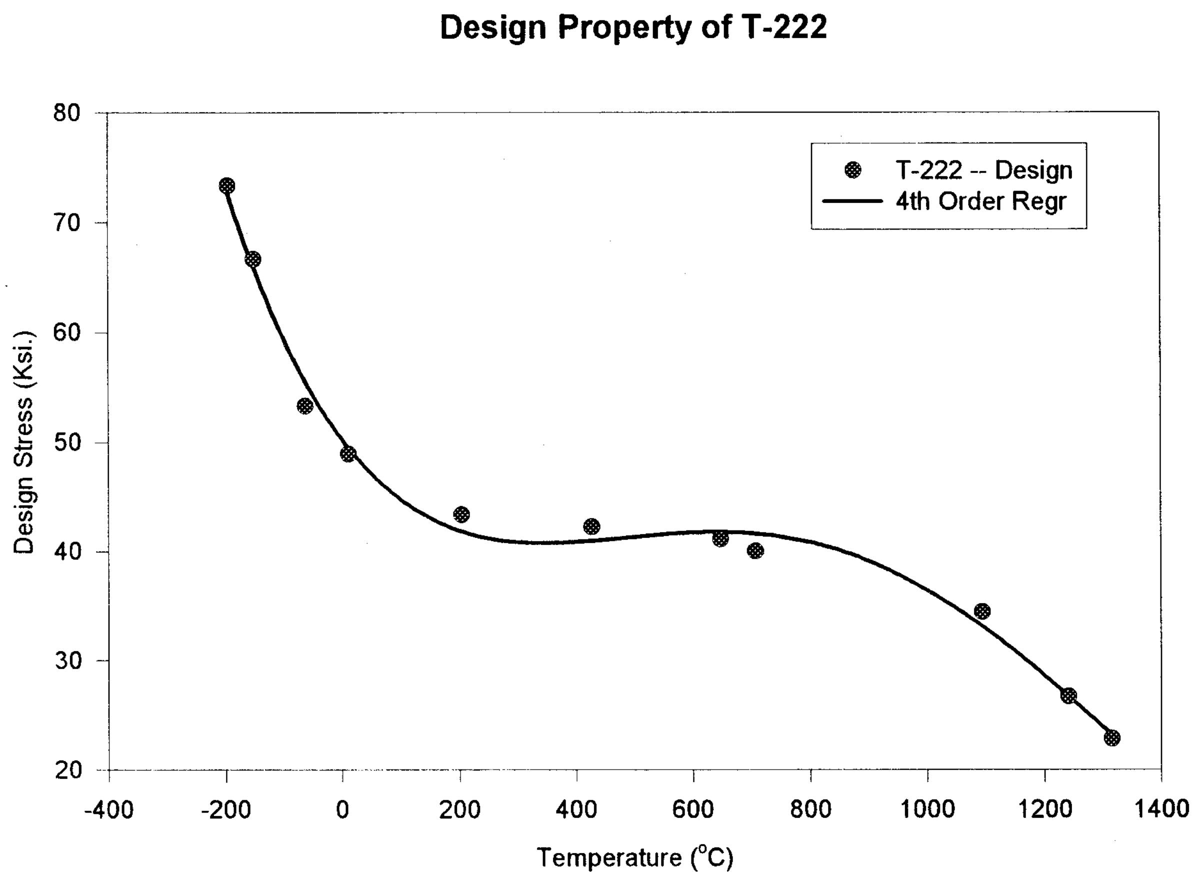
T-111 COMPOSITION

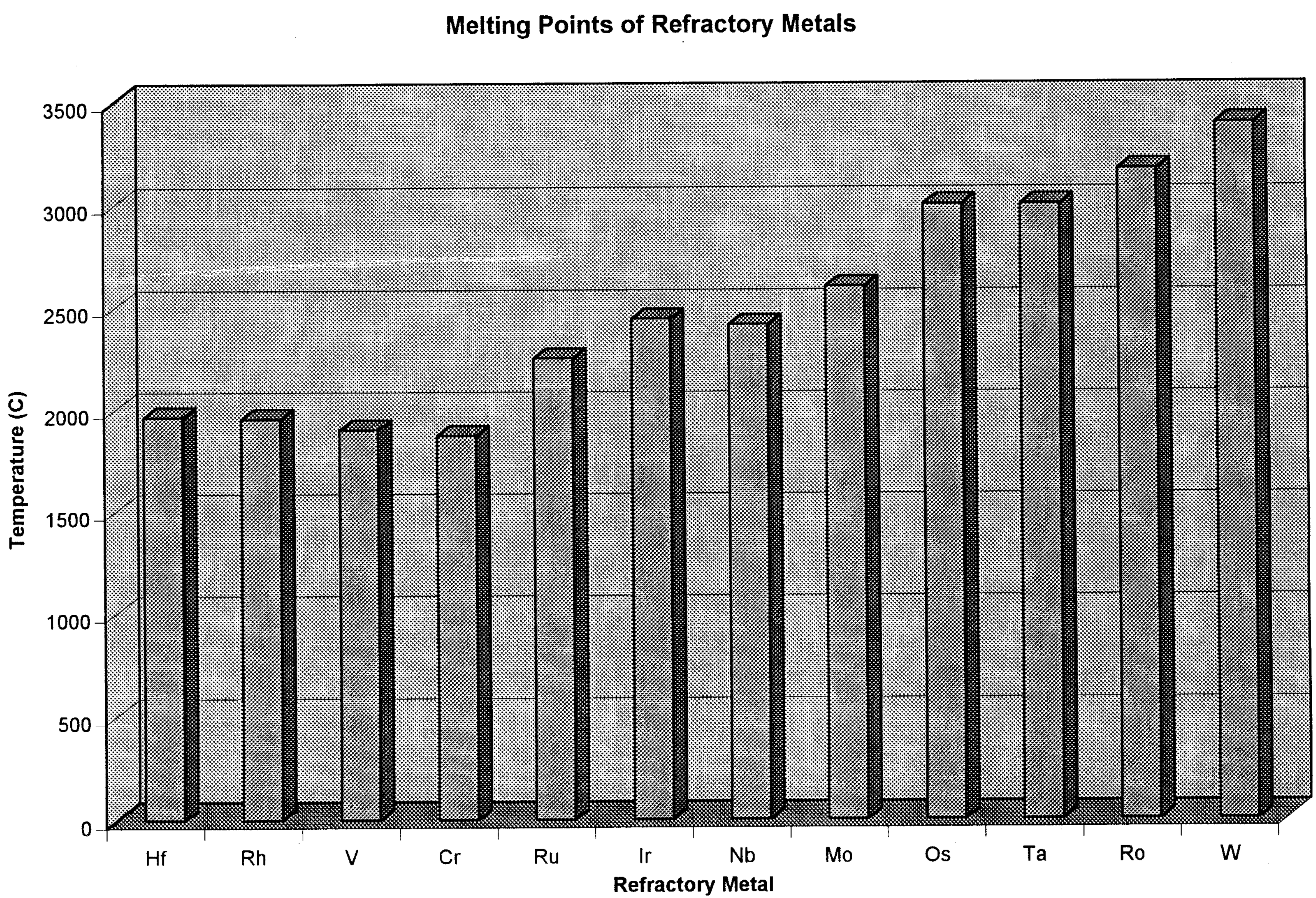
Nominal Composition (wt.%)

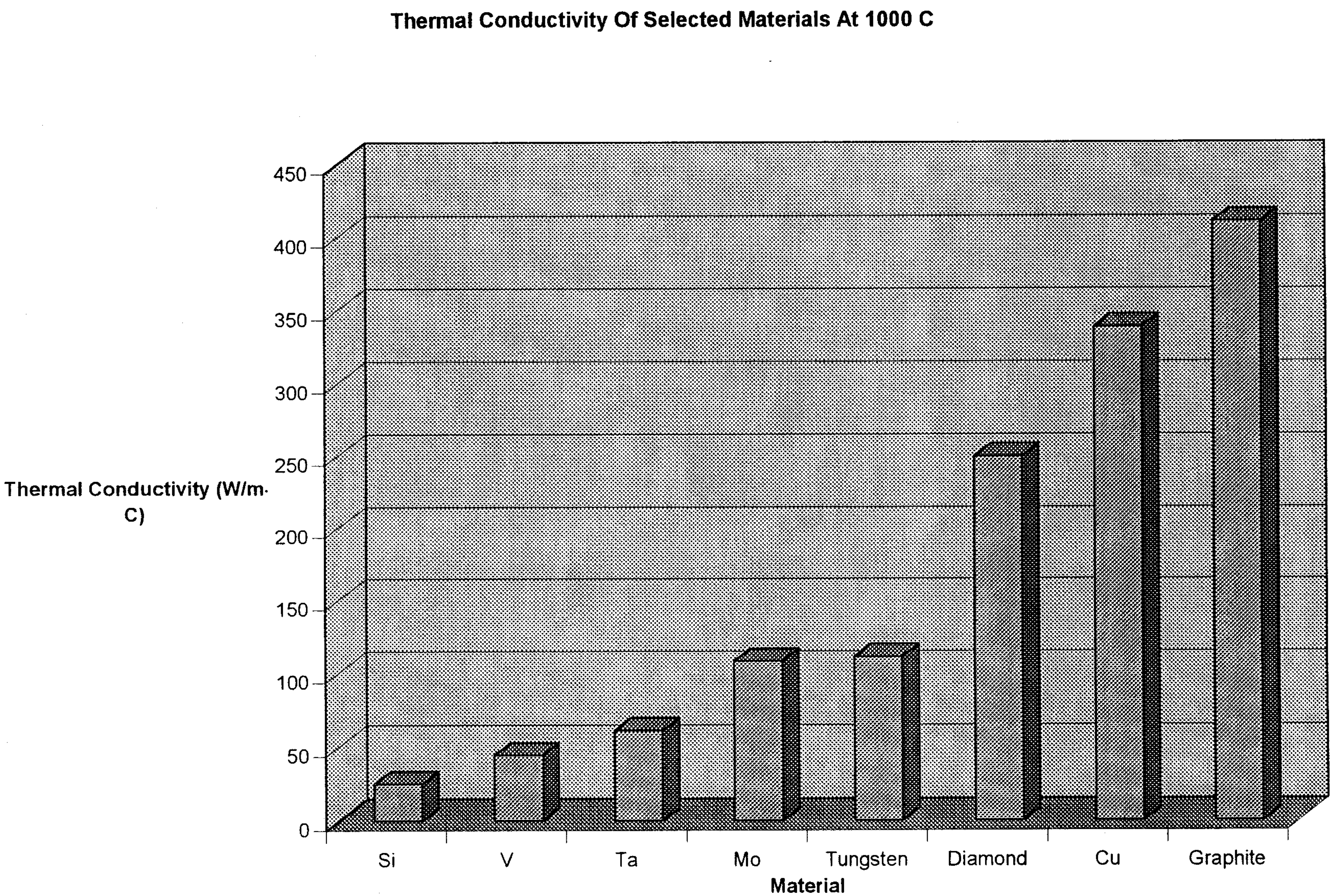
Source	Nominal
Tungsten	8
Columbium	0.1
Molybdenur	0.1
Nickel	
Iron	0.005
Oxygen	0.015
Carbon	0.005
Nitrogen	0.0075
Hydrogen	0.001
Chromium	0.02
Cobalt	0.005
Hafnium	2
Vanadium	0.002
Tantalum	Balance

Commercial Designation: T-111 = Ta-8W-2Hf

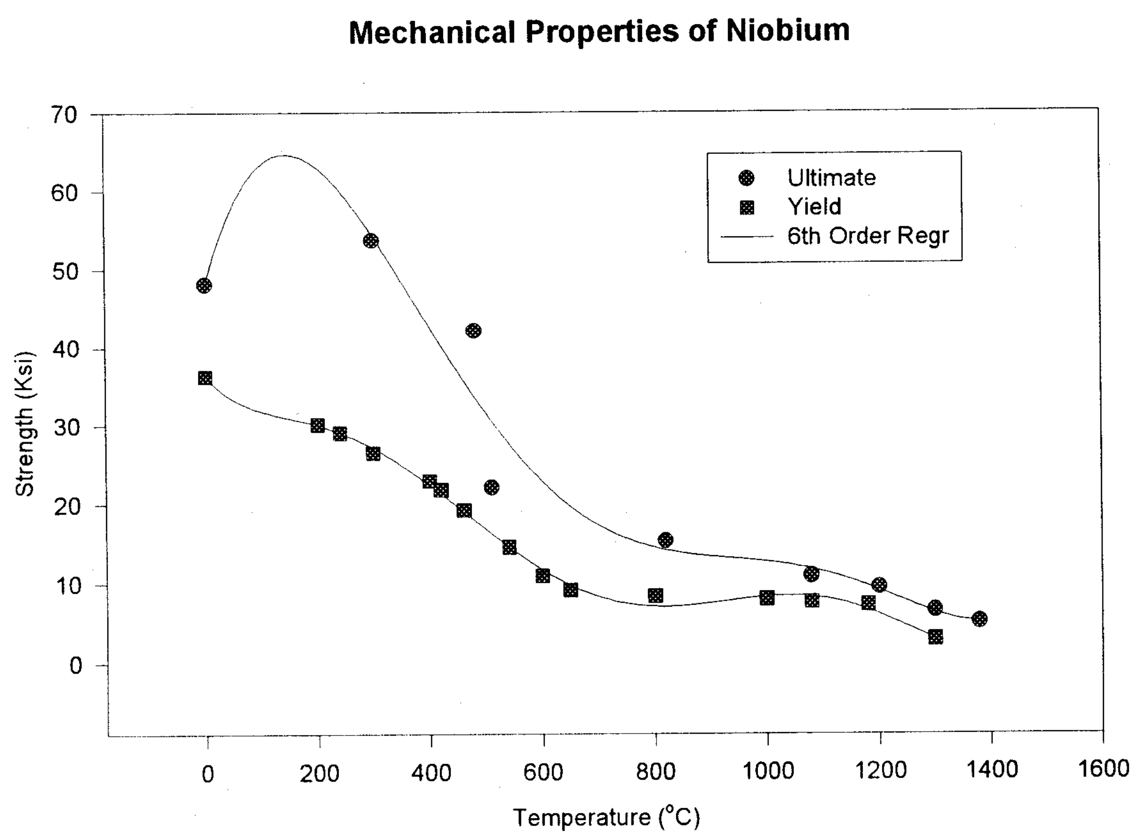

Mechanical Properties of T-222
T-222 -- Ultimate
4th Order Regr
T-222 -- Yield
Ultimate Strength (Ksi)
Yield Strength (Ksi)
Temperature (°C)
240
200
160
120
80
40
0
280
240
200
160
120
80
40
-400
-200
0
200
400
600
800
1000
1200
1400

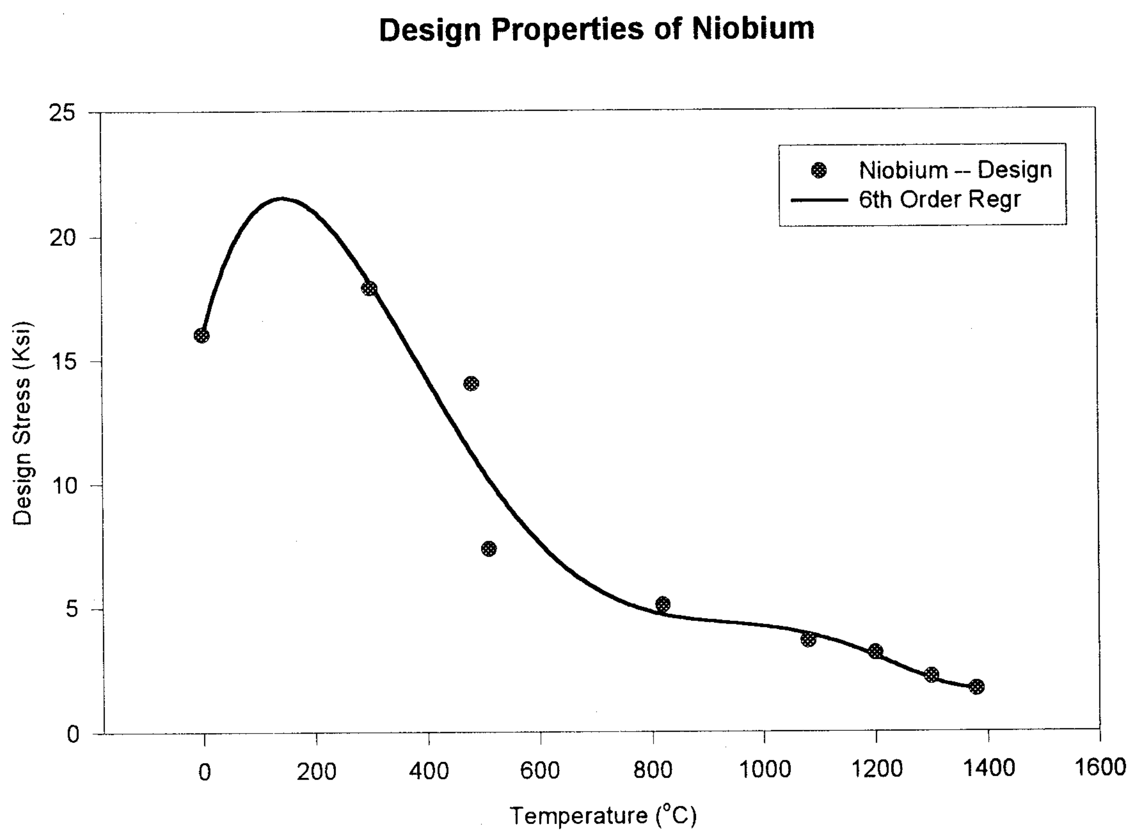

Design Property of T-222
T-222 -- Design
4th Order Regr
Design Stress (Ksi.)
80
70
60
50
40
30
20
-400
-200
0
200
400
600
800
1000
1200
1400
Temperature (°C)

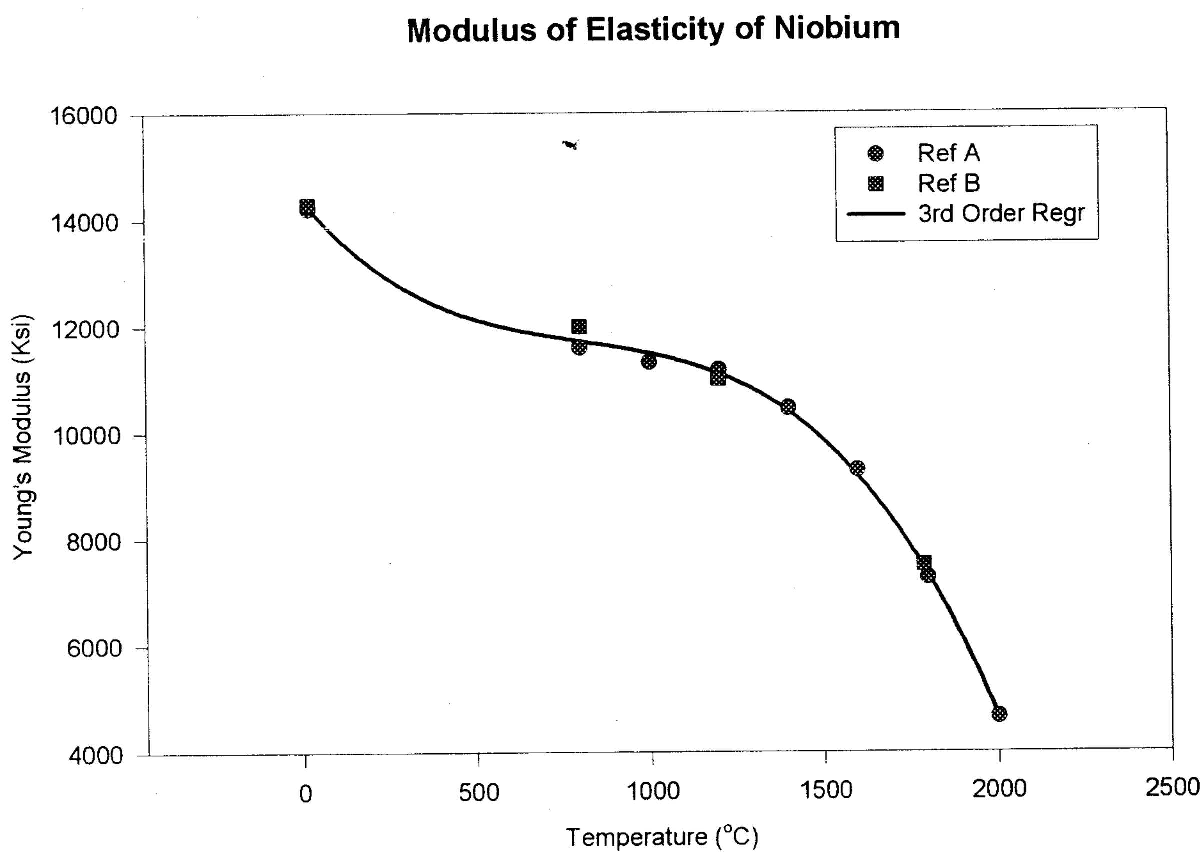

Melting Points of Refractory Metals
Temperature (C)
3500
3000
2500
2000
1500
1000
500
0
Hf
Rh
V
Cr
Ru
Ir
Nb
Mo
Os
Ta
Ro
W
Refractory Metal


Thermal Conductivity Of Selected Materials At 1000 C
450
400
350
300
250
200
150
100
50
0
Thermal Conductivity (W/m-C)
Si
V
Ta
Mo
Tungsten
Diamond
Cu
Graphite
Material

2. Properties of Niobium and its Alloys (Z=41, $[Kr]5s^1 4d^4$)
2.1. Pure Niobium (&Nb-1Zr)



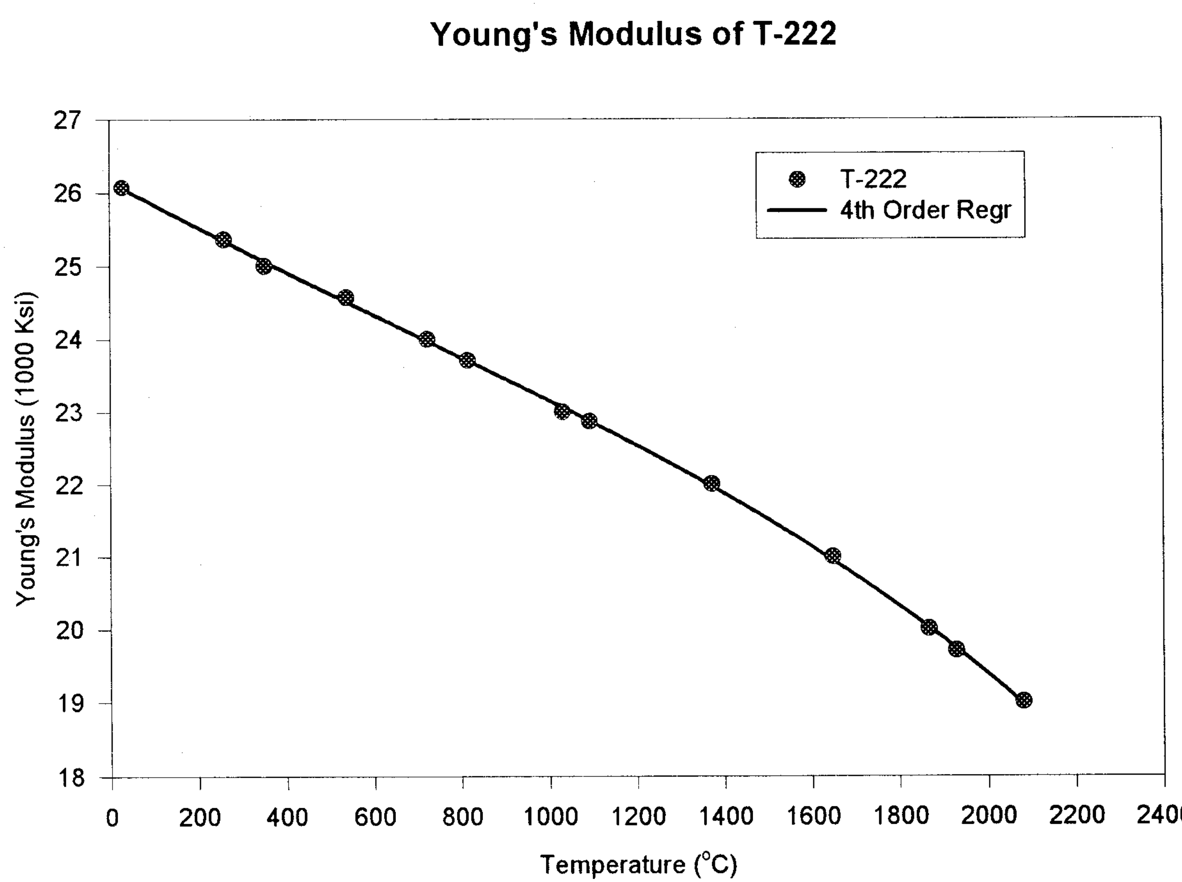

Design Properties of Niobium
25
20
15
10
5
0
Design Stress (Ksi)
0
200
400
600
800
1000
1200
1400
1600
Temperature (°C)
Niobium -- Design
6th Order Regr



Modulus of Elasticity of Niobium
Ref A
Ref B
3rd Order Regr
Young's Modulus (Ksi)
16000
14000
12000
10000
8000
6000
4000
0
500
1000
1500
2000
2500
Temperature (°C)

PHYSICAL PROPERTIES OF NIOBIUM

	Nb
Density (g/cm^3)	8.55
Melting Point (°C)	2468
CTE (ppm/°C)	7.3
Crystal structure	BCC
Thermal conductivity (W/cm °C)	0.54
Specific heat (J/g °C)	0.26


Young's Modulus of T-222
Young's Modulus (1000 Ksi)
Temperature (°C)
T-222
4th Order Regr
27
26
25
24
23
22
21
20
19
18
0
200
400
600
800
1000
1200
1400
1600
1800
2000
2200
2400

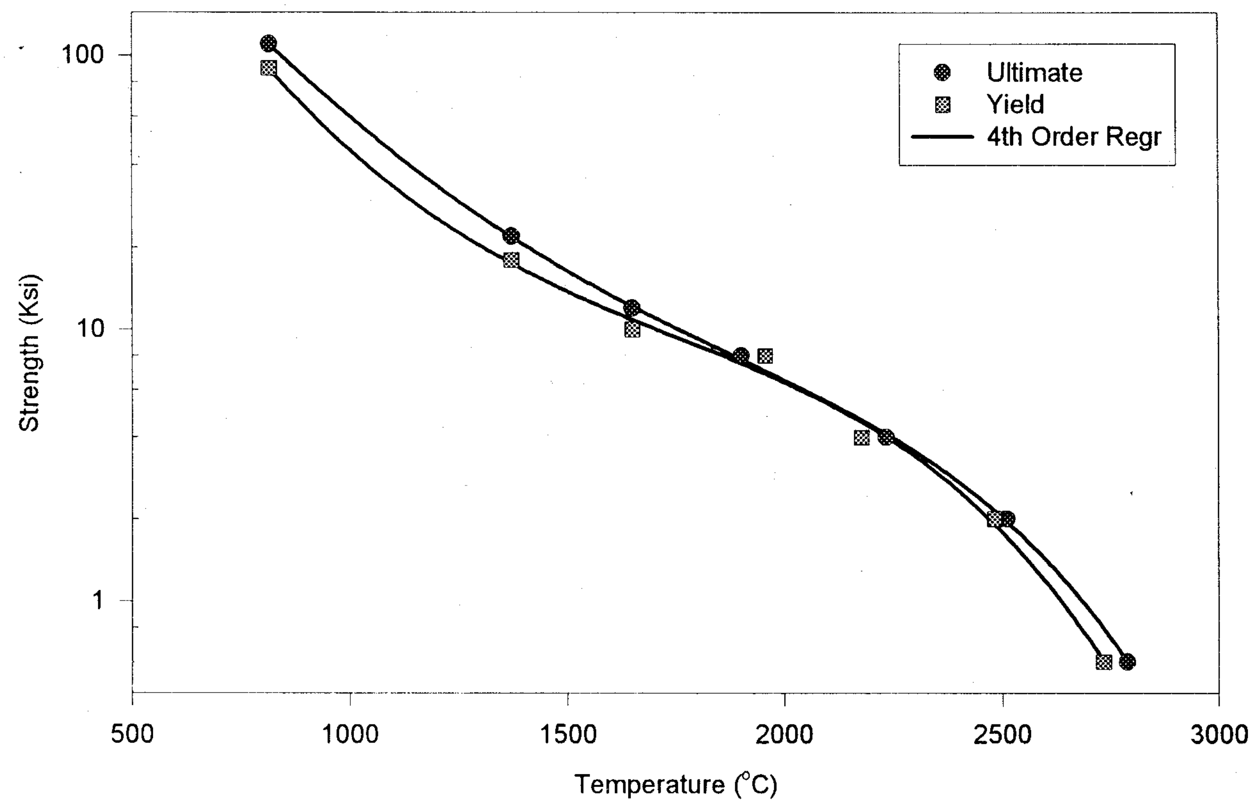
T-222 COMPOSITION

Nominal Composition (wt.%)

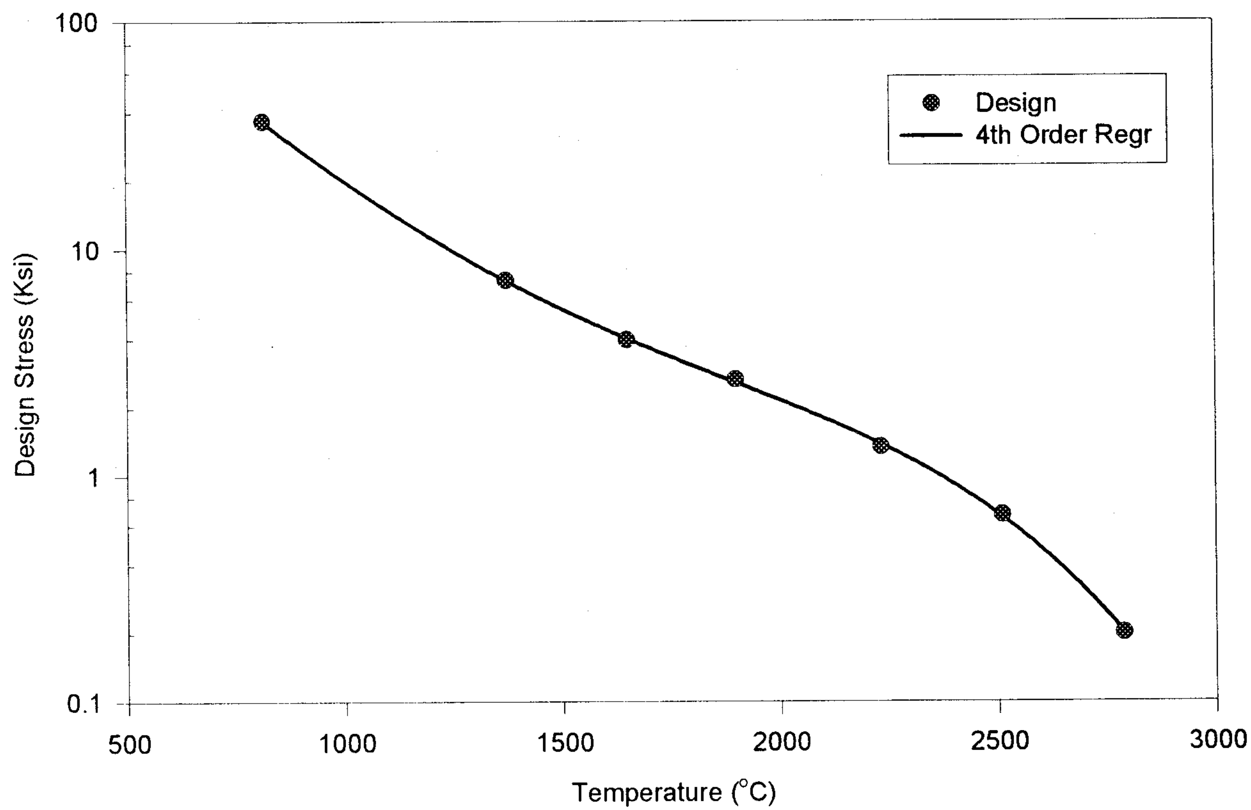
Source	Nominal
Tungsten	9.6
Columbium	
Mlybdenum	
Nickel	
Iron	
Oxygen	
Carbon	0.008
Nitrogen	
Hydrogen	
Chromium	
Cobalt	
Hafnium	2.2
Vanadium	
Tantalum	Balance

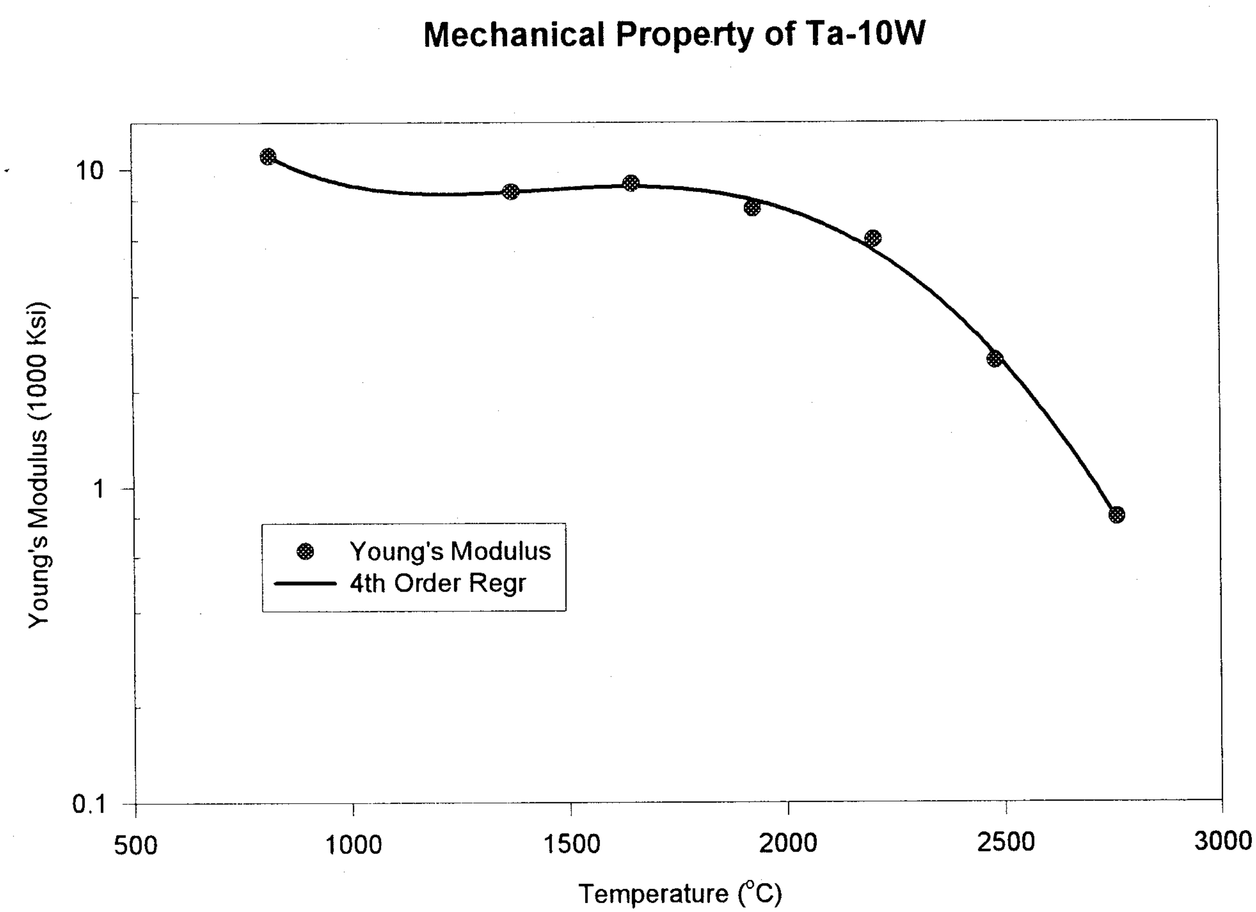
Commercial Designation: T-222 = Ta-9.6W-2.4Hf-0.01C

Mechanical Property of Ta-10W



Design Property of Ta-10W




Mechanical Property of Ta-10W
10
1
0.1
500
1000
1500
2000
2500
3000
Young's Modulus (1000 Ksi)
Temperature (°C)
Young's Modulus
4th Order Regr

Ta-10W COMPOSITION

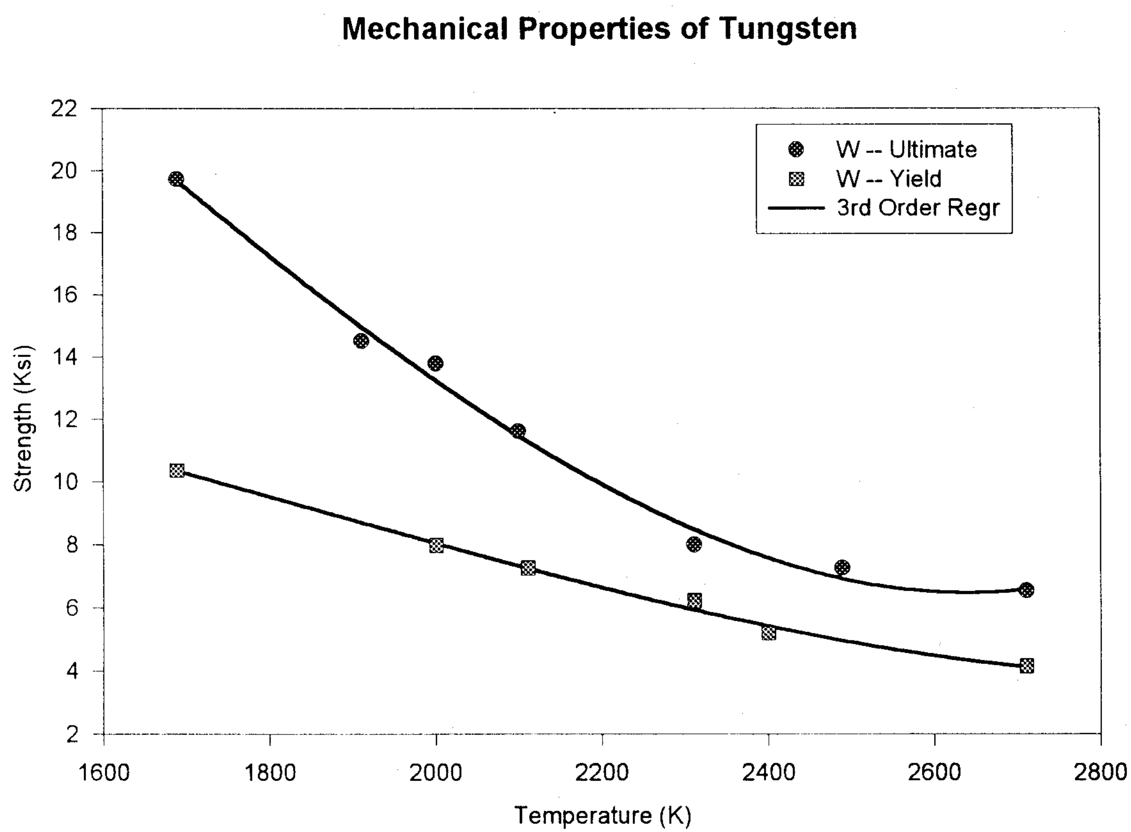
Nominal Composition (wt.%)

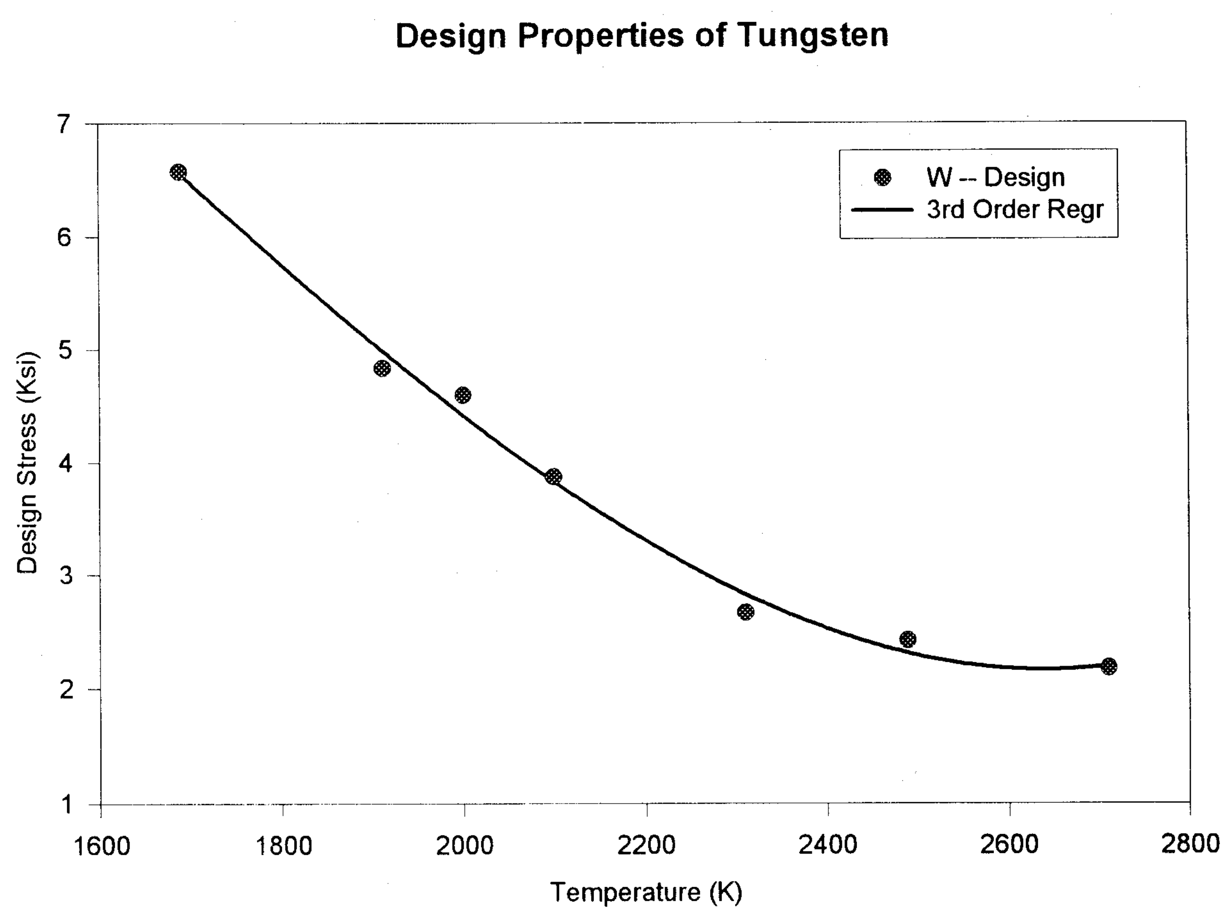
Source	Nominal
Tungsten	8.5
Columbium	
Molybdenum	
Nickel	
Iron	
Oxygen	
Carbon	
Nitrogen	
Hydrogen	
Chromium	
Cobalt	
Hafnium	
Vanadium	
Tantalum	Balance

Commercial Designation: Tantalum

5. Properties of Tungsten and its Alloys (Z=74, [Xe]$6s^2 4f^{14} 5d^4$)

5.1. Pure Tungsten





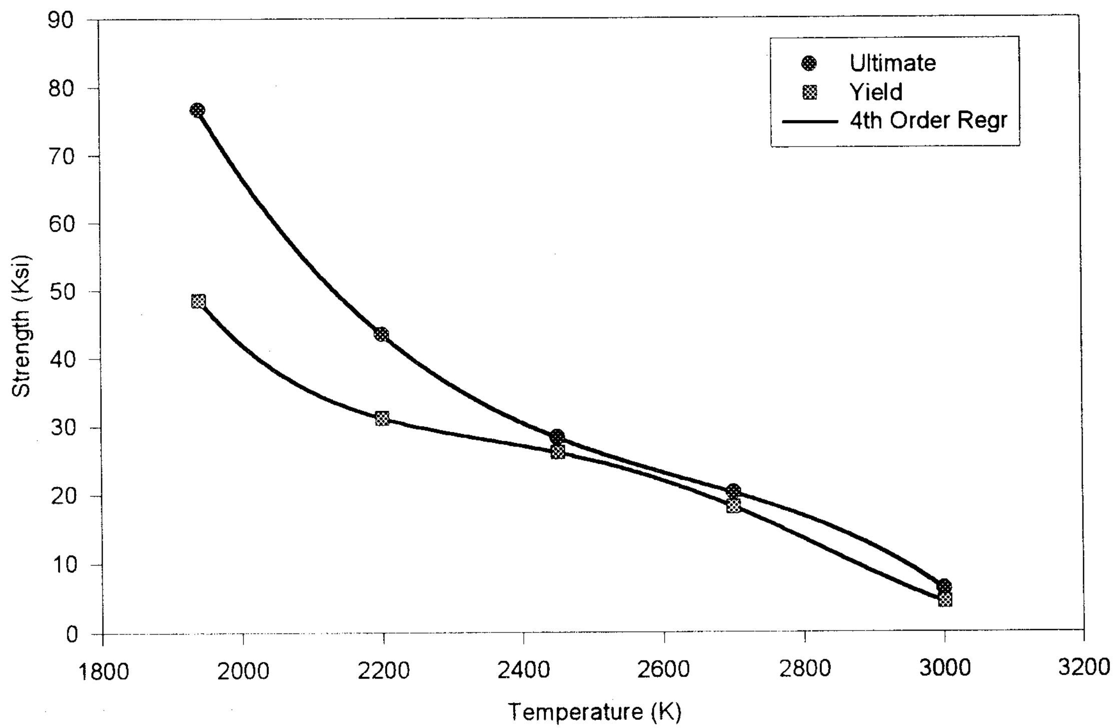
Design Properties of Tungsten
W -- Design
3rd Order Regr
Design Stress (Ksi)
Temperature (K)
1
2
3
4
5
6
7
1600
1800
2000
2200
2400
2600
2800

PHYSICAL PROPERTIES OF TUNGSTEN

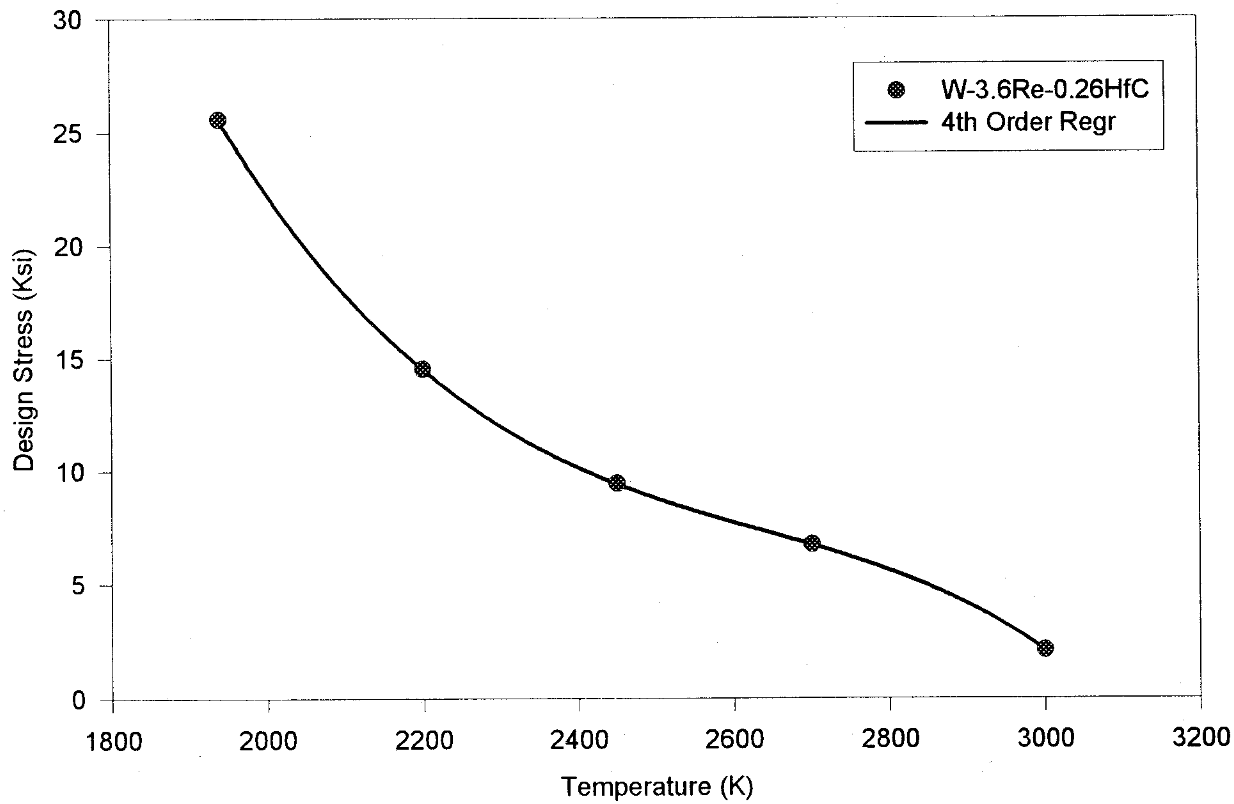
	W
Density (g/cm^3)	19.3
Melting Point (°C)	3410
CTE (ppm/°C)	4.5
Crystal structure	BCC
Thermal conductivity (W/cm °C)	1.7
Specific heat (J/g °C)	0.13

5.2. Selected Tungsten Alloys

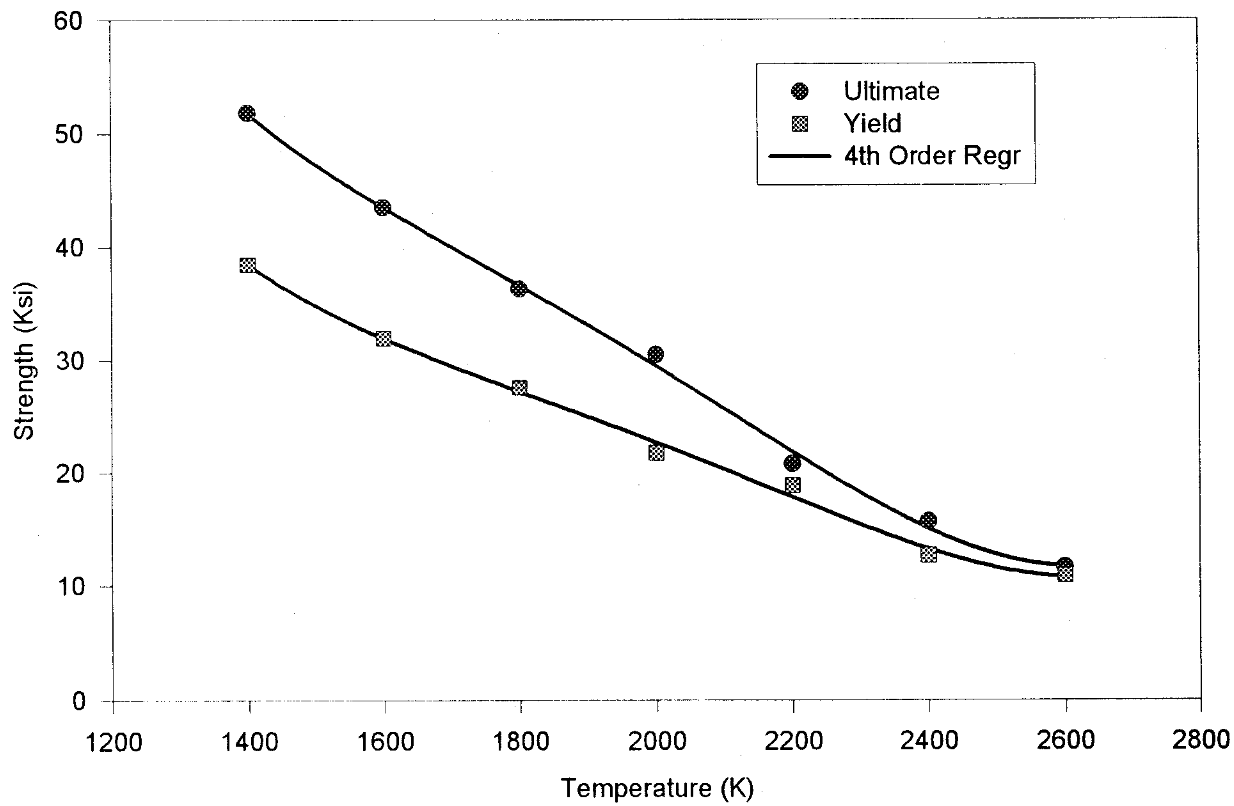
Mechanical Property of W-3.6Re-0.26HfC



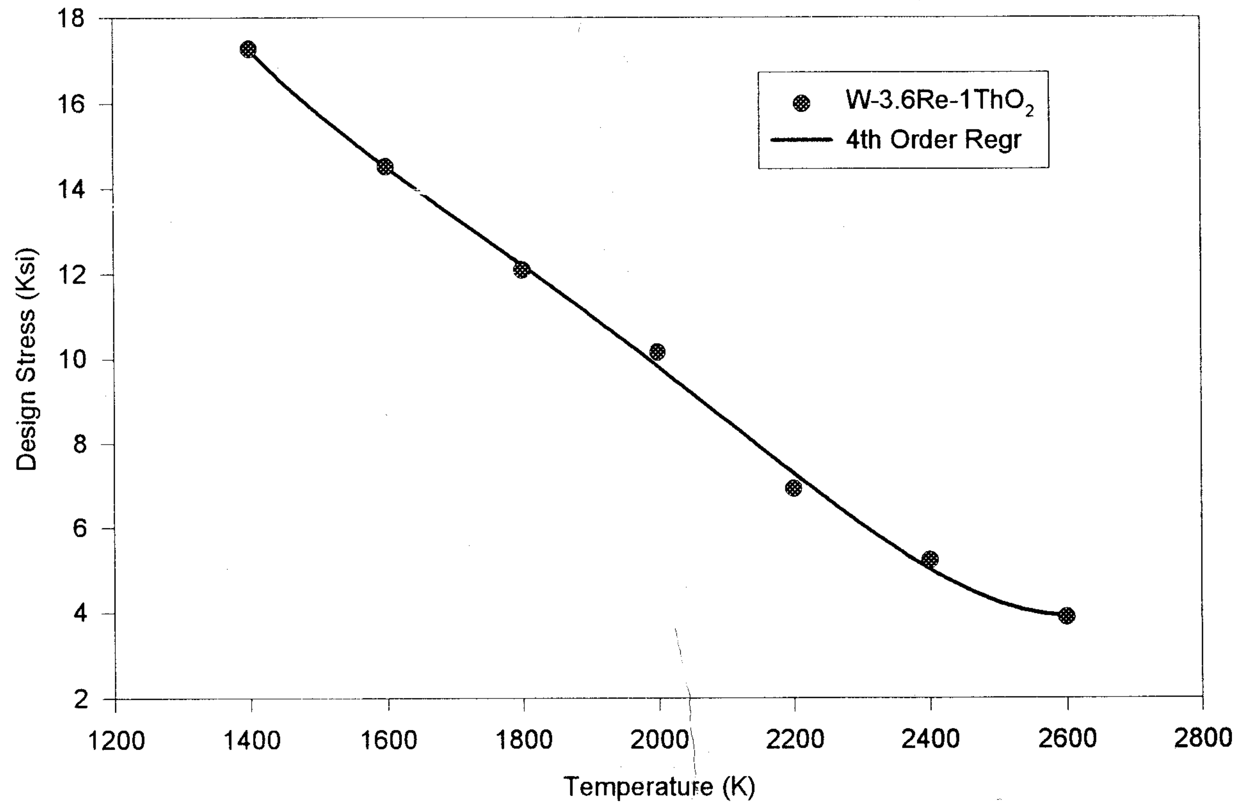
Design Property of W-3.6Re-0.26HfC



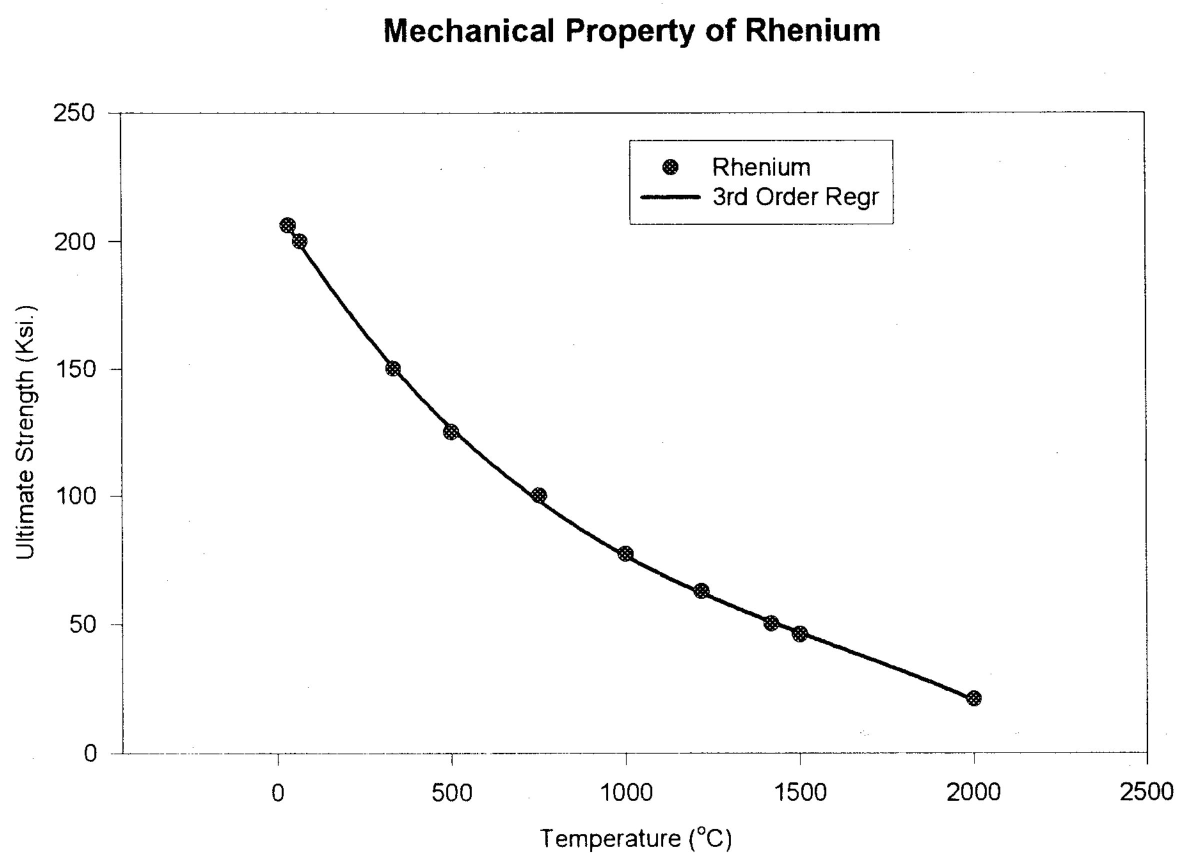
Mechanical Property of W-3.6Re-1ThO_2

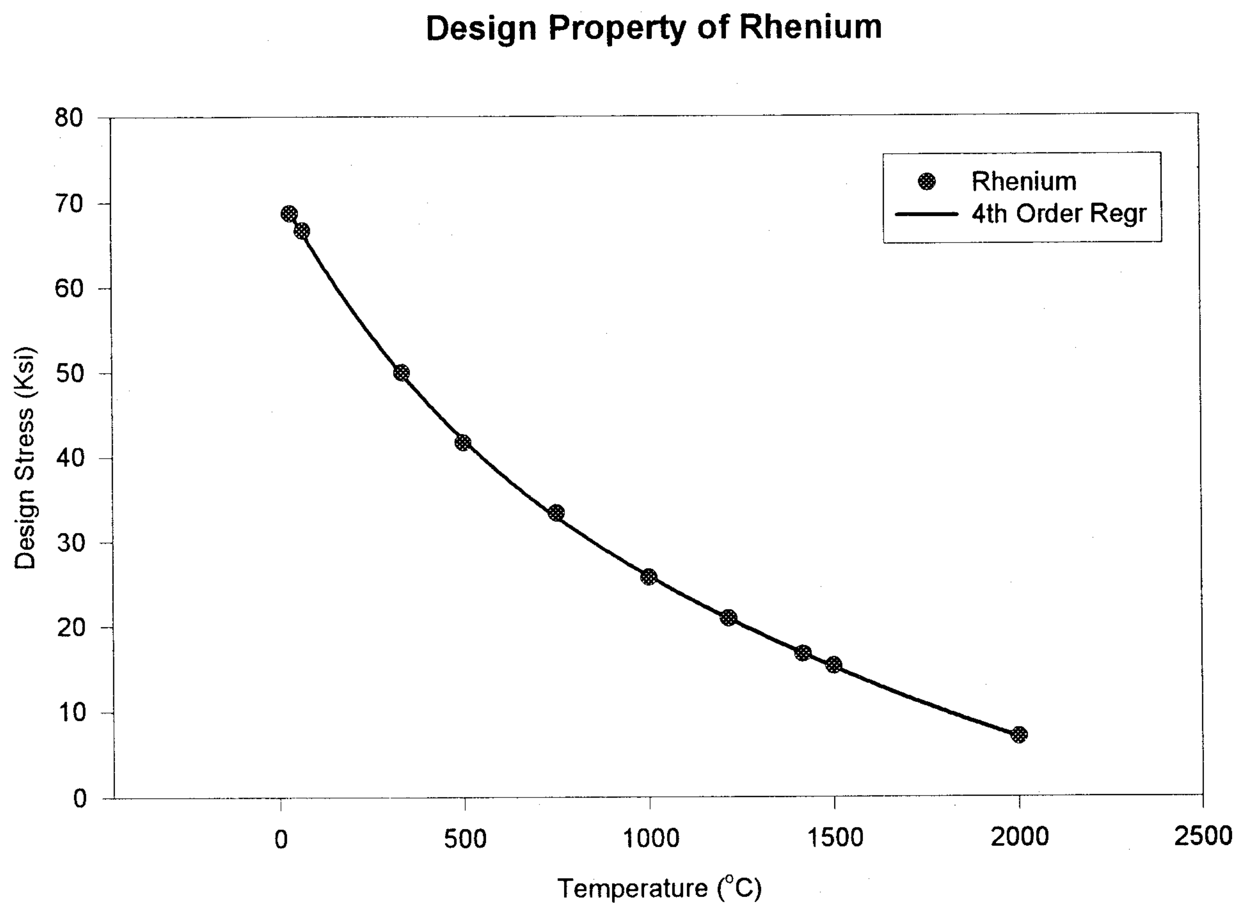


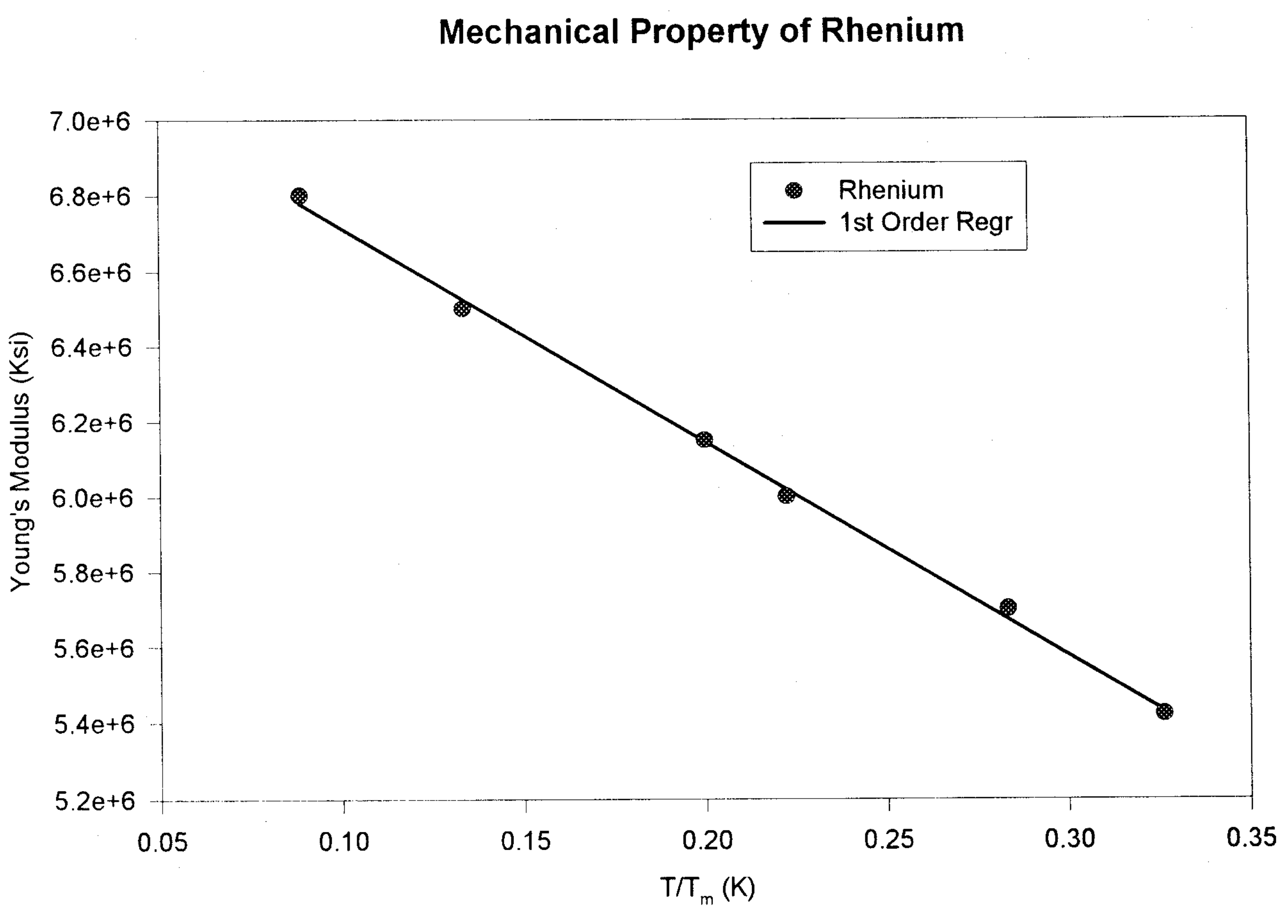
Design Property of W-3.6Re-1ThO$_2$



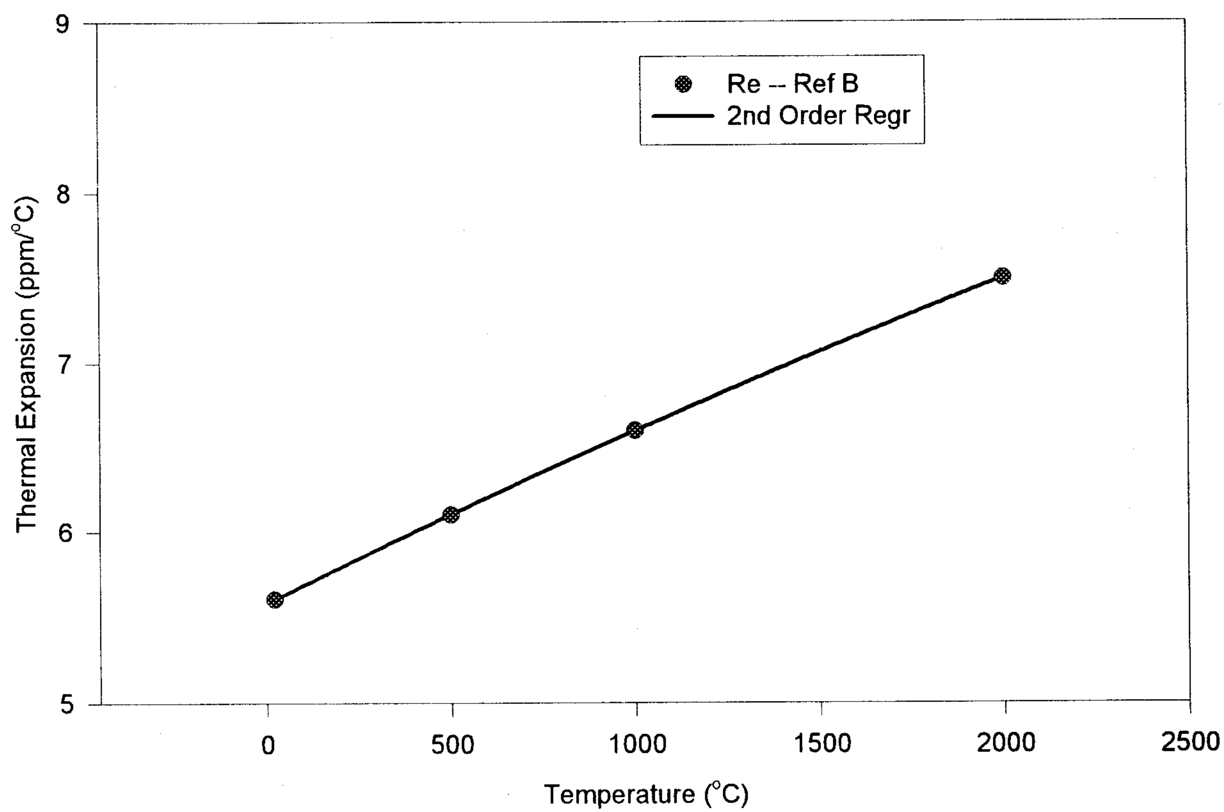
6. Properties of Rhenium and its Alloys (Z=75, [Xe]$6s^2 4f^{14} 5d^5$)




Design Property of Rhenium
Rhenium
4th Order Regr
Design Stress (Ksi)
80
70
60
50
40
30
20
10
0
0
500
1000
1500
2000
2500
Temperature (°C)


Mechanical Property of Rhenium
Rhenium
1st Order Regr
Young's Modulus (Ksi)
7.0e+6
6.8e+6
6.6e+6
6.4e+6
6.2e+6
6.0e+6
5.8e+6
5.6e+6
5.4e+6
5.2e+6
0.05
0.10
0.15
0.20
0.25
0.30
0.35
T/T_m (K)

Thermal Property of Rhenium



PHYSICAL PROPERTIES OF RHENIUM

	Re
Density (g/cm^3)	21
Melting Point (^{o}C)	3180
CTE (ppm/^{o}C)	6.2
Crystal structure	HCP
Thermal conductivity (W/cm ^{o}C)	0.48
Specific heat (J/g ^{o}C)	0.14

7. Comparison with Conventional Alloys, including Cost

Element	Z	A	$/Kg
Fe	26	55.85	67
Si	14	28.086	54
Cu	29	63.55	27
Ti	22	47.9	61
Zr	40	91.22	160
Hf	72	178.49	1200
V	23	50.94	2200
Nb	41	92.906	180
Ta	73	180.947	1200
Cr	24	51,996	100
Mo	42	95.94	110
W	74	183.85	110
Re	75	186.2	5400

COMPARISON OF SELECTED THERMO-MECHANICAL PROPERTIES

FIGURE IX-B-10— Coefficient of Thermal Expansion FOR CTR MATERIALS

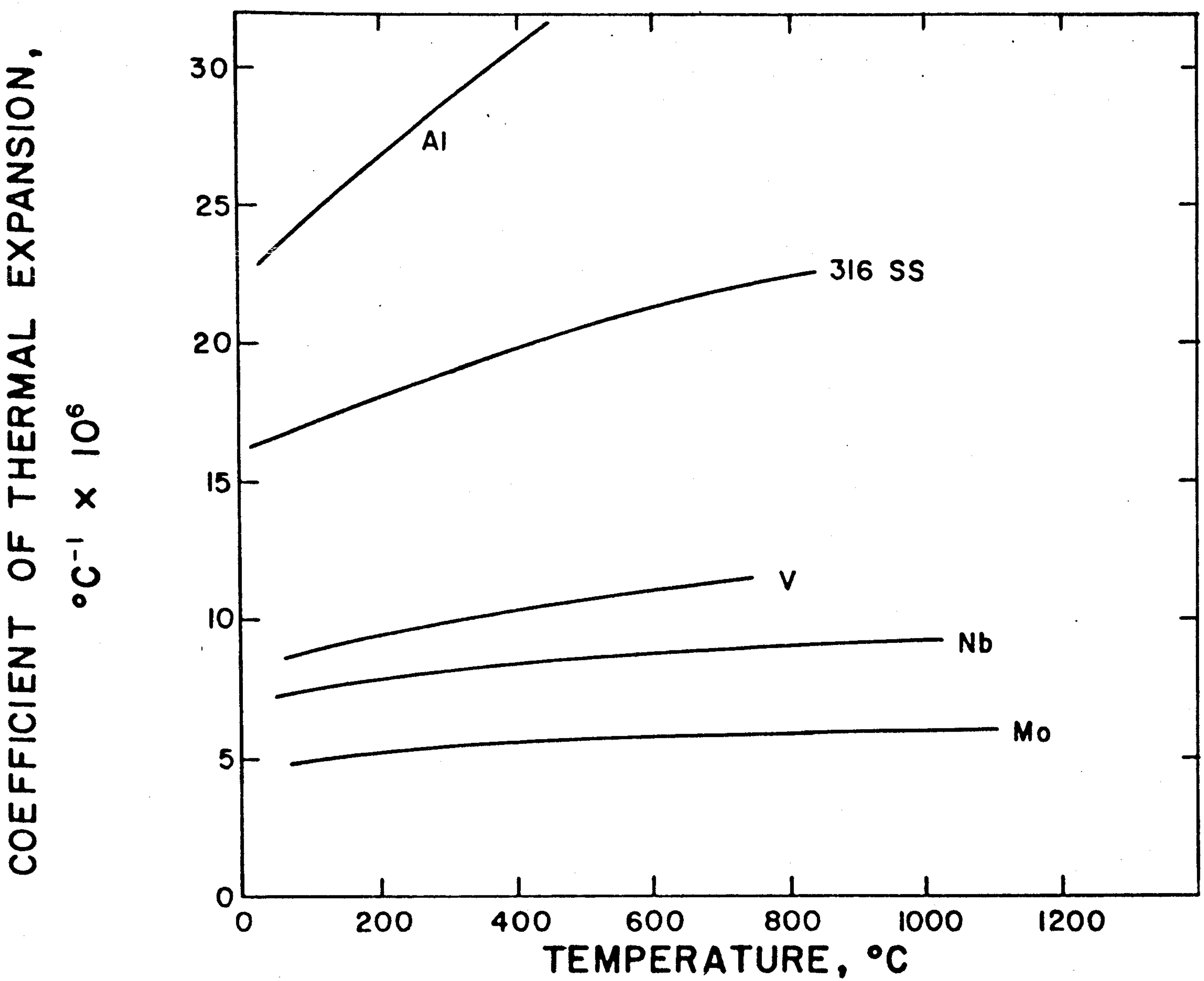


FIGURE IX-B-9— Thermal Conductivity — CTR Materials

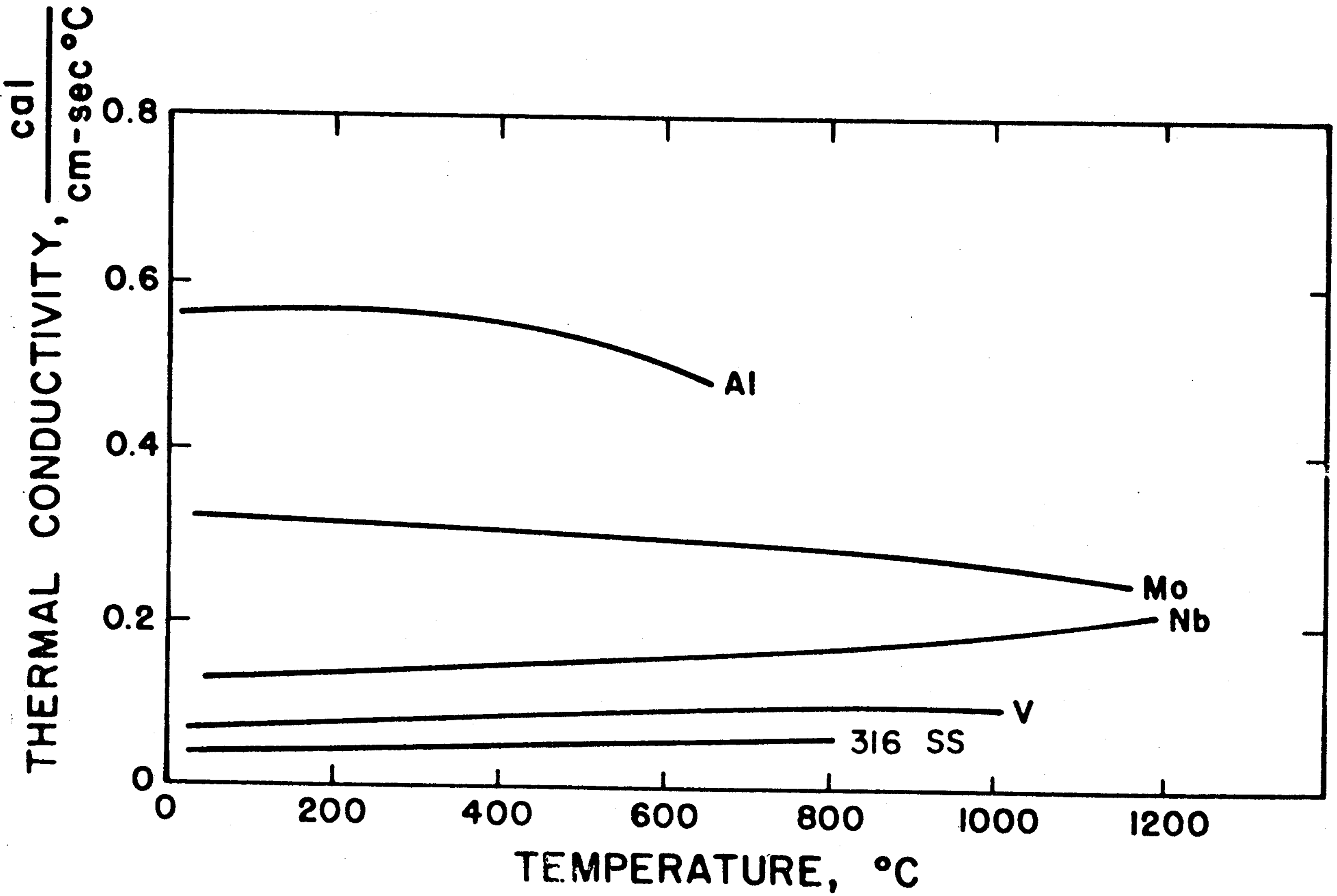


FIGURE IX-B-2 - Electrical Resistivity of CTR Materials

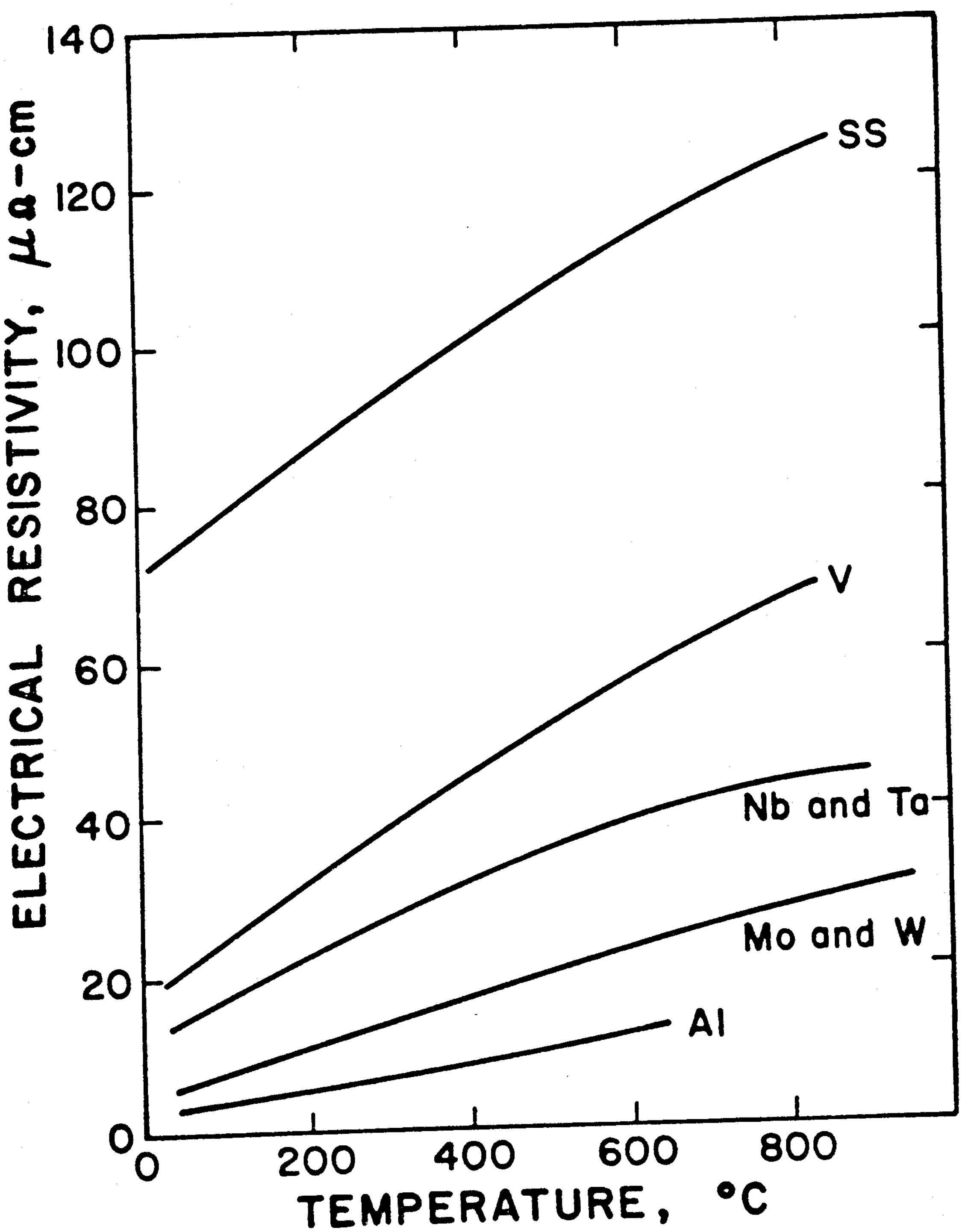
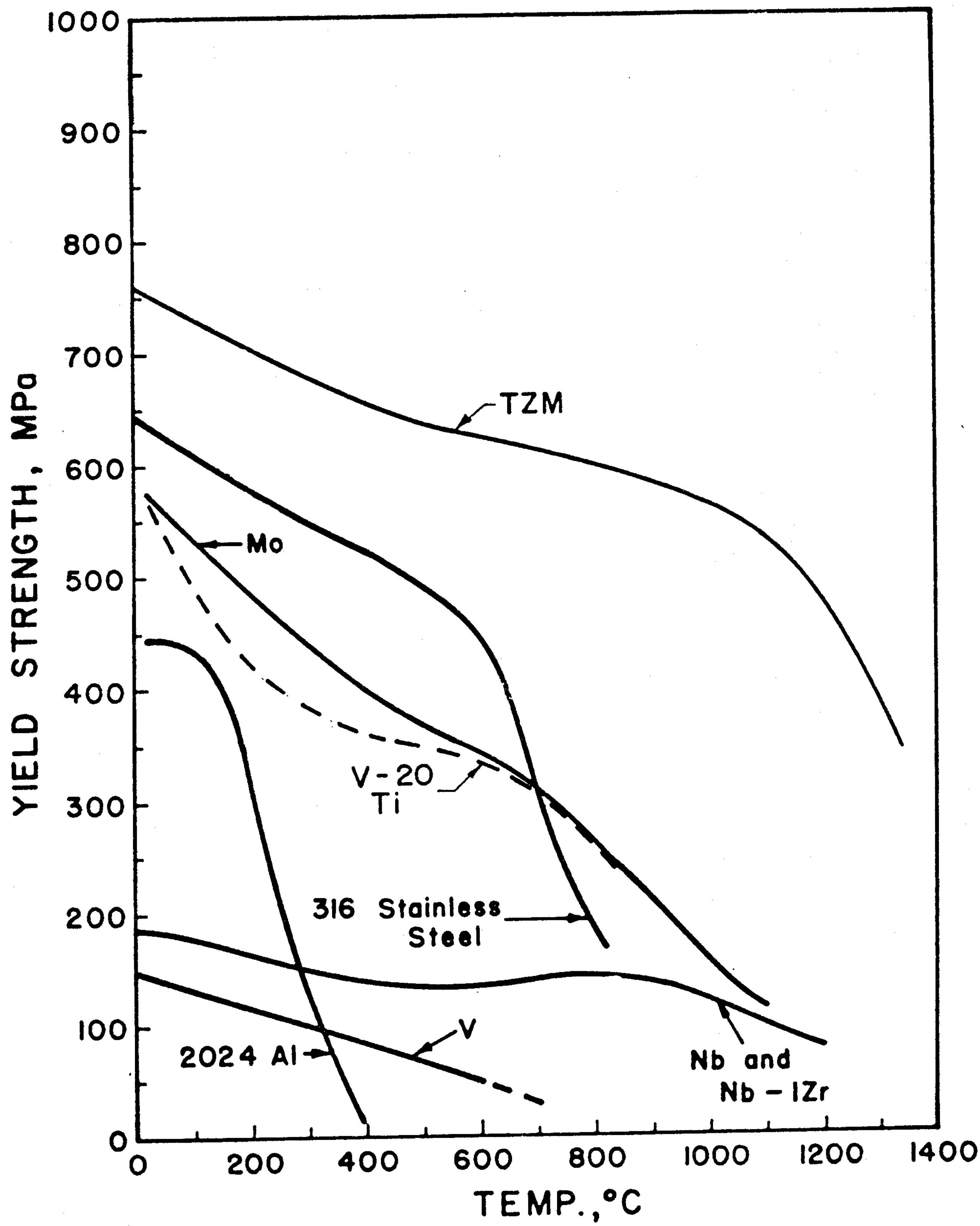


FIGURE IX-B-3

Effect of Temperature on Yield Strength of Potential CTR Materials



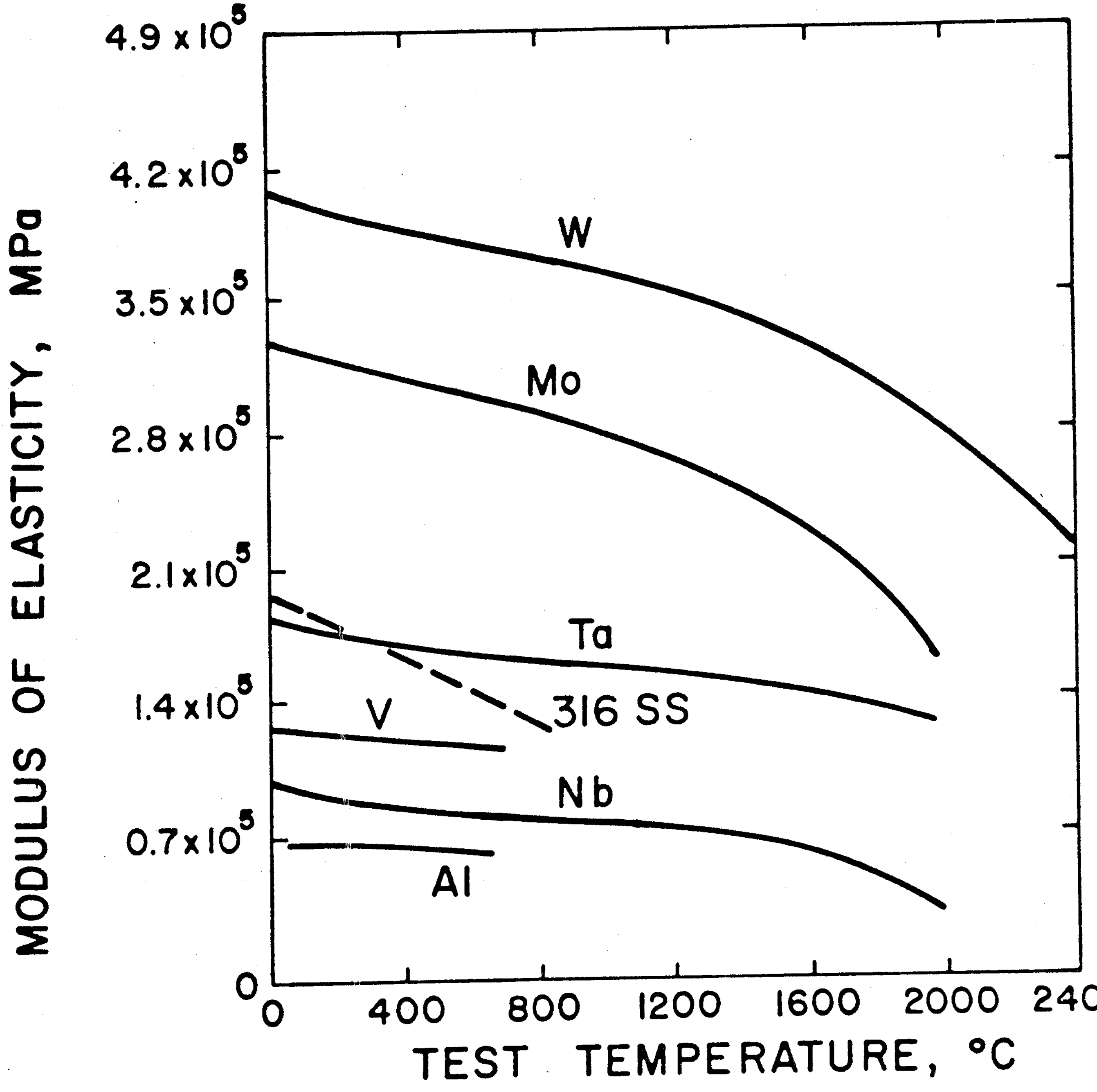


FIG. IX-B-11. MODULUS OF ELASTICITY FOR CTR MATERIALS

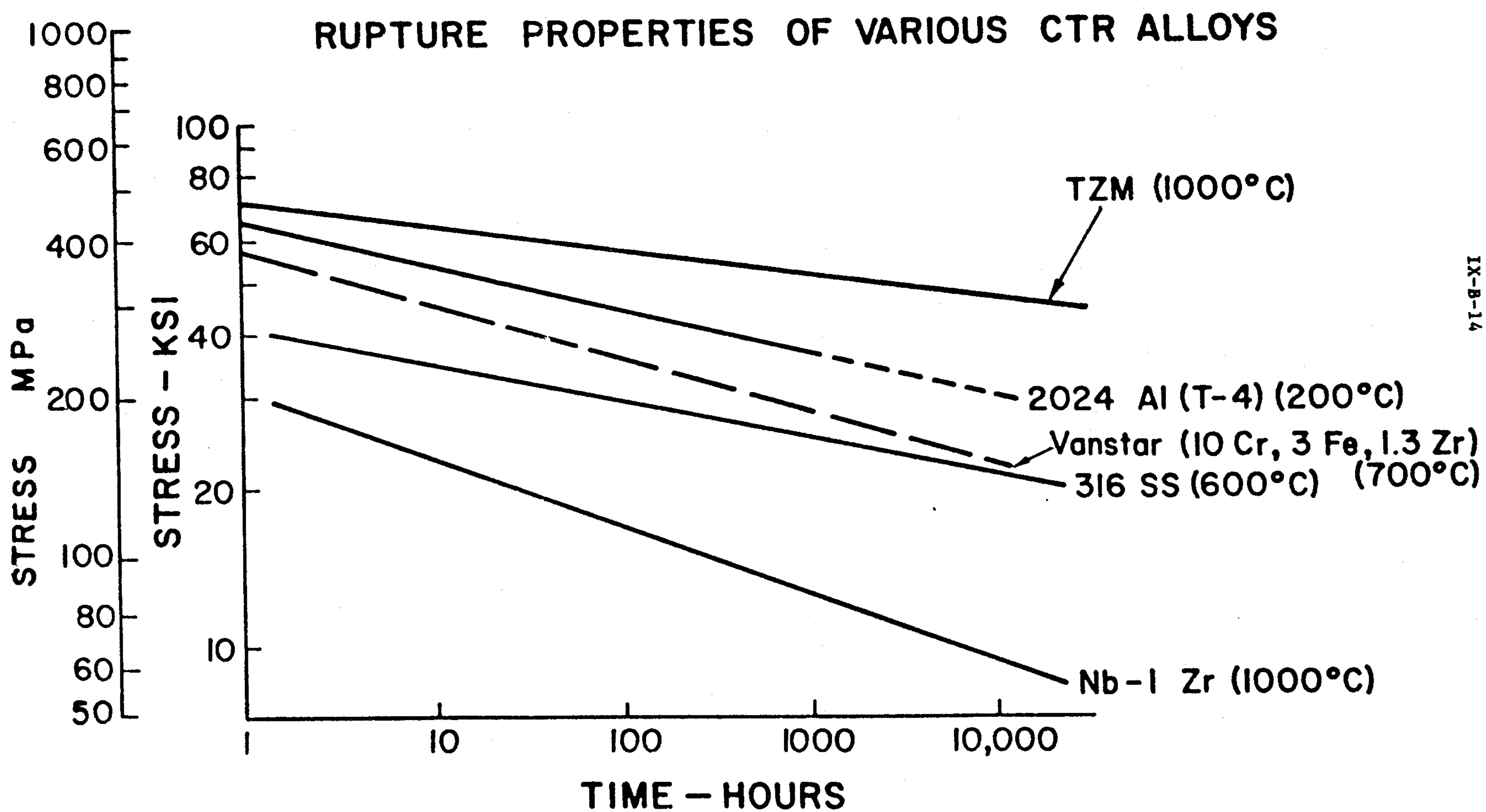

RUPTURE PROPERTIES OF VARIOUS CTR ALLOYS
STRESS MPa
1000
800
600
400
200
100
80
60
50
STRESS - KSI
100
80
60
40
20
10
TZM (1000°C)
2024 Al (T-4) (200°C)
Vanstar (10 Cr, 3 Fe, 1.3 Zr)
(700°C)
316 SS (600°C)
Nb-1 Zr (1000°C)
1
10
100
1000
10,000
TIME — HOURS

FIGURE IX-B-7

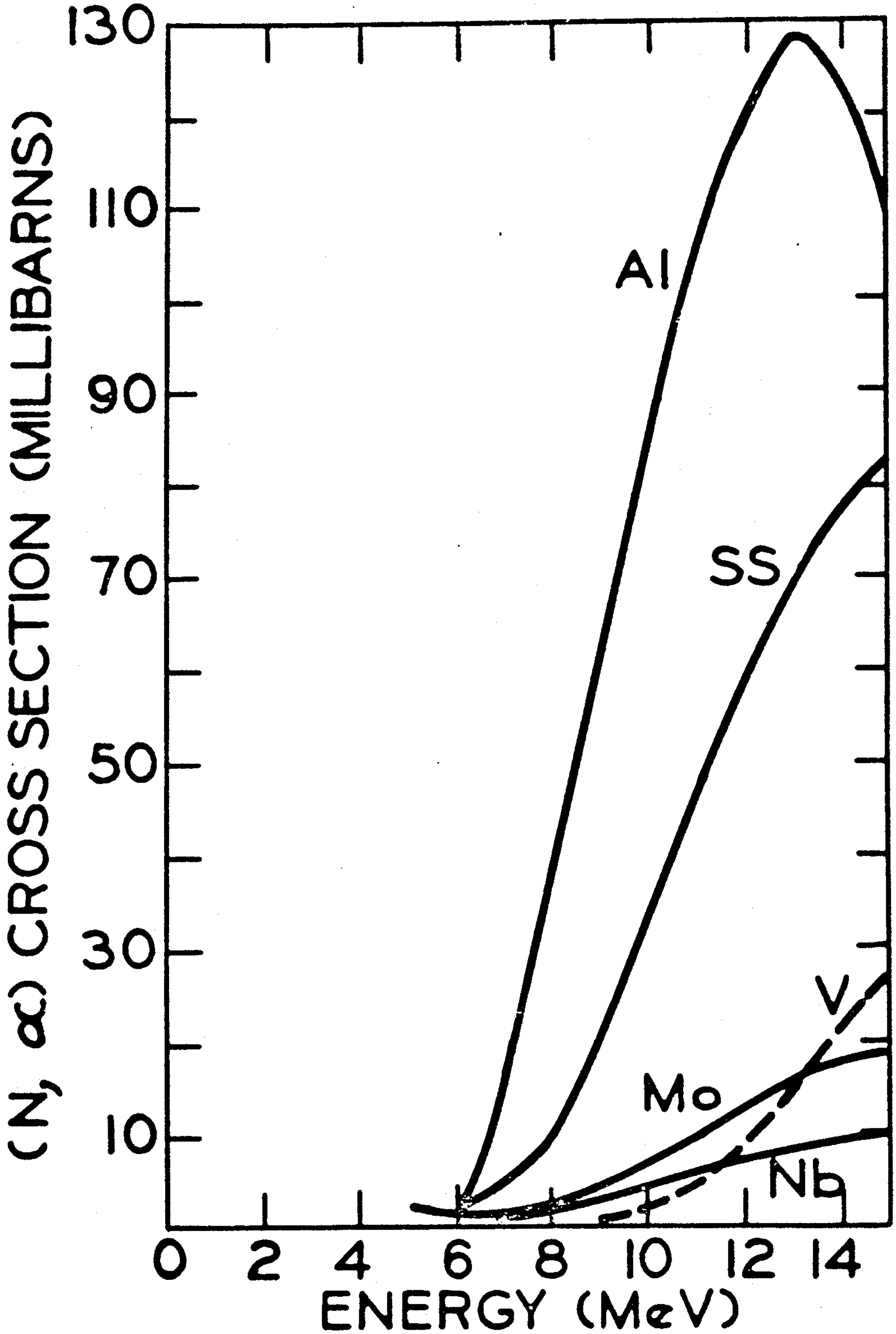


FIG. 19a COMPARISON OF THRESHOLD (N, α) CROSS SECTIONS FOR 316 SS, V, Nb, Mo AND Al

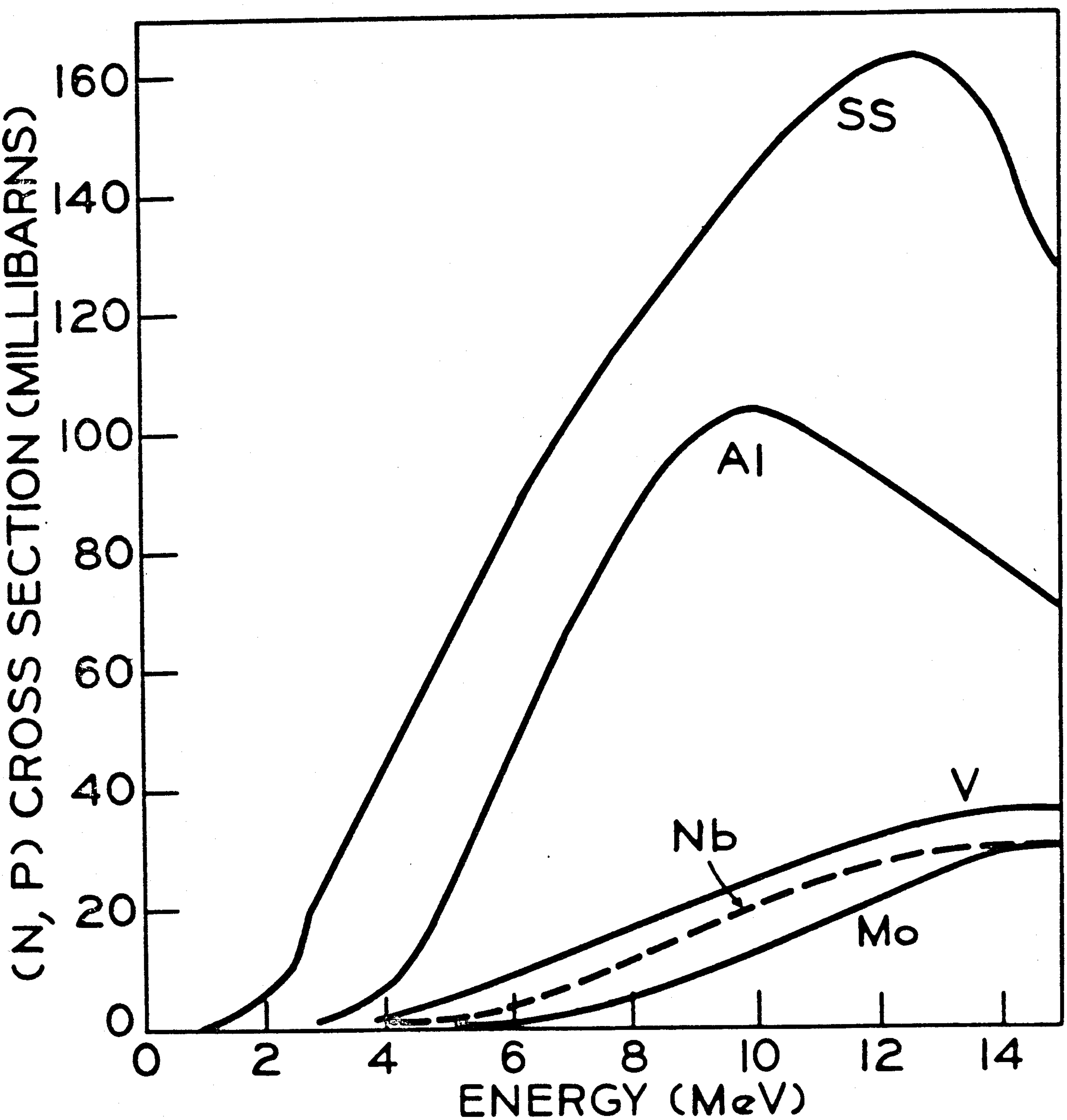


FIG. 19b COMPARISON OF THRESHOLD (N, P) CROSS SECTIONS FOR 316 SS, V Nb, Al AND Mo

8. CORROSION-RESISTANT NICKEL-BEARING ALLOYS

Alloy	%Ni	%Fe	%Cr	Yield Strength at RT(ksi)
Inco-alloy C-276	55	6	16	50
Inconel-718 (up to 980 ^{0}C)	52.5	18.5	19	181
Incoloy 800-HT (up to 980 ^{0}C)	32.5	46	21	20-50

9. COMPATIBILITY WITH LITHIUM AND INTERSTITIAL ELEMENTS

LITHIUM COMPATIBILITY ISSUES:

(1) Solubility of metal in Li,
(2) Impurity Transfer between the metal and Li.

@ Unlike steels, refractory Metals are relatively insoluble in Li (20-50 ppm at 800-1000 ^{o}C).
@ Lithium extracts oxygen from Mo, Nb, and V. If Zr is added, it can reverse the flow of oxygen.
@ Nb and V (no protective coating) will be contaminated with N an C, if Li contains more than 0.001 ppm N.
@ Pure Mo loses C & N to Li in the temperature range (600-1000 ^{o}C).
@ The addition of Zr and Ti stabilizes carbides and nitrides in refractory metals.

FIGURE IX-B-5a EFFECT OF CARBON ON DBTT OF POTENTIAL CTR REFRACTORY STRUCTURAL MATERIALS

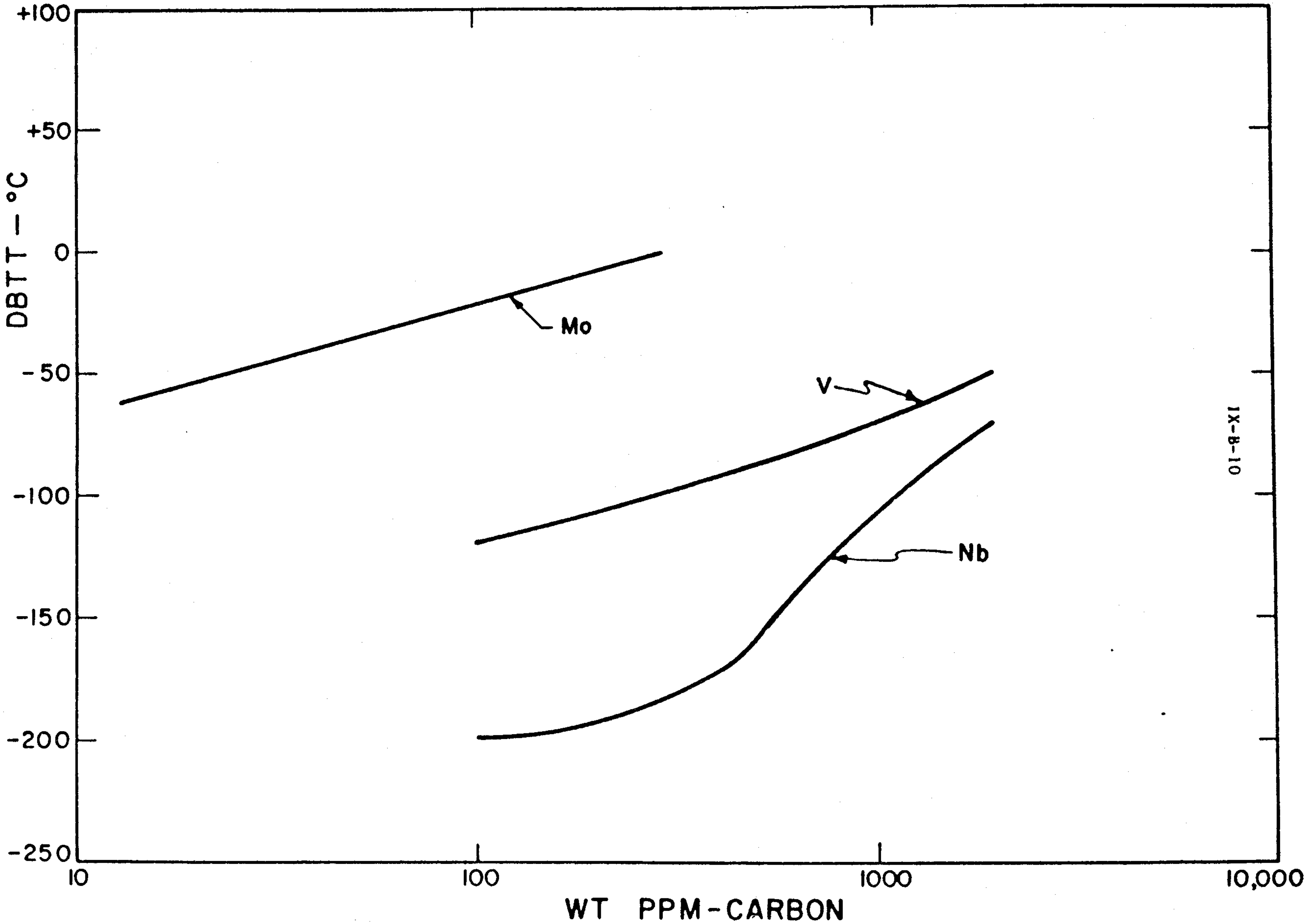
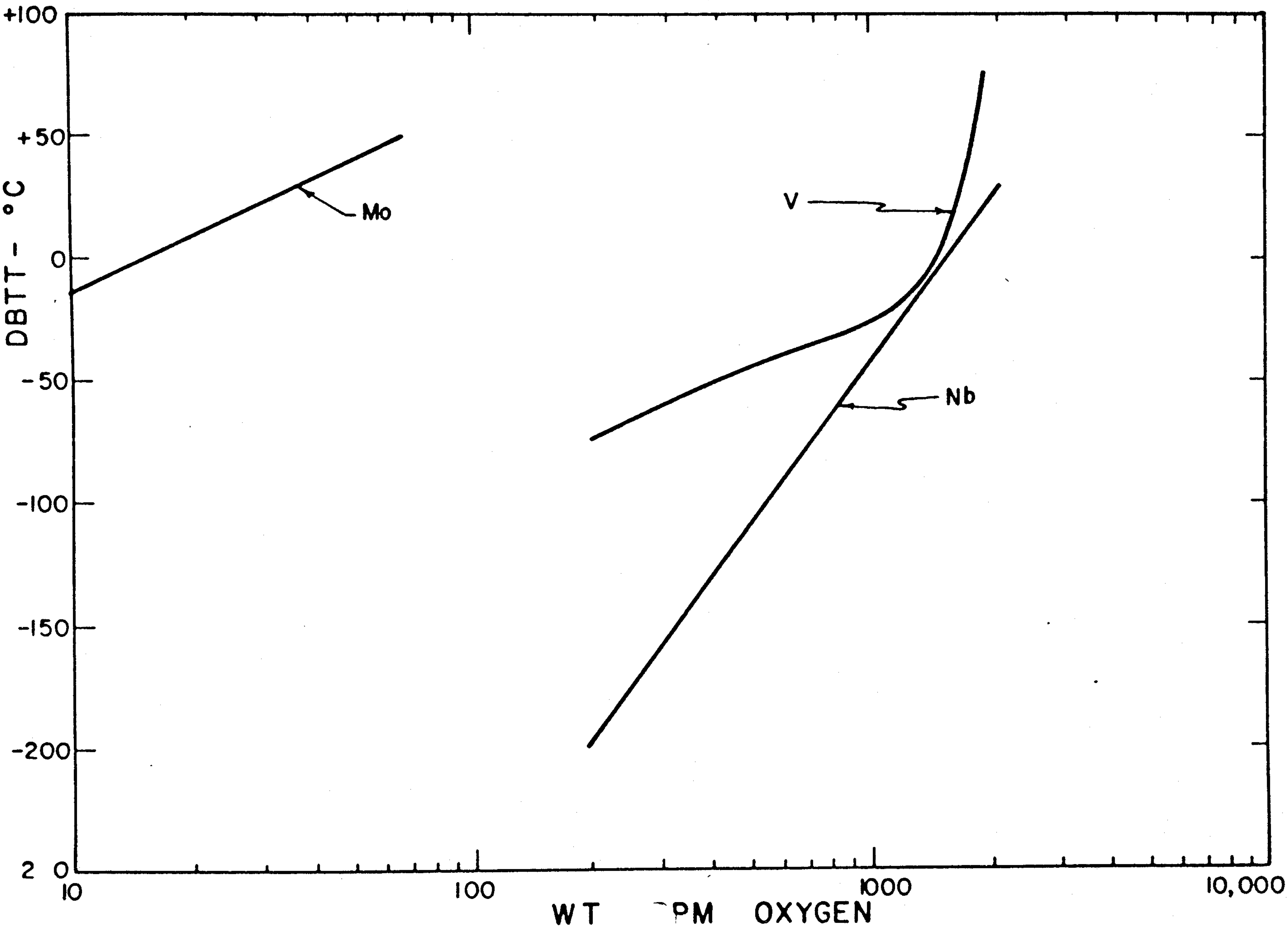


FIGURE IX-B-5b EFFECT OF OXYGEN ON DBTT OF Mo, Nb and V.



IX-B-11

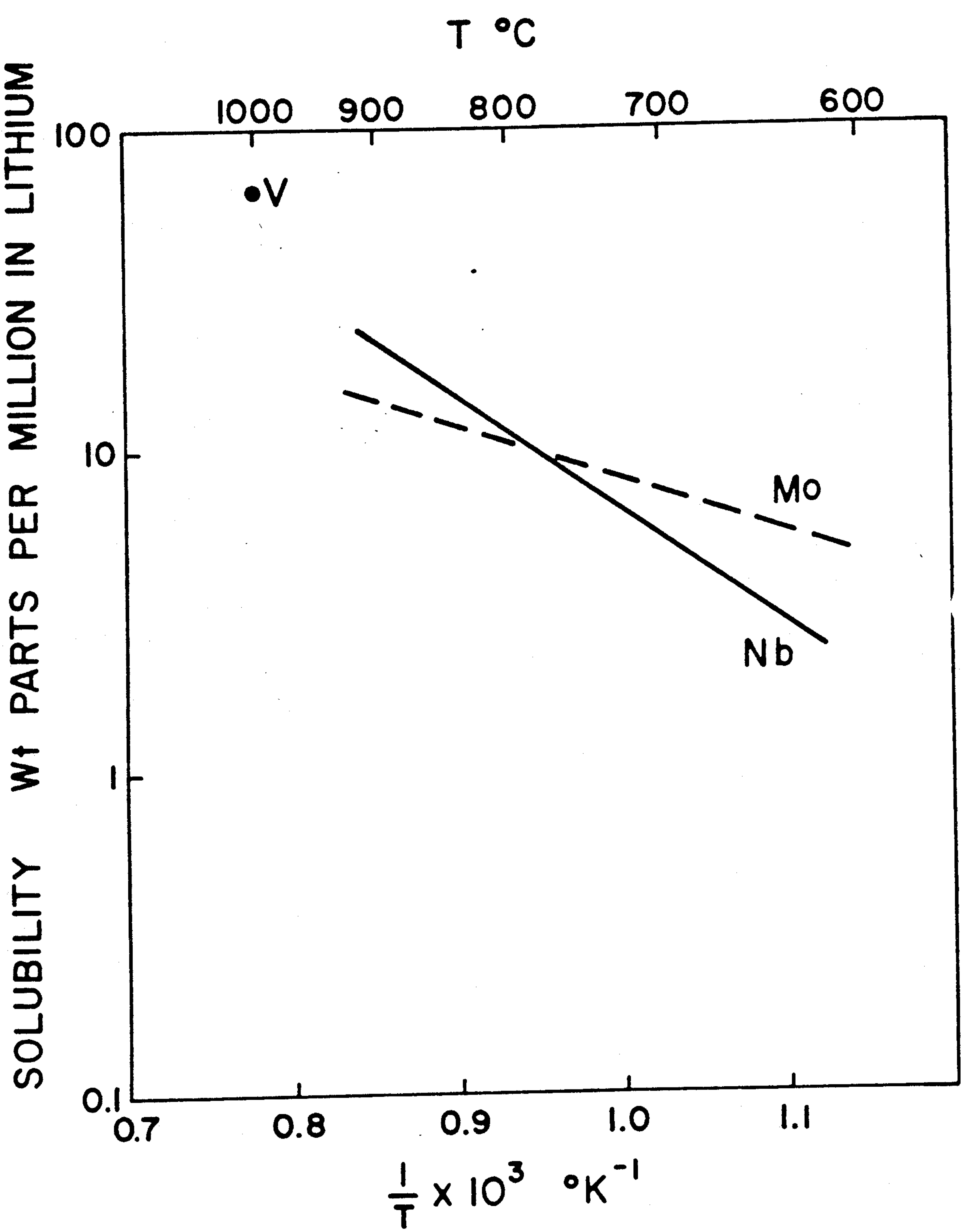


FIGURE IX-B-23 SOLUBILITY OF REFRACTORY METALS IN LITHIUM

FIGURE IX-B-24 TEMPERATURE DEPENDENCE OF THE EQUILIBRIUM DISTRIBUTION COEFFICIENTS FOR INTERSTITIAL ELEMENTS BETWEEN SELECTED REFRACTORY METALS AND LITHIUM

(a) OXYGEN (b) NITROGEN (c) CARBON

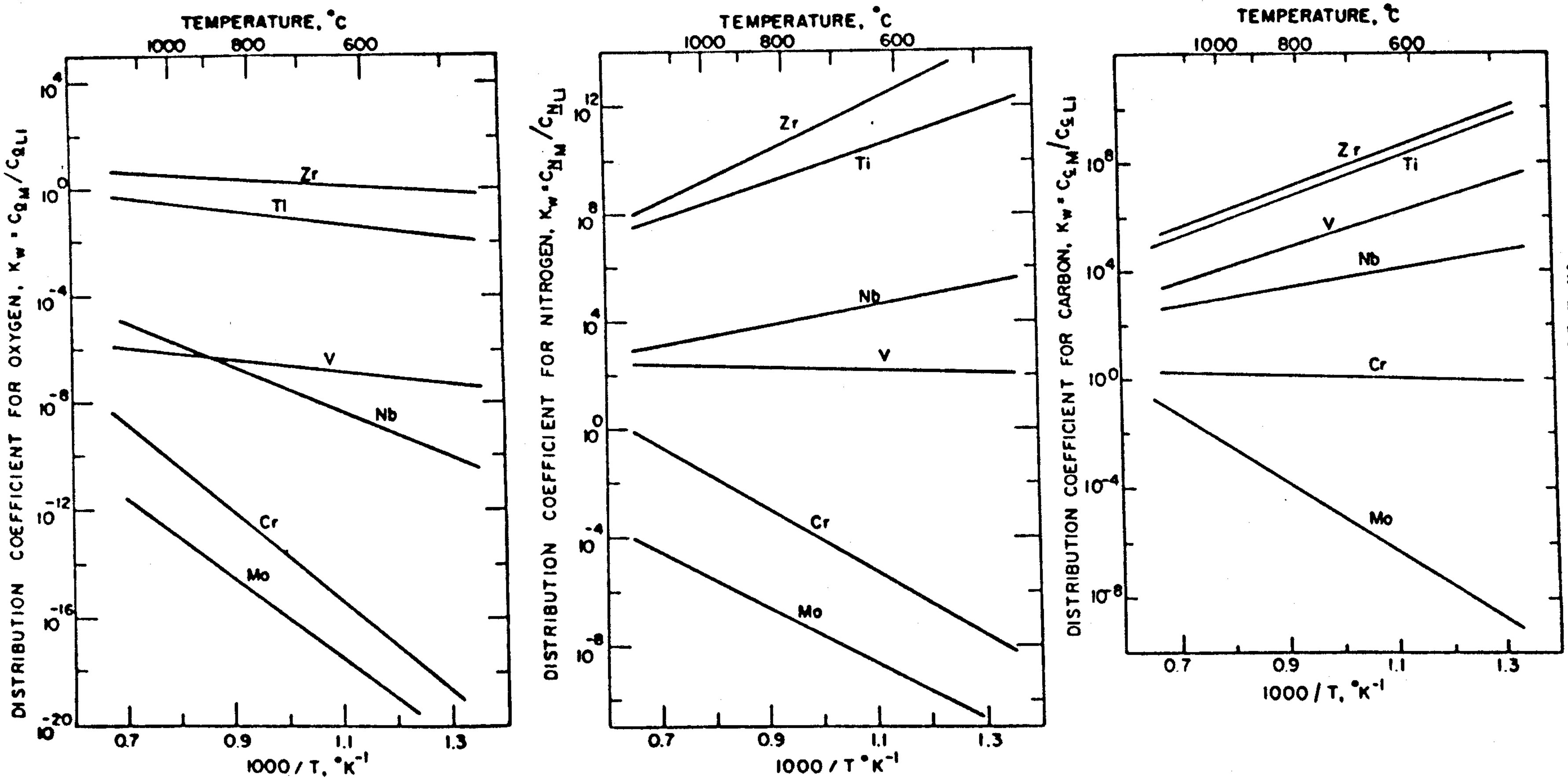
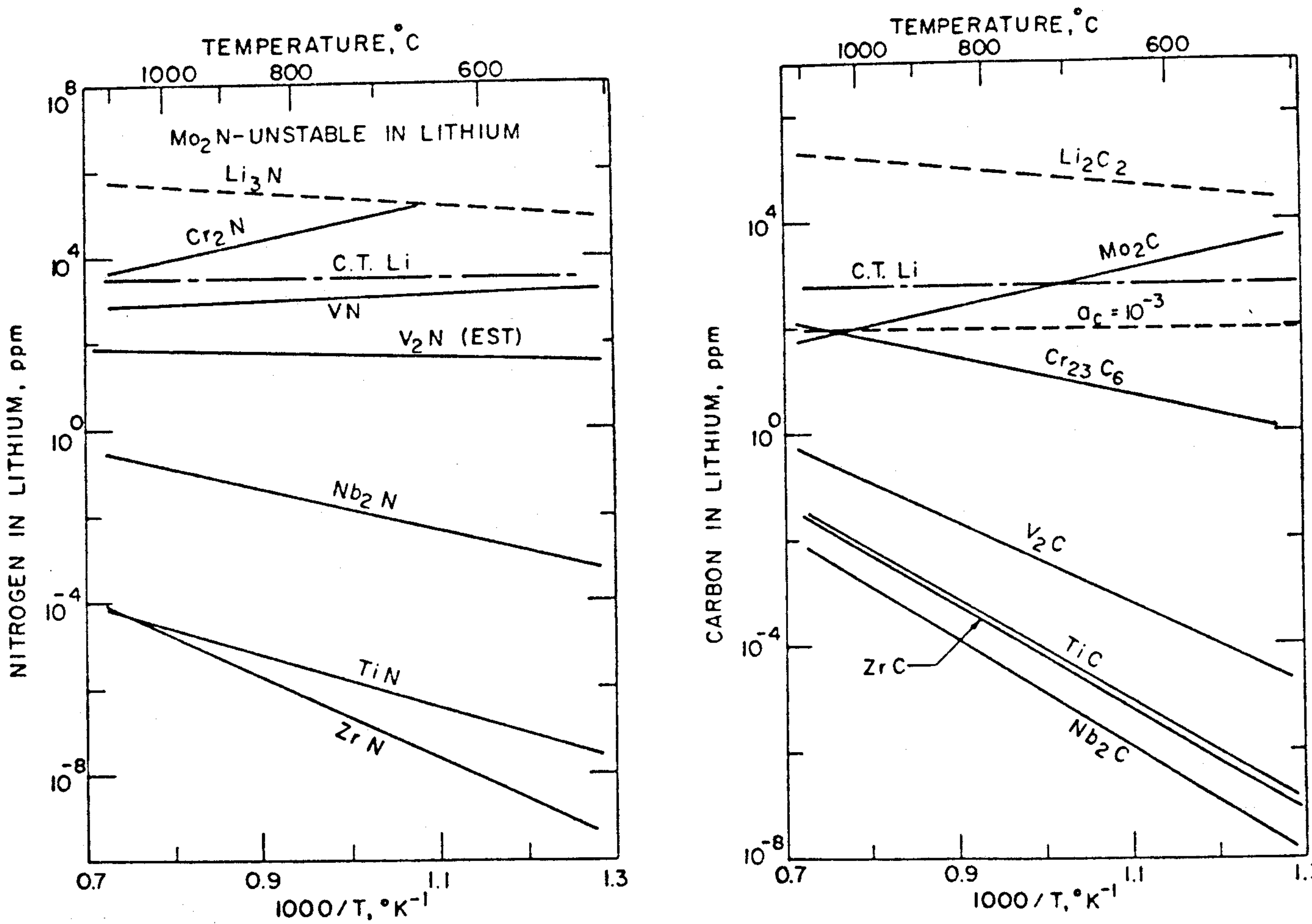


FIG. IX-B-25 TEMPERATURE DEPENDENCE OF THE INTERSTITIAL CONCENTRATIONS IN LITHIUM AT WHICH SELECTED REFRACTORY METAL COMPOUNDS ARE STABLE.*

a) NITROGEN b) CARBON



* COMPOUNDS ARE STABLE ABOVE THE GIVEN LINES.

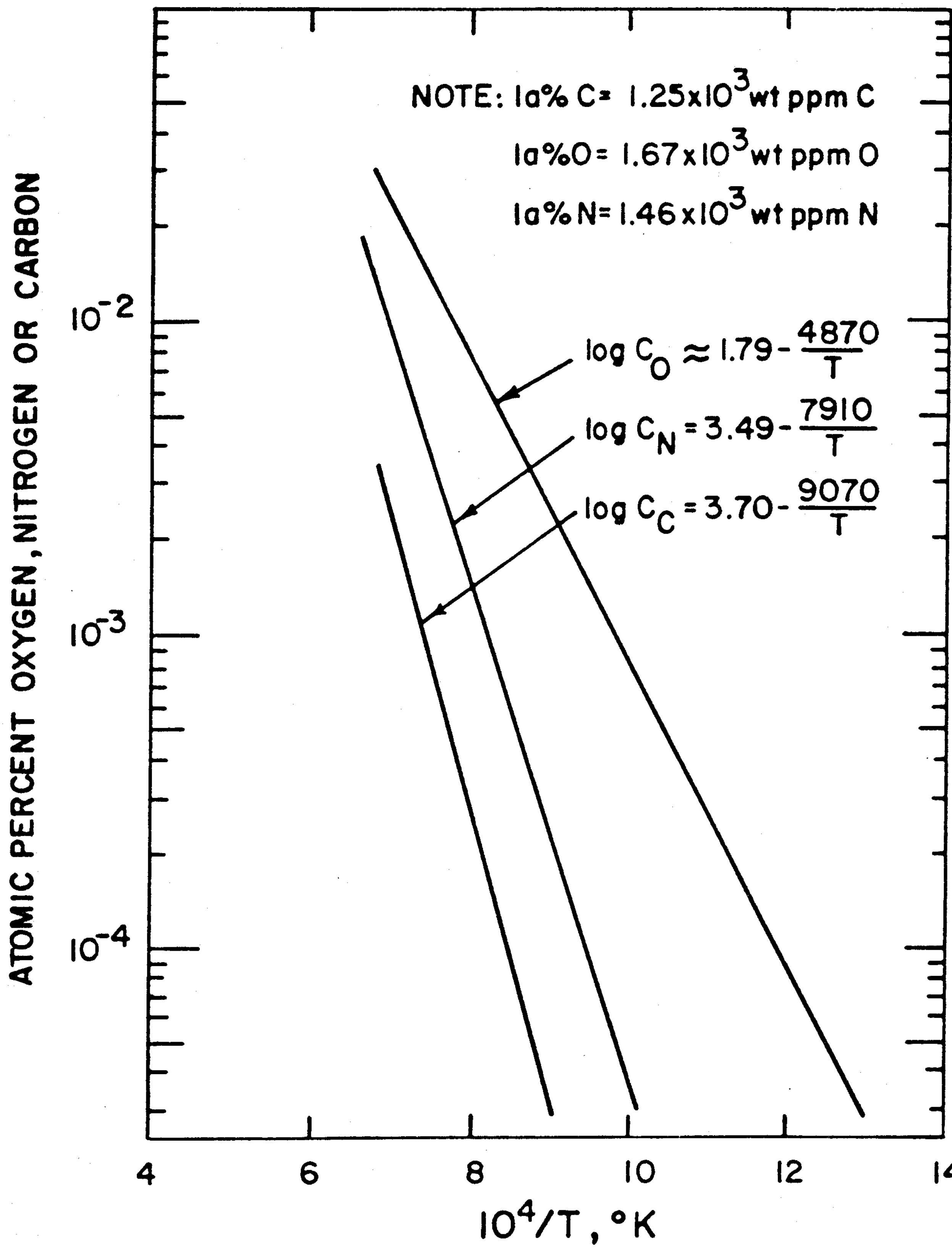


FIGURE IX-B-27 — HIGH TEMPERATURE TERMINAL SOLUBILITY OF OXYGEN, NITROGEN AND CARBON IN MOLYBDENUM

Tritium Permeabilities in Potential CTR Materials

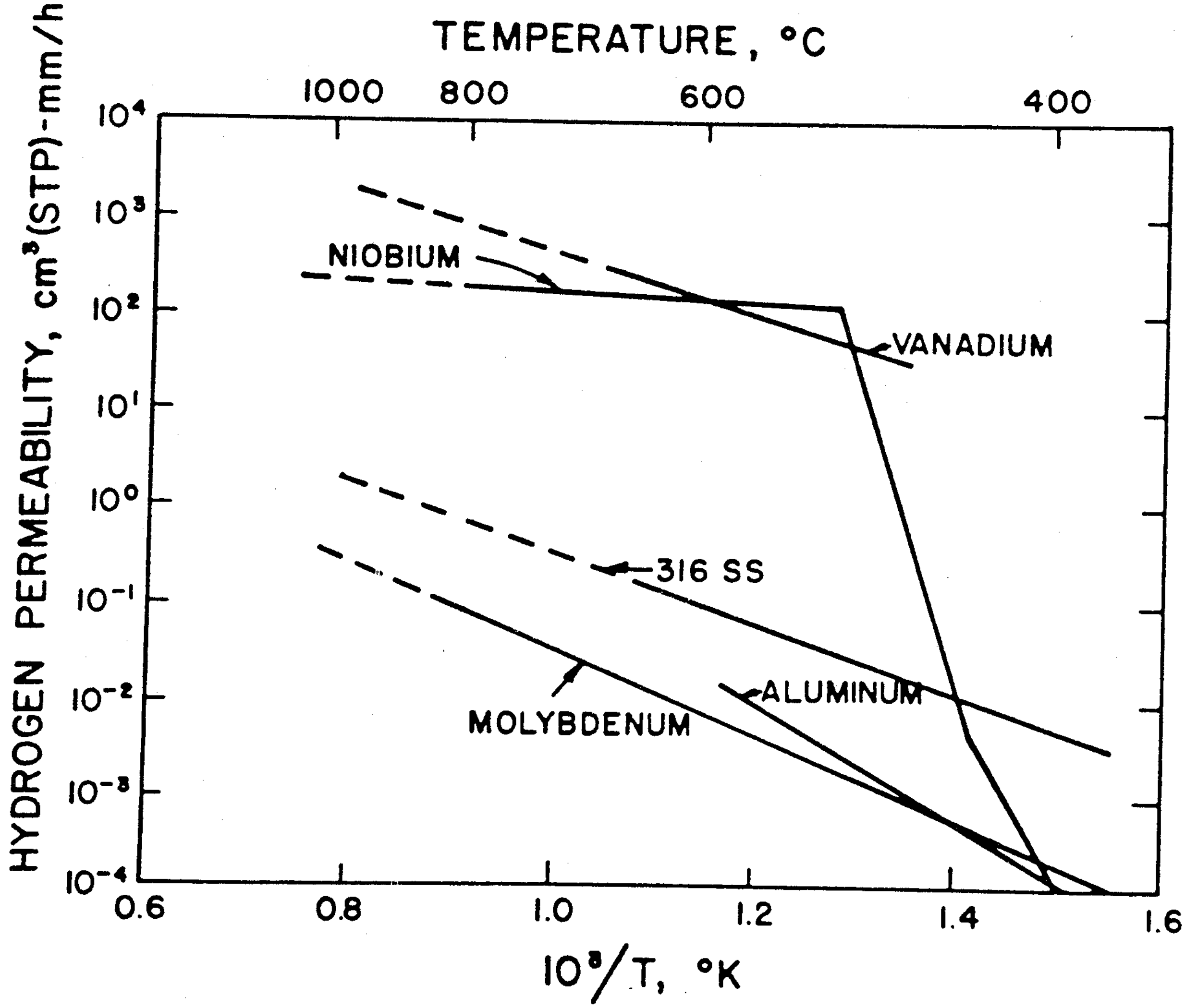


FIG. IX-B-30

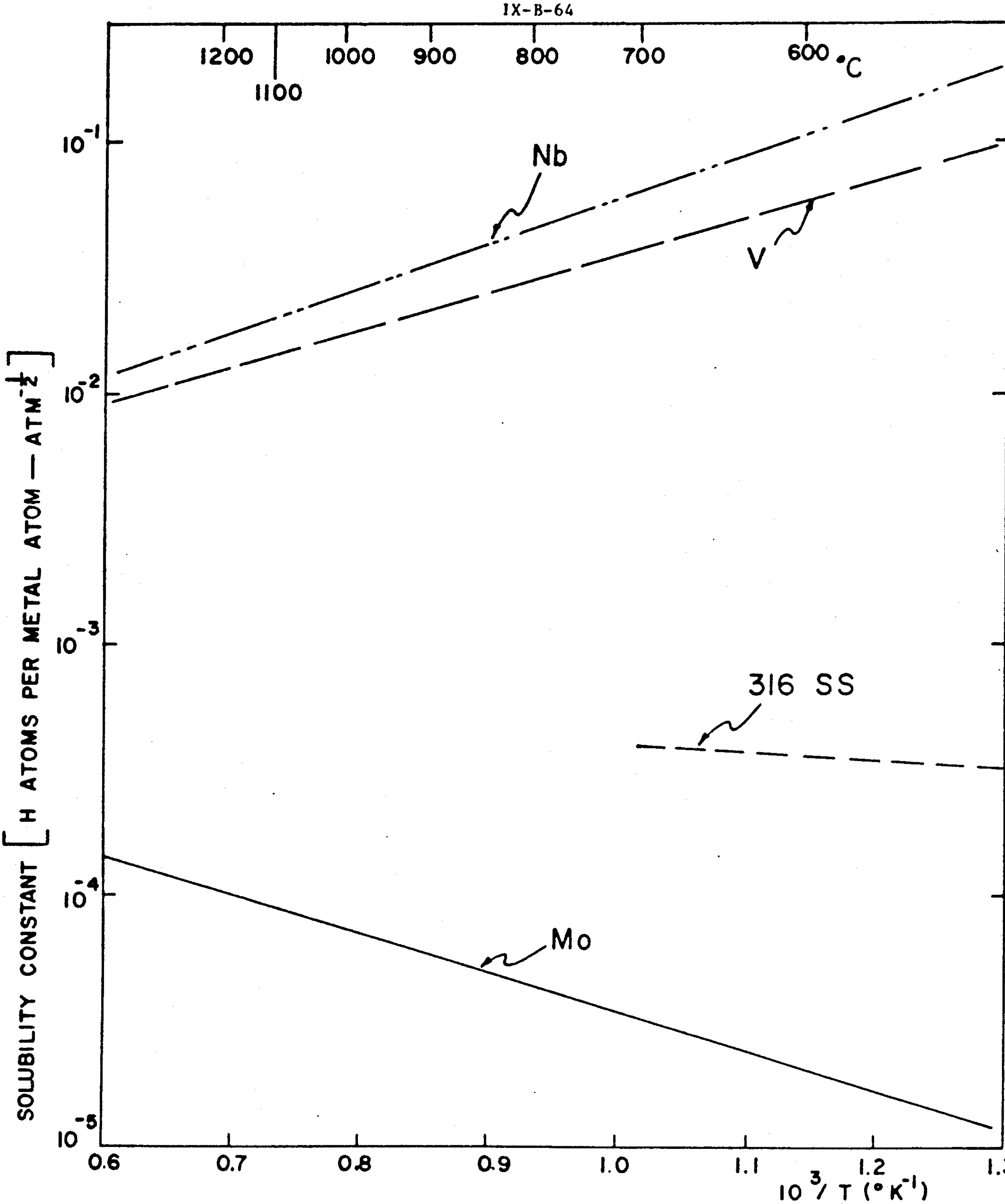


FIGURE IX-B-29 EQUILIBRIUM SOLUBILITY OF HYDROGEN IN SELECTED CTR MATERIALS

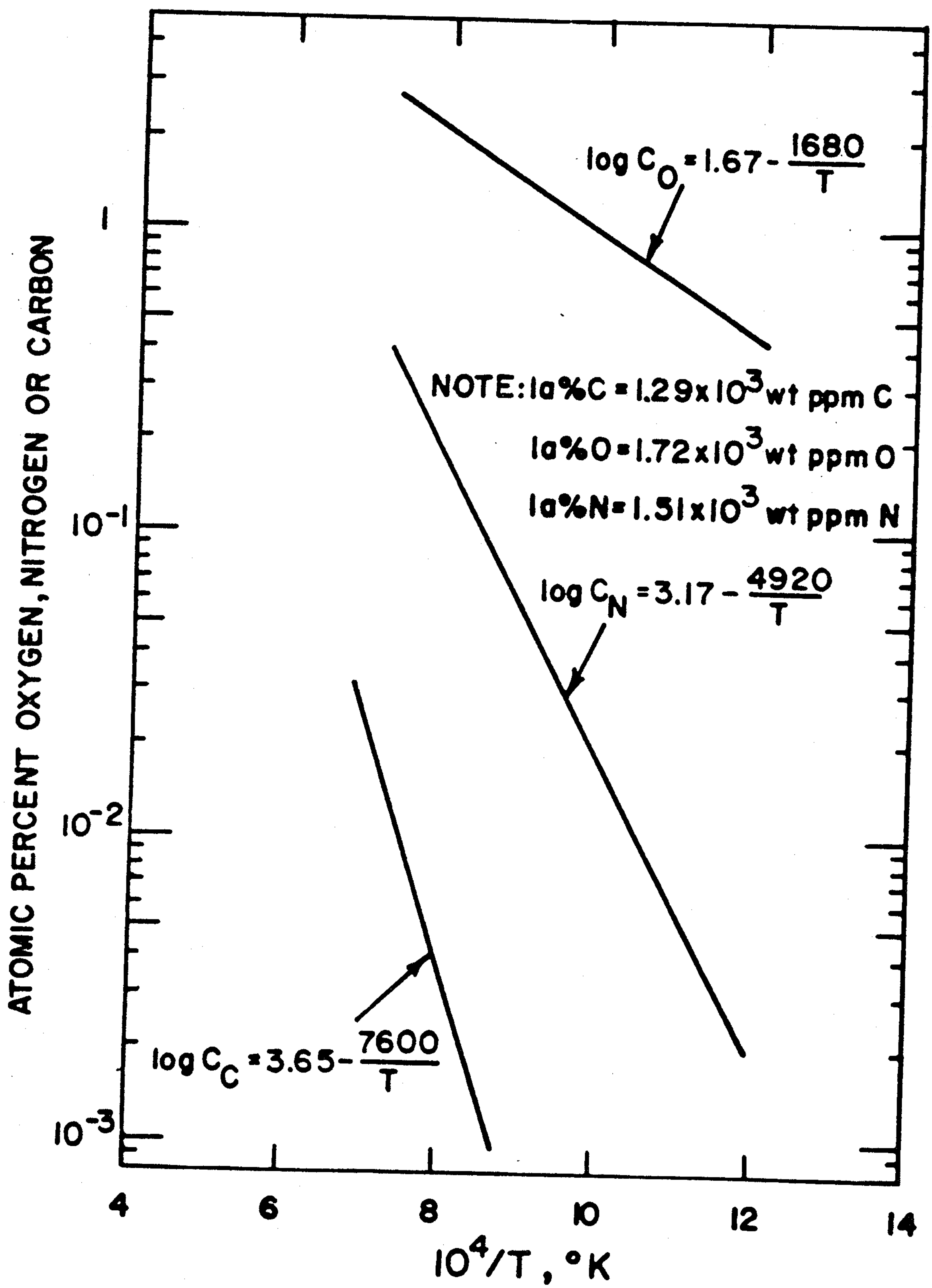


FIGURE IX-B-26—HIGH TEMPERATURE TERMINAL SOLUBILITIES OF OXYGEN, NITROGEN AND CARBON IN NIOBIUM

HELIUM COMPATIBILITY ISSUES:

- **No protective oxide, nitride or carbide will form on refractories at high temperatures.**
- **V and Nb (also Nb-1 Zr) are very sensitive to interstitial impurity contamination. Mechanical properties are severely degraded.**
- **Oxygen diffusion in Mo is slow; its effects may be delayed.**
- **Terminal Solubility of Interstitial Impurities (wppm):**

Element	T, °C	C	O	N
Mo	1000	0.4	15	3
Nb	1000	8	3500	380
V	800	2000	9000	?

COMPATIBILITY WITH LITHIUM SALTS:

- Mo , Ni –bearing alloys and graphite are very resistant to the corrosive effects of $LiF\text{-}BeF_2$ salt mixtures.
- Nb and Fe – base alloys are less corrosion resistant, but may operate up to 600-700 ^{o}C.
- V is prone to corrosion attack by $LiF\text{-}BeF_2$.
- The radiation field will produce free HF^- radicals, which may accelerate corrosion.

10. CONCLUSIONS

1. **Nb alloys are less desirable than Mo, Ta and W alloys, because of sensitivity to interstitial elements.**

2. **Within the Nb group, the alloys (C-103{Nb-10Hf-1Ti}), (WC-3009{Nb-30Hf-9W}) can be used up to 1100-1200 °C.**

3. **The best Mo alloy is TZM, which has an upper temperature limit of 1200-1400 °C.**

4. **Tantalum alloys (T-111{Ta-8W-2Hf}), and (T-222{Ta-9.6W-2.4Hf}) have upper operational temperature limits of 1200 °C and 1400 °C, respectively.**

5. **The Tungsten alloy {W-3.6Re-0.26 HfC} may be used up to 2000 ^{0}C.**

6. **Rhenium and its alloys are excluded because of high costs.**

7. **The alloys Inconel-718, TZM, T-111, T-222, C-103, and WC-3009 are compatible with Flibe up to high temperatures.**